XXIV Encontro Luso Galego de

QUÍMICA

21-23 novembro de 2018
Porto - Portugal

LIVRO DE RESUMOS

Sociedade Portuguesa de Química

U.PORTO
FACULDADE DE CIÊNCIAS
UNIVERSIDADE DO PORTO

Colegio Oficial de
Químicos de Galicia

XXIV Encontro Luso Galego de
QUÍMICA

21 A 23NOVEMBRO 2018

PORTO - PORTUGAL

SOCIEDADE PORTUGUESA DE QUÍMICA

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Este livro de atas foi produzido a partir dos trabalhos submetidos diretamente pelos autores. Apenas foram introduzidas pequenas alterações de edição, o que não alterou o conteúdo científico. A versão final online foi estabelecida para o XXIV Encontro Luso-Galego de Química, de acordo com o modelo publicado. Os autores são responsáveis pelo conteúdo científico dos seus trabalhos.

XXIV ENCONTRO LUSO-GALEGO DE QUÍMICA

Mantendo vivo o evento iniciado em 1985, decorrente da estreita relação existente entre a Delegação do Porto da Sociedade Portuguesa de Química (SPQ) e o Colegio Oficial de Químicos de Galicia (COLQUIGA), O Departamento de Química da Faculdade de Ciências tem o prazer de organizar e receber o XXIV Encontro Luso-Galego de Química, que irá decorrer entre os dias 21 e 23 de novembro de 2018.

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INFORMAÇÕES

LOCAL DO ENCONTRO

O Encontro decorrerá nas instalações da Faculdade de Ciências da U. Porto.

RECEPÇÃO

A recepção para levantamento da documentação do Encontro e informações estará localizada no Átrio do Auditório Ferreira da Silva e estará aberta a partir das 8:30 e durante todo o decorrer do programa científico.

EQUIPAMENTO DE PROJEÇÃO

As salas das comunicações orais estão equipadas com computador (Microsof Office) e sistema de projeção. Cada orador deverá transferir o ficheiro (em power-point) da sua apresentação para o computador da sala pelo menos, no limite, na sessão anterior. Caso pretendam um apontador Laser, com funcionalidade de passagem dos ppt, devem solicitar com antecedência à organização.

APRESENTAÇÕES ORAIS

As lições plenárias terão duração de 45 minutos, incluindo a discussão. As comunicações orais terão duração de 12 minutos, seguidas de 3 minutos de discussão. Atendendo ao número elevado de comunicações orais, pede-se a todos os oradores que cumpram o tempo estipulado de forma a evitar atrasos no programa.

POSTERS

As dimensões máximas do poster deve ser 90 (Largura) x 120 (Altura) Os posters deverão ser afixados apenas no dia em que decorrerá a sessão onde foram alocados, de preferência antes do início do programa científico do respetivo dia. Pede-se aos autores para estarem presentes junto dos painéis durante a sessão de discussão. Os posters deverão ser removidos no final do dia pelos autores da comunicação.

EVENTO SOCIAL

O jantar do encontro será no dia 22 de novembro, às 20 horas.

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PROGRAMA CIENTÍFICO

21 NOVEMBRO 2018 | QUARTA-FEIRA

9:00 - 11:00	**ENTREGA DA DOCUMENTAÇÃO**			
11:00 - 11:30	**SESSÃO DE ABERTURA**			
11:30 - 12:30	**PLENÁRIA DE ABERTURA** **Auditório Ferreira da Silva (AFS)** Stéphane Quideau			
12:30 - 14:00	**ALMOÇO**			
14:00 - 15:00	QAMA 1	QO 1	QA 1	QAMB 1
	QAMA 2	QO 2	QA 2	QAMB 2
	QAMA 3	QO 3	QA 3	QAMB 3
	QAMA 4	QO 4	QSOC 1	QAMB 4
Pausa (5 min)				
15:05 - 16:05	QAMA 5	QO 5	QA 5	QAMB 5
	QAMA 6	QO 6	QA 6	QAMB 6
	QAMA 7	QO 7	QA 7	QAMB 7
	QAMA 8	QO 8	QA 8	QAMB 8
16:05 - 17:00	**PAUSA CAFÉ / SESSÃO DE POSTERS**			
17:00 - 17:45	**PLENÁRIA 1 (AFS)** Tomás Cordero Alcántara			
17:45 - 18:30	QAMA 9	QO 9	CAT 1	QAMB 9
	QAMA 10	QO 10	CAT 2	QAMB 10
	QAMA 11	QO 11	CAT 3	QAMB 11
Pausa (5 min)				
19:00 - 19:45	QAMA 12	SQ 1	CAT 4	QAMB 12
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PROGRAMA CIENTÍFICO

22 NOVEMBRO 2018 | QUINTA-FEIRA

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	QAMA 20	CAT 8	QS 6
	QAMA 21	CAT 9	QS 7
	QAMA 22	CAT 11	QS 8
	QAMA 23	QS 56	QS 9
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11:45-12:30	**PLENÁRIA 2 (AFS)** Carlos Lodeiro Espinõ		
12:30-14:00	**ALMOÇO**		
14:00 - 15:00	QAMA 24	CAT 12	QAMB 15
	QAMA 25	CAT 13	QAMB 16
	QAMA 26	CAT 14	QAMB 17
	QAMA 27	QA4	QAMB 18
Pausa (5 min)			
15:05 - 16:05	QS 10	QSOC 2	QAMB 19
	QS 11	QA 9	QAMB 20
	QS 12	QA 10	QAMB 21
	QS 13	QA 11	QAMB 22
16:05-17:00	**PAUSA CAFÉ / SESSÃO DE POSTERS**		
17:00-17:45	**PLENÁRIA 3 (AFS)** Pilar Goya Laza		
17:45-19:00	QS 14	QA 12	QAMB 23
	QS 15	QA 13	QAMB 24
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	QS 17	EEQ 2	QSUS 7
20:00	**JANTAR DO ENCONTRO**		

PROGRAMA CIENTÍFICO

23 NOVEMBRO 2018 | SEXTA-FEIRA

9:00 - 10:00	QAMA 28	QS 18	QF 1	
	QAMA 29	QS 19	QF 2	
	QAMA 30	QS 20	QF 3	
	QAMA 31	QS 21	QF 4	
Pausa (5 min)				
10:05 - 11:05	BB 1	QS 22	QF 5	
	BB 2	QS 23	QF 6	
	BB 3	QS 24	QF 7	
	BB 4	QS 25	QF 8	
11:05-11:45	**PAUSA CAFÉ/ SESSÃO DE POSTERS**			
11:45-12:30	**PLENÁRIA 4 (AFS)** Manuel António Coimbra (AFS)			
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14:00-15:30	QAMA 32	BB 5	NN 1	QSUS 1
	QAMA 33	BB 6	NN 2	QSUS 2
	QAMA 34	BB 7	NN 3	QSUS 3
	QAMA 35	BB 8	NN 4	QSUS 4
	QI 1	QAMA 36	NN 5	BB 9
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15:30-16:00	**PAUSA CAFÉ/ SESSÃO DE POSTERS**			
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	QI 4	QAMA 39	NN 8	QIE 1
	QI 5	BB 10	NN 9	QIE 2
	QI 6	BB 11	NN 10	QIE 3
	QI 7	BB 12	NN 11	QIE 4
	QI 8	BB 13	NN 12	QI9
17:30	**SESSÃO DE ENCERRAMENTO**			

LIÇÕES PLENÁRIAS - Auditório Ferreira da Silva (AFS)

21 NOVEMBRO 2018 - Quarta-feira

11:30 - 12:30

LP 0: Chiral Iodanes for Asymmetric Oxygen-Atom (and Carbon-Atom) Transfer in Biomimetic Dearomative Transformations of Phenols
Stéphane Quideau

17:00 - 17:45

LP1: Materiales de carbono a partir de lignina. Carbon materials from lignin.
Tomás Cordero Alcántara

22 NOVEMBRO 2018 - Quinta-feira

11:45-12:30

LP2: NanOmics: From sythensis to Environmental and Biomedical Applications

Carlos Lodeiro Espinõ

17:00-17:45

LP3: Ética e integridad en la investigación en química

Pilar Goya Laza

23 NOVEMBRO 2018 - Sexta-feira

11:45-12:30

LP4: Polysaccharides chemistry: from food to food applications

Manuel António Coimbra

COMUNICAÇÕES ORAIS

21 NOVEMBRO 2018 - Quarta-feira

14:00 - 15:00

SALA 1 Auditório Ferreira da Silva

QAMA 1	**GC-MS analysis of Spartina maritima and Puccinellia maritima, two halophytic grasses from Aveiro saltmarshes,** Maria Faustino
QAMA 2	**Efeito da pectina no mecanismo de auto-associação da malvidina-3-O-glucósido,** Ana Fernandes
QAMA 3	**Gunnera tinctoria: A preliminary study about an invasive plant,** Ana Valadão
QAMA 4	**Nanopartículas de lenhina para a encapsulação de piranoantocianinas azuis. Estabilidade em sistemas aquosos,** Paula Araújo

SALA 2 Auditório FC6 (0.29)

QAMB 1	**Evaluation of the removal of doclofenac sodium in water by electrocoagulation,** Gabriel Silva
QAMB 2	**As total y especies de As en arroz comercial en Ecuador y otros países de Latinoamérica y de la Península Ibérica,** Oliva Atiaga
QAMB 3	**Iberian partnership on the study of platinum-group elements (PGE): the case of Tagus estuary,** Carlos Monteiro
QAMB 4	**Efeito de catiões de metais na resistência de geotêxteis à termo-oxidação,** Paulo Almeida

SALA 3 FC6 (1.37)

QA 1	**Hydrochlorothiazide cocrystals screening: a vibrational spectroscopy study,** Marisa Rodrigues
QA 2	**Comparative study of basic and acid tranesterification for assessment of total 3MCPD in oil samples by GC-MS,** Jorge Custodio-Mendoza
QA 3	**A miniaturized chip in a multi-syringe flow system for spectrofluorimetric determination of iodide in urine samples,** Joana Miranda
QSOC 1	**Estudo dos compostos fenólicos presentes em tintas ferrogálhicas medievais obtidas através do uso de reconstruções históricas,** Natércia Teixeira

SALA 4 FC6 (1.42)

QO 1	**2.aryl-4-chloro-2H-chromene: a key intermediate in the synthesis of chromene hybrids,** Djenisa Rocha
QO 2	**(E,E)-cinnamylideneacetophenones as templates for the one-pot synthesis of isoquinuclidines,** Pedro Varandas
QO 3	**Synthesis and biological evaluation of β-functionalized porphyrin with cationic heterocyclic units,** Nuno Moura
QO 4	**Simple Strategies in the β-Functionalization of meso-Tetraaryporphyrins Via Nitro and Formyl Substituents,** Maria Neves

15:05 - 16:05

SALA 1 Auditório Ferreira da Silva

QAMA 5	**Ochratoxin A occurrence and risk assessment in the portuguese wine market,** Liliana da Silva
QAMA 6	**Validation of a liquid chromatography coupled to tandem mass spectrometry (LC-MS / MS) methodology for the monitoring of emergent mycotoxins in plants,** João de Sousa
QAMA 7	**Caracterização química e nutricional de gãos de Chenopodium quinoa Willd (quinoa): uma boa alternativa para produtos alimentares nutritivos,** Eliana Pereira
QAMA 8	**Correlation of aroma characteristics with volatile profile of hops,** Julio Junior

COMUNICAÇÕES ORAIS

21 NOVEMBRO 2018 - Quarta-feira

15:05 - 16:05

SALA 2 Auditório FC6 (0.29)

QAMB 5	**Modelling the Absorption Spectra of Polycyclic Aromatic Hydrocarbons over Seoul, South Korea,** Tiago Dias
QAMB 6	**Variación temporal de las formas geoquímicas de P en sedimentos de la Laguna de Xuño (NO Península Ibérica, Galicia, A Coruña),** Pedro Fraga - Santiago
QAMB 7	**Quantification of Fatty Acid Ethyl Esters in Biodiesel via ATR-FTIR,** Marta Ramos
QAMB 8	**Estudio del suelo rizosférico de la chuquiragua (Chuquiraga Jussieui) en un medio volcánico de clima frío (páramos del volcán Cotopaxi-Ecuador),** Paulina Guevara

SALA 3 FC6 (1.37)

QA 5	**Aplicación de la microextracción en la preparación de muestras de interés toxicológico,** Ana Ares Fuentes
QA 6	**Enantioresolution, chiral recognition mechanisms and binding of xanthone derivatives on immobilized human serum albumin by liquid chromatography,** João do Carmo
QA 7	**Potentiometric detection in liquid chromatographic systems,** Renato Gil
QA 8	**Electrochemical genosensors applied to cardiovascular pharmacogenetics,** *Maria de Fátima Barroso*

SALA 4 FC6 (1.42)

QO 5	**Afinidade e seletividade de porfirinas e ftalocininas catiónicas para diferentes estruturas de ADN: screening competitivo,** Catarina Ramos
QO 6	**Photochromism of fused-naphthopyrans,** Maria de Sousa
QO 7	**A new route to thiazolo[5,4-c]isoquinolines,** Letícia Costa
QO 8	**Halogen bonding and luminescence in supramolecular architectures,** Patricia Vaz

17:45 - 18:30

SALA 1 Auditório Ferreira da Silva

QAMA 9	**Sumo de sabugueiro como ingrediente alimentar com propriedades corantes e bioativas ,** Sandrina Heleno
QAMA 10	**Fracionamento do extrato de acetona das sumidades floridas de Calluna vulgaris (L.) Hull: perfil fenólico e potencial antibacteriano,** Filipa Mandim
QAMA 11	**Deconstructing apple pomace chemistry,** Pedro Fernandes

SALA 2 Auditório FC6 (0.29)

QAMB 9	**Aplicação de argilas pilarizadas em processos de oxidação avançados para o tratamento de efluentes vinícolas,** Vanessa Guimarães
QAMB 10	**Comparison of Advanced Oxidation Processes as a pre-treatment for Sambucus Nigra wastewater,** Leonor Ferreira
QAMB 11	**Monitoring the impact of fertilizers on soil leachates using sequential injection analysis for multiparametric determination,** Carolina da Costa

SALA 3 FC6 (1.37)

CAT 1	**Removal of phenol from aqueous solutions by adsorption and catalytic processes,** Katarzyna Eblagon
CAT 2	**Estudo mecanístico da conversão de CO2 em carbonatos heterocíclicos através de organocatálise,** Ricardo Sendão
CAT 3	**Solketal, a new fuel additive for biodiesel mixtures,** Joana Martinho

COMUNICAÇÕES ORAIS

21 NOVEMBRO 2018 - Quarta-feira

17:45 - 18:30

SALA 4 FC6 (1.42)

QO 9	**Novel porphyrin-flavone conjugates: synthesis and photophysical characterization,** Mariana Mesquita
QO 10	**New routes for the synthesis of marine xanthones with antimicrobial activity,** Daniela Loureiro
QO 11	**Bioguided study in the search for natural antifungal components in the Brazilian Biomas,** Marcelo Silva

19:00 - 19:45

SALA 1 Auditório Ferreira da Silva

QAMA 12	**Recuperação otimizada de antocianinas de Prunus spinosa L. e Ficus carica L. para aplicação como corante alimentar,** Carla Pereira
QAMA 13	**Optimized Acetonitrile Based-Extraction for Determination of Polycyclic Aromatic Hydrocarbons in Cooked Muscle Foods,** Marta da Silva
QAMA 14	**In-house validation method for the determination of 24 pharmaceuticals in clams using QuEChERS-LC-MS/MS ,** Cristina Almeida

SALA 2 Auditório FC6 (0.29)

QAMB 12	**Viability of the conversion of leachate effluents, from a mechanical biological treatment plant for municipal solid waste, to fertilizers,** Jonathan Cardoso
QAMB 13	**Simultaneous removal of sulfamethoxazole and methyl paraben by electro-Fenton treatment,** Antón Puga Pazo
QAMB 14	**Monitoring of several chiral drugs in the Douro river estuary by LC-MS/MS,** Maria Coelho

SALA 3 FC6 (1.37)

CAT 4	**Development of heterogeneous nanostructured catalysts for biodisel production,** Catarina Lino
CAT 5	**Waste oils valorization through biodiesel synthesis using [HMIM]HSO4 ionic liquid as catalyst,** Paulo de Brito
CAT 6	**Kinetic study of the esterification process catalyzed by ionic liquids for fatty acid methyl esters production,** Cristiana Meireles

SALA 4 FC6 (1.42)

SQ 1	**Evaluación de la Exposición a Contaminantes Químicos en el Tratamiento de Residuos Vegetales,** Eugénio Muñoz Camacho
QP 1	**Thermal properties and molecular interactions of alginate/gelatin hydrogel microparticles,** Nadezhda Pilipenko
CAT 10	**Redução de bromato em água na presença de catalisadores metálicos suportados em nanotubos de carbono modificados,** Olívia Salom Soares

COMUNICAÇÕES ORAIS

22 NOVEMBRO 2018 - Quinta-feira

9:00 - 10:00

SALA 1 Auditório Ferreira da Silva

QAMA 15	**Polybrominated diphenyl ethers and their metabolites in European smoked fish products,** Rebeca Cruz
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QAMA 17	**Extracção e quantificação de proantocianidinas totais da farinha da graínha da uva,** Jorge Julião
QAMA 18	**A importância dos polissacáridos do vinho na modulação das interações proteína-tanino,** Elsa Brandão

SALA 2 Auditório FC6 (0.29)

QS 1	**Chalcones as α-amylase and α-glucosidase inhibitors for the management of diabetes mellitus,** Sónia da Rocha
QS 2	**Characterization of the phenolic profile of Caryota urens L. – preliminary evidence on its antidiabetic properties,** Catarina Andrade
QS 3	**Development and application of a synaptosomal model for the study of peroxynitrite - induced lipid peroxidation,** Pedro Nicola
QS 4	**Synthesis and evaluation of self-illuminating photosensitizers for Photodynamic Therapy of Cancer,** Carla Magalhães

SALA 3 FC6 (1.37)

QT 1	**Understanding the Environmental Toxicity of Deep Eutectic Solvents and their Components: A Multitasking Quantitative Structure-Toxicity Relationship Modelling Approach,** Amit Halder
QT 2	**Ring-Shaped Donor-Acceptor Nanoarchitectures for the Removal of Cyperquat Pesticide From the Environment,** Laura Sanchz-Guirao
QT 3	**Computational Evaluation of Vibrational Spectroscopy Techniques as New Candidates for the Rapid, Selective and Univocal Detection of Saxitoxin,** Óscar Iglésias
QT 4	**On the Origin of Drug Recognition Changes and P-Glycoprotein Polyspecificity,** Cátia Bonito

10:05 - 11:15

SALA 1 Auditório Ferreira da Silva

QAMA 19	**Influência da acilação enzimática nas propriedades cromáticas de novos derivados de antocianinas monoglucósidas,** Marta Guimarães
QAMA 20	**Individual phenolic compounds profile from rosé wines aged in contact with different wood chips species (oak and cherry),** Luísa Fontes
QAMA 21	**Estudo da estabilidade e atividade biológica de bagaço de uva (Merlot) após simulação da digestão gastrointestinal e fermentação colónica,** Rúbia Corrêa
QAMA 22	**Valorization of Portuguese elderberries from Varosa Valley,** Sandrine Ferreira
QAMA 23	**Cytinus hypocistis L. plant as source of phenolic compounds with anti-lipid peroxidation activity,** Ana Rita Silva

SALA 2 Auditório FC6 (0.29)

QS 5	**Photodynamic inactivation of antibiotic resistant bacteria using cationic chlorin dyes,** Joana Calmeiro
QS 6	**Amphiphilic porphyrins and phtalocyanine as potential antimicrobial agents,** Sara Gamelas
QS 7	**Microfluidic paper-based analytical devices for the determination of salivary NOx,** Francisca Ferreira
QS 8	**Absorption of mycotoxins using in vitro models of human gastric and intestinal epithelium,** Madalena Sobral
QS 9	**New fluorophores for protein aggregates detection,** Raquel da Silva

COMUNICAÇÕES ORAIS

22 NOVEMBRO 2018 - Quinta-feira

10:05 - 11:15

SALA 3 FC6 (1.37)

CAT 7	**New potential heterogeneous catalysts based on cobalt(II) coordination polymers,** Carla Queirós
CAT 8	**Treatment of oily streams contaminated with lipophilic pollutants by peroxide oxidation using catalysts developed from compost derived from municipal solid waste,** Jose Diaz de Tuesta
CAT 9	**Extraction of laccase from Trametes versicolor growth media using aqueous biphasic systems,** Marguerita da Rosa
CAT 11	**Biomimetic oxygenation of benzofuran derivatives under environmentally benign conditions,** Sónia Pires
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14:00 - 15:00

SALA 1 Auditório Ferreira da Silva

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QAMA 25	**Effect on phenolic composition and biological properties of grape (Vitis vinifera L.) stems during long-term storage,** Irene Gouvinhas
QAMA 26	**In-line phosphate pre-concentration in a flow injection method platform for monitoring fertilizers excess in soil leachates,** Letícia Mesquita
QAMA 27	**Phenolic composition and cell-based antioxidant activity of roots and aerial parts of Eryngium viviparum produced in vitro,** Manuel Ayuso

SALA 2 Auditório FC6 (0.29)

QAMB 15	**Aplicação do processo Fenton no tratamento de efluente gasoso contendo tolueno,** Vanessa de Lima
QAMB 16	**EU multi-class organic micropollutants in Leça River: Spatiotemporal monitoring and fluorescence excitation-emission matrices assessment,** Marta Barbosa
QAMB 17	**Getting inspiration from the surface of plants leaves,** Mariana Fernandes
QAMB 18	**Quantification of enantiomers of psychoactive substances and β-blockers by GC-MS in wastewaters to estimate consumption,** Ricardo Gonçalves

SALA 3 FC6 (1.37)

CAT 12	**Materiais de carbono isentos de metais para o tratamento fotocatalítico de compostos fenólicos,** André Pinto
CAT 13	**Efficient Polyoxomolybdate Catalyst Supported in Mesoporous Silica Nanoparticles for Oxidative Desulfurization Processes,** Fátima Mirante
CAT 14	**Desenvolvimento de processos de produção de aldeídos aromáticos baseados em fotocatalisadores de nitreto de carbono,** Joana Lopes
QA 4	**Looking for beer aging markers using gas-chromatography-mass-spectrometry,** Inês Ferreira

COMUNICAÇÕES ORAIS

22 NOVEMBRO 2018 - Quinta-feira

15:05 - 16:05

SALA 1 Auditório Ferreira da Silva

QS 10	**Sequential flow injection analysis with potentiometric detection for the determination of ammonium and urea in human saliva,** Yanisa Thepchuay
QS 11	**Uso da espectroscopia de infravermelho médio na análise do fluido crevicular gengival,** Ricardo Páscoa
QS 12	**Benzodiazepines: An Integrated Approach Based On Consumption, Risk Assessment And Monitoring Results,** Angelina Pena
QS 13	**Risk assessment of nickel in baby food,** André Pereira

SALA 2 Auditório FC6 (0.29)

QAMB 19	**Desalination Technologies: an Energy Approach,** Sara Sofio
QAMB 20	**E-waste: potential impact of yttrium and lanthanum on embryonic development of Crassostrea gigas,** Bruno Henriques
QAMB 21	**Será possível extrair valor dos smartphones em fim de vida?,** Cláudia Lopes
QAMB 22	**Tratamento de efluentes vinícolas mediado por microalgas,** Leonilde Marchão

SALA 3 FC6 (1.37)

QSOC 2	**What´s the water flavour?,** Sofia Capelo
QA 9	**Interferences minimization using solid phase extraction in a multiparametric sequential injection system,** Tânia Ribas
QA 10	**Dual-Emission ratiometric probe for H2O2 determination,** Rafael Castro
QA 11	**Searching for the most variable m/z values in grape development in a Portuguese vineyard,** Sandia Machado

17:45-19:00

SALA 1 Auditório Ferreira da Silva

QS 14	**New symmetrical indolenine squaraine dyes: synthesis and studies of their photostability, ability of singlet oxygen formation and in vitro phototherapeutic potential,** Eurico Lima
QS 15	**UHPLC-MS a tool to disclose phenolic profiles and/or to validate species medicinal significance,** Diana Pinto
QS 16	**Antioxidant activity of (styryl)pyrazoles and preliminary structure-activity relationship studies,** Vera da Silva
QS 17	**Copper(I)-phosphane complexes as promising anticancer agents,** João Machado

SALA 2 Auditório FC6 (0.29)

QAMB 23	**Aterros sanitários em Portugal - Energia,** Maria dos Santos
QAMB 24	**Caracterização Físico-Química de Amostras no Âmbito da Diretiva Quadro da Água,** Hans Queta
QAMB 25	**Digestão anaeróbia de lamas de ETAR - Biogás e energia,** Fernando Alves
QSUS 7	**Metal-Organic Frameworks de Cu y Sc modificados para la síntesis verde de heterociclos bioactivos,** Daniel Gonzilez-Rodal

SALA 3 FC6 (1.37)

QA 12	**Desenvolvimento e aplicação de um método fluorimétrico para a quantificação de zinco em alimentos para cães,** Rute Martins
QA 13	**Desenvolvimento e caracterização de um sensor potenciométrico para a determinação da atropina,** Ana Rita Pereira
EEQ 1	**Desarrollo de materiales multimedia como recurso didáctico de la enseñanza universitaria de la Química Analítica Instrumental,** Antonio Zapardiel Palenzuela
EEQ 2	**¿Cuánta ciencia puedes aprender con 20 minutos de Los Simpsons? Una propuesta constructivista para la mejora de la comprensión y transmisión del conocimiento científico en el aula,** Ángel Vidal-Vidal

COMUNICAÇÕES ORAIS

23 NOVEMBRO 2018 - Sexta-feira

9:00 - 10:00

SALA 1 Auditório Ferreira da Silva

QAMA 28	**Monitoring the nutritional quality of tomatoes during shelf-life after a post-harvest treatment with Calcium Chloride,** Ana Koch
QAMA 29	**Nutritional and physicochemical characterization of purple and red-fleshed genotypes of potatoes from different geographical regions,** Shirley Sampaio
QAMA 30	**Atividade antioxidante de fenolipidos em emulsões alimentares O/A - Correlação entre a atividade antioxidante e propriedades químicas,** Marlene Costa
QAMA 31	**Efeito da irradiação na estabilidade de vitaminas essenciais em azedas (Rumex induratus) armazenadas a 4 °C,** José Pinela

SALA 2 Auditório FC6 (0.29)

QS 18	**Characterization of nanoformulations produced with the aqueous extract from Annona muricata L.,** Ana Clara Grosso
QS 19	**Computational studies with oxindole frameworks,** Luís Fernandes
QS 20	**Evaluation of in vitro anti-diabetic potential of 2,3-diarylxanthones through the inhibition of α-glucosidase,** Clementina dos Santos
QS 21	**The influence of age on the toxicity induced by mitoxantrone: in vivo studies with mice,** Rita Guedes

SALA 5 FC6 (1.46)

QF 1	**Improving Vibrational Mode Interpretation Using Bayesian Regression,** Filipe Teixeira
QF 2	**Thermophysical study of the solvation of alcohols in ionic liquids,** Inês Vaz
QF 3	**Interaction of biocompatible star-shaped block copolymers with 2D cell membrane models: a thermodynamic study,** Emílio Lage
QF 4	**Selective vibrational excitation as a tool for conformational control,** Igor Reva

10:05 - 11:05

SALA 1 Auditório Ferreira da Silva

BB 1	**Bio-guided fractionation of extracts of Geranium molle L.: relationship between phenolic profile and biological activity,** Vânia Graça
BB 2	**Evaluation of antioxidant function in liver samples collected in young and middle age animal subject to a plan of daily physical exercice,** Mónica da Silva
BB 3	**Honey biomimetic fructo-oligosaccharides production by nonenzymatic reactions,** Elisabete Coelho
BB 4	**Ganoderma lucidum as a promising ingredient for cosmeceutical application: safety assessment and in vitro skin permeation studies,** Oludemi Taofiq

SALA 2 Auditório FC6 (0.29)

QS 22	**Síntese de 2,1-benzisoxazoles e espiroindolin-3-onas derivados de ácidos (tio) barbitúricos potencialmente bioativos,** Samuel Silvestre
QS 23	**In vitro evaluation of the photoreactivity of natural phenolic antioxidants,** Brandon Aguiar
QS 24	**Synthesis of barbiturate substituted squaraine dyes and evaluation of their interaction with bovine serum albumin,** Vanessa Gomes
QS 25	**Ionic Systems Approaches for Pharmaceuticals,** Luis Branco

SALA 5 FC6 (1.46)

QF 5	**Physical and Chemical characterization of anthocyanins from Purple-Fleshed Sweet Potato,** Hélder Oliveira
QF 6	**Thermal behavior investigation of hydrogenated waste cooking oil and beeswax for Phase Change Materials,** João Baptista
QF 7	**Thermodynamic modelling of binary mixtures containing naturally occurring phenolic acids,** Sérgio Vilas-Boas
QF 8	**Modelos teóricos para simular el efecto del potencial eléctrico sobre los desplazamientos de las frecuencias vibracionales de piridina adsorbida en un electrodo de plata,** Juan Otero

COMUNICAÇÕES ORAIS

23 NOVEMBRO 2018 - Sexta-feira

14:00-15:30

SALA 1 Auditório Ferreira da Silva

QAMA 32	**Its tea time! Mycotoxins in teas and herbs destined to prepare infusions,** Sofia Duarte
QAMA 33	**Identification of biogenic amines in wines using a dispersive solid phase extraction clean-up/concentration method,** Juliana Milheiro
QAMA 34	**Pirano-Estiril-Flavílios – novos pigmentos 'bio-inspirados' e a modelação da sua cor através de sistemas micelares,** Vânia Gomes
QAMA 35	**Phlorotannins from Fucus vesiculosus: potential for prevention of diabetes and obesity,** Marcelo Catarino
QI 1	**Rectifying heat flows with polyoxometalate anisotropic structures,** Filipa Sousa
QI 2	**Optimization of the synthesis of imprinted hollow TiO2 microspheres,** Vanessa Ferreira

SALA 2 Auditório FC6 (0.29)

BB 5	**Disclosing the occurrence of (β1→3) and (β1→4) mixed-linkage β-glucan in yeast cell wall,** Ana Rita de Bastos
BB 6	**Simultaneous dehydration and extraction of broccoli by-products by microwave hydrodiffusion and gravity,** Sónia Ferreira
BB 7	**Purification platform for monoclonal antibodies based on aqueous biphasic systems formed by glycine-betaine ionic liquids,** Ana Filipa Rufino
BB 8	**Nutritional and chemical characterization of fruits and stems of Lycium barbarum L.,** Tânia Pires
QAMA 36	**Evaluation of solid-state fermentation with white-rot fungi on the nutritive value of grape stalks as herbivore feed,** Valéria Costa-Silva
QAMA 37	**Microencapsulação como estratégia para a compatibilização da microalga Spirulina platensis em matrizes hidrofílicas (iogurtes),** Isabel Fernandes

SALA 6 FC4 (0.11)

NN 1	**Temperature-switch nanomagnetic logic gates for cellular hyperthermia,** Rute Pereira
NN 2	**Targeting and killing the ever-challenging ulcer bug,** Daniela Lopes-de-Campos
NN 3	**Carbon nanodots from olive mill wastewater as sensors for nitroanilines and nitrophenols,** José Prata
NN 4	**Fighting bacterial resistance: a novel nanosystem for N-acetyl-cysteine (NAC) delivery,** Ana Rita Pinto
NN 5	**Hybrid Supercapacitors: Textiles with Energy,** Joana Teixeira
NN 6	**Nanoagents with CO-releasing molecules to treat rheumatoid arthritis,** Andreia Marinho

SALA 7 FC4 (0.22)

QSUS 1	**Metal-organic framework based materials towards sustainable processes,** Luís Cunha-Silva
QSUS 2	**Utilização de uma Metodologia Superfície-Resposta para Maximizar a Extração de Ácido Rosmarínico,** Amílcar António
QSUS 3	**Novel choline amino acids ionic liquids based aqeous two-phase systems for the purification of DNP-amino acids,** Elena Gomez
QSUS 4	**Valorization of wood wastes from the agro-food industry – a sustainable approach to obtain cosmeceutical products,** Manuela Moreira
BB 9	**Influência de ambientes lipídicos na interação de polifenois em modelos de membranas: impacto na adstrigência oral,** Ana Reis
QSUS 5	**High throughput NMR methodology for ionic liquids screening: extracting polyphenols,** Raquel Barrulas

COMUNICAÇÕES ORAIS

23 NOVEMBRO 2018 - Sexta-feira

16:00-17:30

SALA 1 Auditório Ferreira da Silva

QI 3	**Multifunctional Porphyrin-based Nano-Metal-Organic Frameworks,** Flávio Figueira
QI 4	**Functional lamellar coordination polymers,** Ricardo Mendes
QI 5	**Protective effects of Mn(III)-Schiff base-dicyanamide complexes on H2O2-induced oxidative stress: catalase mimics or radical scavengers?,** Laura Rodríguez-Silva
QI 6	**From molecular to supramolecular catalysts for water splitting,** Marcelino Maneiro
QI 7	**A novel platinum(II) porphyrin for photodynamic therapy,** José de Almeida
QI 8	**Breathing Metal-Organic Frameworks Based on a Polyphosphonate Organic Linker,** Filipe Paz

SALA 2 Auditório FC6 (0.29)

QAMA 38	**Design of a full solar powered food dryer for home excess production,** Lisete Fernandes
QAMA 39	**Improving Gluten Free Bread Quality Using By-Products and Underexploited Resources,** Rita Martins
BB 10	**Homogeneous and heterogeneous photocatalytic activation of PMS and PS for wastewater disinfection,** Sonia Guerra Rodríguez
BB 11	**Atividade neuro-protetora e anti-inflamatória produzida por extratos de C. ficifolia,** Tiago Coutinho
BB 12	**Volatiles and α- and -acids: comparative analysis of hops clones, spontaneous and cultivars, in Bragança region,** Hugo Goes
BB 13	**Evaluation of antioxidant function at renal level in respnse to chronic exercise and age,** Paulo Nunes

SALA 6 FC4 (0.11)

NN 7	**Nanoestruturas híbrido-magnéticas para remediação in situ,** Lisandra Alves
NN 8	**Topical delivery of cyclosporine A using lipid nanoparticles,** Ana Barbosa
NN 9	**Metal-free nanomaterials for the oxygen reduction reaction,** Sofia Meirinho
NN 10	**Hydrophilic carbon nanomaterials - a novel insight into antioxidant therapeutic applications?,** Andreia Veloso
NN 11	**Rational optimization of the microwave-assisted synthesis of bright ternary AgInS2/ZnS quantum dots,** José Soares
NN 12	**Limpeza e branqueamento de têxteis de algodão em cru usando nanopartículas fotossensíveis,** Maria de Barros

SALA 7 FC4 (0.22)

QSUS 6	**A greener approach to obtain sulfur-free fuels based on the Venturello catalyst and a solvent-free system,** Diana Julião
QIE 1	**Phase behavior of binary mixtures of fames and alkanes,** Nuno Branco
QIE 2	**High pH Reversed-Phase Preparative Chromatographic Separation of Nadolol Racemates using C18 Adsorbents,** R. Arafah
QIE 3	**Innovative photonic crystals and phosphors based coatings for wood,** Kevin Tomaz
QIE 4	**Surface Tension for the ternary system dimethyl carbonate + p-xileno+ n-decane in function of the temperature (288.15 K – 308.15 K),** Santiago Castelo
QI9	**Crown ether palladium compounds: a strategy for encapsulating potassium cations in crown ether rings,** Fátima Lucio-Martinez

SESSÃO DE POSTERS

21 NOVEMBRO 2018 - Quarta-feira

SESSÃO I

QUÍMICA ORGÂNICA (QO)
QUÍMICA ANALÍTICA (QA)
QUÍMICA AMBIENTAL (QAMB)
QUÍMICA AGRO-MAR-ALIMENTAR (QAMA)
CATÁLISE E FOTOCATÁLISE (CAT)
SEGURANÇA QUÍMICA (SQ)
QUÍMICA DOS POLÍMEROS (QP)

22 NOVEMBRO 2018 - Quinta-feira

SESSÃO II

QUÍMICA E SAÚDE (QS)
QUÍMICA AGRO-MAR-ALIMENTAR (QAMA)
QUÍMICA AMBIENTAL (QAMB)
QUÍMICA ANALÍTICA (QA)
QUÍMICA TEÓRICA E MODELAÇÃO MOLECULAR (QT)

23 NOVEMBRO 2018 - Sexta-feira

SESSÃO III

BIOQUÍMICA E BIOTECNOLOGIA (BB)
EDUCAÇÃO E ENSINO DA QUÍMICA (EEQ)
NANOQUÍMICA E NANOTECNOLOGIA (NN)
QUÍMICA INDUSTRIAL E ENGENHARIA (QIE)
QUÍMICA INORGÂNICA (QI)
QUÍMICA SUSTENTÁVEL (QSUS)
QUÍMICA-FÍSICA (QF)

SESSÃO DE POSTERS

21 NOVEMBRO 2018 - Quarta-feira

	QUÍMICA ORGÂNICA
QO 12	**Synthesis of new quercetin-based derivatives with potential antioxidant activity,** Sónia Maria Gomes Pires
QO 13	**Halogen-exchange and amination of chlorinated thioxanthones,** Filipa Daniela Freitas Barbosa
QO 14	**Synthesis and characterization of ammonium-photosensitizers ,** Sara Raquel Duarte Gamelas
QO 15	**New pyrrole-based fluorophores: Synthesis, structures and luminescent properties,** Raquel Silva
QO 16	**Click chemistry synthetic approach for discovery of new potential bioactive chalcones,** Ana Rita Franco
QO 17	**Initial steps of the total synthesis of neofiscalin A, a natural antimicrobial alkaloid,** Ana Patrícia da Costa Marques
QO 18	**Synthesis, characterization and photophysical properties of thioglycerol-porphyrins and -phthalocyanines,** Joana Calmeiro
QO 19	**Synthesis of dipyrrolic compounds for fluoride detection,** Flávio Alberto da Silva Figueira
QO 20	**Desenvolvimento de Novos Conjugados do GPE com Propriedades Potencialmente Sinérgicas,** Sara Reis
QO 21	**Identification of other organic compounds, beyond fatty acids, from terrestrial and aquatic species by gc-ms,** Ana Maria da Seca
QO 22	**Aggregation-induced emission enhancement of chiral boranils,** Patricia vaz
QO 23	**Síntese e Avaliação da Fotocitotoxicidade de Corantes Aminoesquarílicos Conjugados com Colesterol,** Maria de Fátima Machado
QO 24	**Synthesis and characterization of tris(3-Hydroxy-4-pyridinonate) gallium(III) complexes,** Silvia Vinhas
QO 25	**Towards the synthesis of a polyoxygenated xanthone,** Mariana da Costa Almeida
QO 26	**Synthesis of functionalized tetrahydroquinolines, and its further transformation into hexahydropyrroloquinoline-2,3-diol by aminocyclization.**, Artem Drogalin
QO 27	**Avaliação química da Phyllanthus welwitschianus Müll.Arg ,** Dina Mendonça
QO 28	**Preparação das formas enantiomericamente puras do ácido 2-azanorbornano-3-exo-carboxílico através de reacções de aza-Diels-Alder assimétricas ,** José Rodriguez-Borges
	QUÍMICA ANALÍTICA
QA 14	**Avaliação de métodos analíticos para determinação de teobromina em presença de cafeína,** Flávio Almeida
QA 15	**Ionic liquid-embedded C18 for solid phase extraction,** Marieta Leite de Castro Passos
QA 16	**¿Es la filtración un problema en la determinación de compuestos orgánicos en aguas?,** Estefania Concha-Graña
QA 17	**Efecto de la presión aplicada al análisis de gases por FT-IR,** Jose Manuel Andrade Garda
QA 18	**Técnicas analíticas para la identificación y caracterización de plásticos de juguetes,** Carmen Moscoso-Perez
QA 19	**Pharmaceutical cocrystallization techniques: advances and challenges.,** Marisa Abreu Rodrigues
QA 20	**Histamine detection by electrochemical sensors employing commercial and non-commercial instrumentation,** Ricarda Torre
QA 21	**Development of a genoassay for the transgenic soybean detection using a surface response methodology,** Maria de Fátima Barroso
QA 22	**Exploring the acetylacetone derivatization for the GDME extraction and determination of formaldehyde,** Rui Miguel Ramos
QA 23	**Modificación de electrodos con dispersiones de nanotubos de carbono en polivinilpirrolidona y su aplicación a la evaluación del contenido de polifenoles en vino,** Antonio Zapardiel Palenzuela
QA 24	**Determinación de microplásticos en mejillones,** Jose Manuel Garda
QA 25	**Merging zones approach in a flow-based platform for the determination of the total protein content in microbiological samples**, Susana Vidigal
	QUÍMICA E AMBIENTE
QAMB 26	**Phenolic compounds concentration by membrane technology from autohydrolysis liquors of paulownia leaves,** Paula Rodríguez Seoane
QAMB 27	**Lead elimination from aqueous solutions using entrapped grape marc in calcium alginate beads,**Benita Cid
QAMB 28	**Validation of a simple method for Sulphur determination in wastes,** Isabel Brás
QAMB 29	**Comparación del poder coagulante/floculante de la simiente de acacia, del quitosano y del sulfato de aluminio para el tratamiento de purines porcinos,** Elena Falqué López
QAMB 30	**Development of a simple, cheap and eco-friendly strategy to reuse PVPP,** Sandrine Dos Santos Ferreira
QAMB 31	**Caracterização de solos florestais queimados ,** Maria João Fernandes
QAMB 32	**Resynthesis of LiCoO2 from discarded lithium-ion cell phone batteries and its electrochemical performance,** Jair Scarminio
QAMB 33	**Children exposure to polycyclic aromatic hydrocarbons at school environments: Exposure levels and health risks,** Marta Oliveira
QAMB 34	**Determinación de elementos traza en muestras de agua de la ría de vigo (no españa),** Elena Falqué López
QAMB 35	**Monitoramento de grupos funcionais oxigenados na superfície de hydrochars por espectroscopia no infravermelho,** Flávio de Almeida

QAMB 36	**Fotocatálise heterogénea usando UV-LEDs e TiO2 imobilizado aplicada ao tratamento de efluentes agro-industriais,** Leonilde Marchão
QAMB 37	**Degradação do ácido oxâmico por ozonização fotocatalítica na presença de nitreto de carbono,** Carla Orge
QAMB 38	**Recovery of Co and Li compounds and resynthesis of LiCoO¬2 from discarded cell phone batteries,** Jair Scarminio
QAMB 39	**Effects of artificial weathering on microplastics of packaging materials,** Carmen Moscoso-Perez
QAMB 40	**PLS-DA model for biomonitoring of Coffea arabica leaves exposed to increased atmospheric CO2,** Gustavo Galo Marcheafave
QAMB 41	**Valorisation of wastes as biosorbents for the simultaneous removal of pharmaceuticals and personal care products,** Antón Puga Pazo
QAMB 42	**Combinação de agentes físico-químicos na degradação de geotêxteis - o projeto GeoSinergismo,** Paulo Almeida

21 NOVEMBRO 2018 - Quarta-feira

	QUÍMICA AGRO-MAR-ALIMENTAR
QAMA 40	**Sweeteners in beverages: occurrence and risk evaluation,** André Monteiro Pereira
QAMA 41	**Comparison of ion exchange resins at industrial scale and enological stabilizers treatments for tartaric stabilization of white Port wine: Impact on wine physicochemical and sensory profile,** Daniela Moreira
QAMA 42	**Rheology of chestnut starch gels with the addition of common biopolymers,** Ramon Moreira
QAMA 43	**ice cream enriched with aqueous extract of thymus citriodorus by-product: phenolic compounds and antioxidant activity evalutation,** Ana Catarina Silva Ferreira
QAMA 44	**Produção e deteção de y-glutamil-S-etenil-cisteína (GEC) em 24 acessos de Vicia narbonensis L.** Marta Amorim
QAMA 45	**Histamine detection by electrochemical sensors employing commercial and non-commercial instrumentation** Ricarda daniela da torre
QAMA 46	**Identificação em vinhos de uma nova família de compostos derivados da cortiça - Corklinas,** Joana Azevedo
QAMA 47	**Vicinal diketones and nitrogenous compounds monitoring during lager beer fermentation: effects of yeast re-pitching,** Ana Cristina Rebola Pereira
QAMA 48	**Evaluation of the phenolic composition and antioxidant and antimicrobial activities of grape (Vitis vinifera L.) stems extracts from the Moscatel variety of different geographic regions,** Irene Pereira Gouvinhas
QAMA 49	**Comparative analysis of sensory properties of French fries made by vacuum and deep fat frying,** Ana Cristina Vilas Boas Correia
QAMA 50	**Nutritional and physicochemical characterization of purple and redfleshed genotypes of potatoes from different geographical regions,** Shirley de Lima Sampaio
QAMA 51	**Optimisation of a method to predict red wine colouring matter instability,** Juliana Milheiro Ferreira
QAMA 52	**Variação anual das famílias de proteínas salivares de diferentes indivíduos,** Susana Isabel Soares
QAMA 53	**Transferencia de metales pesados a Lolium perenne en suelos tratados con purín de vacuno,** Maria Luisa Marcos
QAMA 54	**Comparison between extracts from acacia dealbata link flowers obtained by microwave hydrodiffusion and gravity (mhg) and distillation techniques,** Paula Rodríguez Seoane
QAMA 55	**Water adsorption isotherms of dextrinized potato starches,** Ramon Moreira
QAMA 56	**Structure characterization of water soluble polysaccharides from two species of Cinnamomum,** Maria Filomena de Jesus Raposo
QAMA 57	**Effect of different conservation treatments for unfiltered wort and beer samples during storage,** Ana Cristina Rebola Pereira
QAMA 58	**Macronutrients and secondary metabolites from seeds of coix lachryma-jobi l.: potential prebiotics for ibd complementary treatment,** Thelma de Barros Machado
QAMA 59	**Comparative analysis of phenolic composition from two different oak wood species used for wine aging: (Q. petraea L. and Q. pubescens Willd),** Ana Cristina Vilas Boas Correia
QAMA 60	**Edible macro and microalgae: assessment of chlorophylls and carotenoids ,** Sílvia Bessada
QAMA 61	**Tartrazine determination and quantification in foodstuffs and beverages,** Liliana João Gatões da Silva
QAMA 62	**Hibiscus sabdariffa L. calyces as a source of anthocyanins rich extracts to be used as a natural food colouring agent,** Filipa Sofia Dinis Reis
QAMA 63	**Polycyclic aromatic hydrocarbons levels in commercial meagre fishes,** Marta Madalena Oliveira
QAMA 64	**Low pressure assisted volatile compounds extraction for carbonyl compounds study in coffee beans,** João Rodrigo Santos
	CATÁLISE
CAT 15	**Preparation and characterization of natural and pillared clays for catalytic wet peroxide oxidation of 4 nitrophenol,** Jose Luis Díaz de Tuesta
CAT 16	**Titanate nanotubes/Carbon dots nanocomposites: Advanced materials for photodegradation of organic pollutants ,** José Virgílio Prata
CAT 17	**Michael addition of indole to α,β-unsaturated steroidal ketones as a synthetic route to new bioactive compounds,** Samuel Martins Silvestre

CAT 18	**Materiales de carbono derivados de biomasa implicados en la síntesis de quinoxalinas. Consideraciones mecanísticas,** María Elena Mayoral
CAT 19	**Overview on Calcium diglyceroxide Biodiesel Catalyst,** Ana Paula Dias
CAT 20	**Acidic waste cooking oil valorization by biodiesel synthesis catalyzed by hydrogen sulfate 1-butyl-3-methylimidazolium,** Ana Caroline Baú
CAT 21	**Photoinduced water splitting with a Mn(III) supramolecular box,** Lara Rouco Méndez
CAT 22	**Optimization and kinetic study of esterification reaction of oleic acid using [HMIM]HSO4 as catalyst,** Paulo Miguel Pereira de Brito
CAT 23	**Synthesis, Characterization of TiO2 modified by (P, Mo) (P, W) and (Si, W) co-doping and its visible light photodegradation,** Abderrahim El Mragui
CAT 24	**NiCeAl-LDH/g-C3N4 as photocatalyst for light-driven hydrogen production,** Hanane Boumeriame
CAT 25	**Materiales híbridos de carbono/ZnO en la síntesis verde de heterociclos nitrogenados,** María Elena Mayoral
	SEGURANÇA QUÍMICA
SQ 2	**Correlación entre accidentabilidad y economía en el sector de la construcción y sus efectos en plantas químicas,** Eugenio Muñoz Camacho
	QUÍMICA DOS POLÍMEROS
QP 2	**Study of polymer additives migration on coated wires,** Sandra Cristina de Matos
QP 3	**Micro-structured Fluorescent Powders for Detecting Latent Fingerprints on Different Types of Surfaces ,** Hélio Lopes Barros
QP 4	**Selective capture of beta-pinene by molecularly imprinted polymers: freundlich isotherms obtained by gc-ms,** Humberto Eduardo Ferreira
QP 5	**Análise de Componentes Principais aplicada ao estudo da oxipropilação do resíduo da semente da Araucaria angustifólia,** Stephany Cunha de Rezende
QP 6	**Freundlich isotherms: development of calculation models to determine adsorption of beta-pinene-minus from liquid solutions,** Humberto Eduardo de Carvalho Santos Ferreira
22 NOVEMBRO 2018 - Quinta-feira	
	QUÍMICA E SAÚDE
QS 26	**Bacterial sensitivity metal ion in aqueous solution by microcalorimetric techniques,** José Luis Soto
QS 27	**Chemical and microbiological characterization of Serra da Estrela cheese: A traditional Portuguese dairy product,** Luísa Maria Fontes
QS 28	**Quantification of Bisphenol A in human saliva by HPLC-FD,** Virgínia Maria Ferreira Gonçalves
QS 29	**Síntese e avaliação do potencial de uma cianina esquarílica derivada da indolenina como sonda para deteção da BSA,** Jorge Daniel Marques Machado
QS 30	**Thermal properties of peloids using mineral water from galicia,** José Luis Soto
QS 31	**Bisphosphonate-Based Materials: Development of a 3-in-1 Multidelivery System for Osteoporosis Treatment,** Jéssica Maria da Silva Barbosa
QS 32	**Breast cancer and prostate cancer cell lines as target of benzophenones: in vitro assays,** Djenisa Rocha
QS 33	**D-Pinitol [(1S,2S,4S,5R)-6-metoxiciclohexano-1,2,3,4,5-pentol] de Mimosa caesalpiniifolia para tratamento preventivo de diabetes mellitus,** Marcelo José Dias Silva
QS 34	**Valorisation of scabiosa stellata l.: a medicinal plant that grows wild in algeria,** Diana Pinto
QS 35	**Estudio de la actividad antitumoral de complejos de vanadio con ligandos hidrazona derivados de pyridoxal,** Lucía Mato López
QS 36	**Prostate cancer: antitumor effect of chalcones on androgen-dependent and androgen-independent prostate cancer cell lines,** Bruno Miguel Guedes Horta
QS 37	**A new strategy against malaria – antimalarial ionic liquids derived from aminoquinolines and fatty acids,** Ana Teresa Teixeira da Silva
QS 38	**Envisioning bladder cancer in liquid biopsies by high resolution mass spectrometry,** Joana Cordeiro
QS 39	**Phytochemical analysis and anti-aging activities of compounds from juniperus brevifolia bark,** Ana Maria da Seca
QS 40	**Especiación de complejos de vanadio(v) con ligandos hidrazona derivados de 2,6-diformil-4-metilfenol y estudio de su interacción con el adn,** Lucía Mato López
QS 41	**Pinpointing protein differences between chromophobe renal cell carcinoma and renal oncocytoma,** Susana Jorge
QS 42	**Antioxidant activity of chalcones related to the scavenging of hypochlorous acid,** Thaise Martins
QS 43	**Disposable electrochemical biosensors for early diagnosis of chronic kidney disease,** Marta Neves
QS 44	**Structure-based virtual screening approach to identify alpha-glucosidase inhibitors,** Luísa Amaral
QS 45	**Design and development of a !PAD device for magnesium determination in saliva,** Juliana Isabel Aguiar
QS 46	**Novel 16E-arylidene-5a,6a-epoxydehydroepiandrosterone derivatives: synthesis and cytotoxicity evaluation,** Vanessa Sofia Figueiredo de Brito
QS 47	**Unraveling the splicing events underlaying nasopharyngeal carcinoma progression by label free quantitative mass spectrometry analysis ,** Luis André Carvalho

QS 48	**Tomato glycoalkaloids as new drug candidates: an overview of mechanisms of action and clinical applications,** José Pinela
QS 49	**Enantioseparation of xanthone derivatives of proteinogenic amino acids on cellulose tris(3-chloro-4-methylphenylcarbamate) stationary phase.** , Virgínia Maria Ferreira Gonçalves
QS 50	**Development of in vitro and ex vivo methods for the evaluation of dipeptidyl peptidase-4 activity,** Carina Isabel Coelho Proença
QS 51	**Avaliação in vitro das atividades antioxidante e de inibição da acetilcolinesterase de extratos de Hibiscus sabdariffa,** Ana Clara F M T Grosso
QS 52	**Looking for more active, less toxic antimicrobials ,** Joana Rita Costa
QS 53	**4-Azasteroid derivatives as inhibitors of prostate cells proliferation: study of three-dimensional quantitative structure–activity relationship (3D-QSAR),** Vanessa Sofia de Brito
QS 54	**Enhanced extraction of chlorophylls from Spartina patens and Puccinellia maritima and their potential as photosensitizers,** Maria Vicente Faustino
QS 55	**Effect of heptaphylline and two related secondary metabolites on cervical (HeLa) and prostate (LNCaP and PC-3) cancer cell lines,** Bruno Miguel Guedes Horta
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QUÍMICA

RESUMOS DAS LIÇÕES PLENÁRIAS

Chiral Iodanes for Asymmetric Oxygen-Atom (and Carbon-Atom) Transfer in Biomimetic Dearomative Transformations of Phenols

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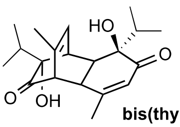
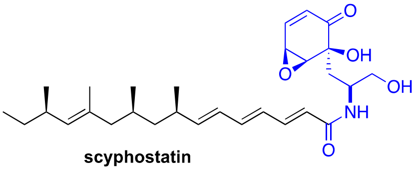
The chemistry of hypervalent organoiodine compounds, also referred to as iodanes, has unarguably experienced an impressive development since the early 1990s, as evidenced by both the diversity of iodane reagents that are available today and the number of chemical transformations that these metal-free reagents can promote.[1] Major current research efforts focus on the design of chiral λ^3- and λ^5-iodane structures for asymmetric synthesis and organoiodine-catalyzed versions thereof.

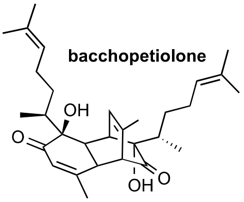
The focal reaction of our own contributions to this field has been the dearomatization of phenols, which constitutes a powerful tactic for the rapid construction of highly functionalized molecular architectures, and often an ultimate key transformation in the biogenesis of numerous natural products.[2] In particular, *ortho*-quinonoid cyclohexa-2,4-dienones can be efficiently generated by iodane-mediated oxygenative phenol dearomatization during which the iodane reagent regioselectively transfers an oxygen atom at a substituted *ortho*-carbon center of an appropriate starting phenol.[2] Novel chiral λ^5-iodanes were developed to control the configuration of this carbon center upon its sp2 to sp3 hybridization change, and these reagents were successfully utilized in the asymmetric and biomimetic synthesis of, inter alia, bis(thymol), bacchopetiolone, and the polar head of scyphostatin.[3]



bis(thymol)



scyphostatin



bacchopetiolone

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Materiales de carbono a partir de lignina. Carbon materials from lignin

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En las últimas décadas el estudio sobre el aprovechamiento de la lignina ha experimentado un gran aumento debido, en parte, al desarrollo de una industria paralela a la ya tradicional de producción de pasta para papel, como es el caso de la biorrefineria que usa como materia prima productos lignocelulósicos. La lignina es el segundo polímero natural en abundancia después de la celulosa y el primero si se considera como fuente renovable de productos aromáticos. La mayor parte de la lignina que se produce en el mundo es como co-producto en la industria de pasta para papel, siendo el proceso kraft el más ampliamente usado. El uso más común de la lignina es quemarla, una vez evaporadas las lejías negras, en las propias plantas de pasta para papel, para recuperar los reactivos químicos de las cenizas de combustión al tiempo que se aprovecha la energía generada en la propia planta. La obtención de productos químicos renovables, bicombustibles y materiales de alto valor añadido, a partir de lignina, puede ser esencial para el desarrollo integral del concepto de biorrefineria. En este sentido, nuestro grupo de investigación ha sido pionero en el estudio de distintas vías de aprovechamiento de la lignina, preparando diversos materiales de carbón a partir de diferentes tipos de lignina [1,2]. Así, se han preparado carbones activos, tamices moleculares, carbones con alto grado de ordenamiento, materiales carbonosos con porosidad jerarquizada por nanomoldeo, fibras y tubos de carbón etc. Los métodos de preparación de estos materiales, su caracterización y funcionalización, así como algunas aplicaciones de los mismos constituyen los objetivos de este trabajo que se presenta en este Encontro Luso Galego de Química.

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NanOmics: From sythensis to Environmental and Biomedical Applications

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The traditional classification of the Chemistry field divides the mother of Science into small pieces such as Analytical Chemistry, Inorganic Chemistry, Organic Chemistry, Chemical Engineering, Physical Chemistry, Biochemistry, Medicinal Chemistry, Nanochemistry among others. However, nowadays, this division is nonsense, because the current research world is made on connections to other complementary fields such as biology, geology, medicine, leading more interdisciplinary research, with multifunctional applications and the most important one, based on collaborations. In two simple words, we could speak about a modern translational chemistry. In connection with this idea of multifunctional applied research, our team has been involved during the last ten years in different research project developing new connections between the synthesis of nanomaterials, dyes, and sensors, with applications in the fields of biomedicine, biochemistry, environmental toxicology, and bioanalytics. From the detection of metals, anions, to imaging the delivery of drugs, to the OMICS (Proteomics, Genomics, and Metallomics) studies to personalize medicine. In this talk, I will overview our research with different systems and case studies developed in recent years with applications in biomedicine, proteomics, and environmental fields.

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Ética e integridad en la investigación en química

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La integridad en la práctica científica es un presupuesto esencial para el progreso y avance de la ciencia. Las malas prácticas científicas como pueden ser la fabricación, la falsificación y el plagio, así como otra serie de conductas cuestionables son claramente perjudiciales para la investigación, se traducen en la pérdida de confianza entre científicos así como entre estos y la sociedad, y dañan la imagen pública de la ciencia. Los agentes implicados, investigadores, instituciones y agencias financiadoras deben potenciar la integridad en la investigación mediante la formulación y el cumplimiento de códigos de conducta. En esta conferencia, tras unas breves consideraciones sobre ética y química, se abordarán las malas prácticas científicas, sus causas, incidencia, y efectos, así como algunas iniciativas planteadas a nivel institucional e internacional para promocionar la integridad científica. A lo largo de la conferencia, se incidirá en los aspectos mas relacionados con la química.

Polysaccharides chemistry: from food to food applications

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Chitosan, a polysaccharide with animal and fungi origin, composed by (β1→4)-GlcN residues, and pectic polysaccharides, derived from plant cell walls, composed by (α1→4)-GalA repeating units, are examples of polysaccharides with chemical peculiarities that can be used as the basis of novel food applications. These polysaccharides, usually available as food industry by-products, can be used for the replacement of the use of sulfur dioxide in beverages preservation and for the acrylamide mitigation in biscuits. Chitosan, due to its nontoxicity, biocompatibility, and antimicrobial properties, is able to form edible films. Therefore, chitosan becomes a suitable candidate for a wide range of beverage applications including clarification, preservation, encapsulation, and packaging [1]. However, for food applications, the use of chitosan in the form of films has been limited due to their high degradability in aqueous acidic media and low resistance. To overcome this limitation, the cross-linking of chitosan with genipin, a natural and non-cytotoxic compound extracted from gardenia fruit, has been proposed, enhancing the films mechanical strength and chemical stability, rendering them practically insoluble in acidic aqueous solutions [2]. This allows to exploit chitosan antimicrobial and antioxidant properties for wine preservation as an alternative to the use of sulfur dioxide [3].

Polymeric sugar acid structures, like those present in pectic polysaccharides, having a high ratio of carboxylic groups in relation to the reducing end, has been shown to provide the required medium acidity to minimize the formation of acrylamide in cooked foods. Although relevant for all diets, this property is even more important for fructose-rich foods, such as the biscuits eaten by diabetics, where the content of acrylamide formed is usually high. As the main route for acrylamide formation is the reaction between reducing sugars and asparagine, this reaction is minimized at low pH. These conditions can be provided by deesterified and purified pectic polysaccharides without contributing to the sour taste usually associated with acid foods [4].

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QUÍMICA

RESUMOS DAS COMUNICAÇÕES POR ÁREA

Bio-guided fractionation of extracts of Geranium molle L.: relationship between phenolic profile and biological activity

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Geranium molle L. (Fig. 1) has been used in the Portuguese folk medicine for the treatment of various ailments including cancer [1]. However, contrary to many *Geranium* species, the bioactivity and the phytochemical composition of *G. molle* are virtually unexplored.

The first phase of this study consisted in the chemical characterization (nutritional value, free sugars, organic acids, fatty acids and tocopherols) of a *G. molle* sample from Trás-os-Montes, north-eastern Portugal. The bioactive properties of infusion and decoction (common forms of consumption) and of different organic extracts obtained by sequential extraction were also evaluated. *G. molle* was shown to be rich in carbohydrates and proteins, providing tocopherols and essential fatty acids. Amongst the various extracts, the acetone extract was found to have the highest content of phenolic compounds as well as the highest antioxidant and cytotoxic activities [2].

Following this preliminary evaluation, the most active extracts (acetone and methanol) were fractionated by column chromatography and the resulting fractions were evaluated for their antioxidant and cytotoxic activities. The bio-guided fractionation of the extracts resulted in several fractions with improved bioactivity in comparison with the corresponding crude extracts. The fractions obtained from the acetone extract consistently displayed the lowest EC_{50} and GI_{50} values and presented the highest content of total phenolic compounds. The phytochemical composition of the most bioactive fractions of the acetone and methanol extracts was included about thirty identified compounds, mainly flavonoids and phenolic acids, which could be identified for the first time in *G. molle* [3].

Fig.1 Geranium molle L.

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Evaluation of antioxidant function in liver samples collected in young and middle age animals subject to a plan of daily physical exercise

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The active and regular practice of physical exercise has a beneficial influence on the human healthy. According to the WHO, adults aged 18–64 should do at least 150 minutes of moderate-intensity aerobic physical activity throughout the week or do at least 75 minutes of vigorous-intensity aerobic physical activity throughout the week or a combination of moderate and vigorous intensity activity [1]. A correct prescription of exercise allows an extension of the functional limitation of the organism, producing a modulation of the homeostasis as a result of the adaptation to this physical activity. Factors such as age and sedentary lifestyle seem to have the opposite effect. In this way, physical exercise can work preventively on the damages associated with these factors and thus cause a decrease in the appearance of diseases related to these factors [2,3].

This study aims to determine if this daily exercise plan performed in young animals (32 weeks of life) and middle age (62 weeks of life) are cable to promote hepatic physiological changes both in antioxidant system and mitochondrial. Liver samples from 28 male Wistar rats were randomly distributed into two groups: non-exercised or exercised, submitted to a treadmill exercise program (5 days / week, 30 minutes / day at a speed in cm/m defined at the beginning of each month by performing a stress test) for 24 or 54 weeks.

Clinical biomarkers of liver damage (albumin, total protein, ALT, TG) show no liver injury. Oxidative stress biomarkers (lipid peroxidation and GSH/GSSG) show that young animals suffer oxidative stress at lipid and GSH levels, contrarily to middle aged animals. This may result from an adaptive response to the exercise program carried out. Antioxidant enzymes (SOD, CAT, GR, GPx, GST) show an increased activity in middle age animals compared to the young animals. This may result as a consequence of the aging process. The plan of physical exercise performed caused an increase in the first line defence antioxidants (SOD and CAT), while GPx and GST shows a slight but significant decrease. For GR, there were no significant differences. The aging process show a direct effect on complex I of mitochondria electron transporter chain, resulting in an increased of the enzymatic activity of this complex. Otherwise, complex II an IV weren't affected by aging. Physical exercise shows a significant increase in complex I related with age, contrarily to complex II and IV, which shows a slight decrease. This shows that the complex I responds differently from complex II and IV, to the aging process and to physical exercise. Regarding cell O_2 consumption, data shows that complex I and II are stimulated in both ages. These results confirm that the exercise may somehow model the redox status of hepatocyte and mitochondrial function, although age seems to be more relevant.

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Honey biomimetic fructo-oligosaccharides production by nonenzymatic reactions

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Fructo-oligosaccharides (FOS) are fructose containing oligosaccharides with D-fructose residues mostly linked by (β2→1) linkages, being considered prebiotic compounds, with several functional proprieties. Due to these proprieties, FOS became highly important at a commercial level, emerging the interest of increasing its production with purity in an economically competitive way. FOS can be produces through the inulin hydrolysis, transfructosylation reactions using enzymes or microorganisms, and more recently non-enzymatic transglycosylation reactions, similarly to what occurs in honey. Model solutions showed the occurrence of oligosaccharide synthesis without the intervention of enzymes, showing that honey oligosaccharides may result from nonenzymatic reactions using the beehive temperature conditions (35ºC). The FOS inulobiose [Fru(β2→1)Fru] and blastose Fru(β2→6)Glc] were identified in all model solutions, whereas 1-kestose [Fru(β2→1)Fru(β2↔α1)Glc] and neokestose [Fru(β2→6)Glc(α1↔β2)Fru] were present in all samples except in solutions at pH 2.0. Moreover, maltose, isomaltose, sophorose, gentiobiose, cellobiose, panose, and inulotriose were also identified in some model solutions. Some of these oligosaccharides such as 1-kestose, neokestose, panose [1], inulobiose, inulotriose and blastose [2] are reported to have prebiotic effect.

The present work aims to produce honey-like FOS at different temperatures (35, 60, and 80ºC) through transglycosylation reactions in sucrose and fructose solutions. Their purification was achieved using activated charcoal. The solutions were prepared with 20 g Suc:Fru (1:3) in water, evaporated until 16.7%, and kept at 35ºC, 60ºC e 80ºC. The temperature of 35ºC simulates the hive conditions [3] and the temperatures of 60ºC and 80ºC were used to observe their influence in FOS production.

FOS were produced and quantified by gas chromatography coupled with mass spectrometry (GC-MS) after oligosaccharide derivatization as alditol acetates, without acid hydrolysis. The FOS produced in higher extend were inulobiose, kestose, and blastose. At 35ºC, the beehive temperature, after 1 month, inulobiose (0.04% of total sugars) and kestose (0.05%) were formed. At a temperature of 60ºC, only after two weeks, the amount of inulobiose, kestose, and blastose increased to 0.85%, 0.49%, and 0.37%, respectively. For a temperature of 80ºC, in 1 week, a higher yield of inulobiose, kestose, and blastose were obtained, reaching 4.1%, 0.19%, and 0.5%, respectively, showing that the process of FOS production using nonenzymatic transglycosylation reactions was more effective at 80ºC. However, at 60ºC the formation of high amounts of dehydrated sugars are avoided.

It was possible to produce in an easy and economical way, via nonenzymatic production, honey biomimetic fructo-oligosaccharides with reported prebiotic effects.

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Ganoderma lucidum as a promising ingredient for cosmeceutical application: safety assessment and *in vitro* skin permeation studies

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As the global cosmetic market continues to grow steadily, there is a continuous demand for product diversification resulting in the emergence of products with different claims and functional properties [1]. Because of the rising consciousness and awareness among consumers about the origin, safety and environmental implications of some of the ingredients used in cosmetic formulations, there is an increasing demand for the use of green and more sustainable raw materials during product formulation. Mushrooms are globally consumed not only because of their nutritional properties but also for their medicinal potential and more recently their utilisation as cosmeceutical ingredients due to their richness in several bioactive compounds [1]. In the present study, the *Ganoderma lucidum* ethanolic extract was evaluated for antioxidant, anti-inflammatory, anti-tyrosinase, antimicrobial and cytotoxic effects, and further characterized in terms of phenolic acids and triterpenoids using HPLC-DAD-ESI/MSn. The obtained extract was incorporated in a base cosmetic cream to ascertain bioactive properties sustainment. The extract and its corresponding formulation were further submitted to *in vitro* safety evaluation using MTT and LDH assays in Keratinocyte (HaCaT) and Fibroblast (HFF-1) cell lines and, also *in vitro* skin permeation studies using a Franz diffusion apparatus with pig ear skin as permeation membrane. Ganoderic acids C2 (38.7±0.2 mg/g), A (36.77±0.04 mg/g) and H (41.1±0.4 mg/g) were the most abundant triterpenic acids in the extract, and protocatechuic, *p*-hydroxybenzoic and syringic acids were the identified phenolic acids. Anti-inflammatory activity (EC_{50},112±1 μg/mL), anti-tyrosinase activity (EC_{50}, 2.81±0.01 mg/mL) and broad-spectrum antimicrobial activity (MICs up to 20 mg/mL) were observed for the extract. Cell viability of HaCaT and HFF-1 cells were maintained at 100 μg/mL extract exposure, but a ~50% decrease was observed in the cell viability of both cell lines after exposure to the final formulation. The cumulative amounts of triterpenoids and phenolic acids that penetrated the *stratum corneum* and epidermis-dermis (i.e. target sites) after 8h detected by HPLC-DAD-ESI/MSn indicate lower mean concentration in the receptor chamber, while a reduction in bioactives concentration in the donor compartment showed that compounds might be retained in skin layers. The results showed promising cosmeceutical properties of the ethanolic extract obtained from *G. lucidum*.

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Disclosing the occurrence of (β1→3) and (β1→4) mixed-linkage β-glucan in yeast cell wall

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Saccharomyces yeast cell wall is a layered network of **β**-glucans, mannoproteins and chitin that determines the cellular morphology and integrity during cell growth, division and under stress conditions. The Saccharomyces cell wall glucans are generally described as (**β**1→3), (1**β**→6)-and (**α**1→4)-linked glucans [1]. Recently, it was reported the presence of (**β**1→4)-linkages in brewing yeast *Saccharomyces pastorianus* cell wall glucans. Moreover, *S. pastorianus* cell wall showed to be a dynamic structure that modifies as response to the fermentative stress conditions, increasing both **α**- and **β**-(1→4)-linked glucans [2]. Despite the essential role for the occurrence of these linkages for the yeast tolerance during the brewing process [3], it is important to disclose the structure of these glucans for further relate with their function to the cell.

As the structural analysis of the yeast glucans is hampered by their insolubility, in this study the alkali insoluble (8M KOH) *S. pastorianus* glucans were hydrolysed with an endo-1,3-β-D-Glucanase (Zymolyase) and further with an endo-1,3:1,4-β-D-Glucanase (Lichenase). The hydrolysates were further fractionated by BioGel P2 size exclusion chromatography (SEC-P2). The eluted fractions from SEC-P2 were analysed with evaporative light scattering detection, and the glycosidic-linkage composition of representative molecular weight fractions was determined as partially methylated alditol acetates by gas chromatography-quadrupole mass spectrometry (GC-qMS).

Oligosaccharides produced with the hydrolysis of (**β**1→3)-linked glucan with zymolyase showed different molar ratios of Glc linkages and the main linkage observed was (1→4)-Glc. This result suggests that the hydrolysis of endo (**β**1→3)-Glc linkages produces oligosaccharides with (**β**1→3) and (1→4)-Glc that could occur as mixed linkages. To support this evidence, *S. pastorianus* cell wall glucans were hydrolysed with Lichenase, an endohydrolase that has the ability to cleave all (**β**1→4)-bonds that immediately follows (**β**1→3) linkages. It does not hydrolyze homopolymers of (1→3)-β-D-glucans nor (1→4)-β-D-glucans. Size-exclusion chromatography of lichenase hydrolysate showed a chromatographic profile consistent with the main presence of tetrasaccharides (DP4), with no signal for the DP2/DP1 retention times. This result confirms that *S. pastorianus* cell wall (1→3)-β-D-glucans are not a homopolymer, as reported and accepted in yeast cell wall general structure, but mixed with (**β**1→4)-Glc residues.

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Simultaneous dehydration and extraction of broccoli by-products by microwave hydrodiffusion and gravity

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In the frozen-food industry of broccoli, stalks, leaves, and inflorescences remains account for 45% of the initial broccoli heads, resulting in a large amount of by-products with low economic value and considerably high environmental impact. In turn, broccoli by-products have high nutritional value and are rich in bioactive compounds such as glucosinolates, phenolic acids, flavonoids, and polysaccharides that act as dietary fibre [1]. These should be studied and valuated. However, due to their high moisture content, the valorisation requires stabilization to inhibit enzymes, prevent microbial growth, and degradation of the product [2]. Moreover, the selection of processing techniques should consider the bioactive compounds of interest. Therefore, in this study, broccoli by-products were stabilized by dehydration using microwave hydrodiffusion and gravity (MHG), a technology that allows the simultaneous dehydration and recovery of the water-soluble diffused compounds [3]. Moreover, MHG impact on carbohydrates extraction was evaluated by six boiling water sequential extractions of 1 h each, applied to the remaining dehydrated broccoli by-products (dBB), and for comparison, also applied to the initial broccoli by-products (iBB).

The hydrodiffusion allowed to obtain a dried material with 12% moisture in 43 min when 550 g of broccoli by-products were used. Diffused water contained up to 317 μg/mL gallic acid equivalents of phenolic compounds, 11 mg/mL free sugars, 9 mg/mL amino acids, and 356 μg/mL glucosinolates, depending on the type of by-product used. Further carbohydrate extraction of dBB reached higher yields in comparison with iBB. Beyond free glucose and fructose, a total of 76% of dBB pectic polysaccharides were extracted, whereas only 60% of pectic polysaccharides were extracted from iBB.

This work shows the potential of MHG for dehydration of broccoli by-products, allowing their stabilization while recovering water-soluble compounds by diffusion. Additionally, the MHG dehydration works as a pre-treatment that improves the extraction of polysaccharides. Water-soluble material recovered by diffusion and boiling water extraction, rich in free sugars and pectic polysaccharides, respectively, may be valuable as ingredients for food applications. These results indicate that MHG technology has potential to be used for industrial by-products stabilization and further valorisation.

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Purification platform for monoclonal antibodies based on aqueous biphasic systems formed by glycine-betaine ionic liquids

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The production of monoclonal antibodies (mAbs) has been firstly described in 1975, by Köhler and Milstein [1]. Since then, their therapeutic role in the treatment of several diseases has been demonstrated, being in some cases the only available therapy [2]. Currently, they are produced through well-developed biological processes, shifting the bottleneck to the downstream processing. Protein A affinity chromatography is the "gold standard" of the pharmaceutical industry to purify mAbs. However, it is an extremely expensive technique, covering up to 80% of the mAbs global production costs [2]. As an alternative technique, ionic-liquid-based aqueous biphasic systems (IL-based ABS) can be foreseen as promising alternatives for the mAbs downstream processing. However, ABS imidazolium-based ILs are the most investigated systems, which may raise some toxicity and biodegradability concerns [3].

In this work, novel ABS formed by glycine-betaine analogous ILs (AGB-ILs) and K_2HPO_4/KH_2PO_4 at pH 7 were studied to develop novel purification routes for mAbs, directly from cell culture supernatants. These AGB-ILs are prevenient from a natural and renewable source and are non-toxic, thus giving a biocompatible and greener character to the process [4]. The phase diagrams and tie-lines of ABS composed of AGB-ILs and phosphate buffer at pH 7 were firstly characterized at 25 ºC and atmospheric pressure. Based on the obtained results, it was found that the ability trend of the AGB-ILs to form two-phase systems is in accordance with their Kamlet Taft (KT) solvatochromic parameters, in particular with their hydrogen-bond basicity. Then, these systems performance for the extraction and purification of anti-human interleukin-8 (anti-IL-8) mAbs directly from Chinese Hamster Ovary (CHO) cell culture supernatants was evaluated. Recovery yields ranging from 20 to 100% were obtained, with purification factors up to 1.6 in a single-step. Moreover, the purification factor can be increased up to 3.5 by using higher concentrations of IL and in the framework of a three-phase partitioning approach, in which mAbs can be recovered in the solid state at the interface of the ABS.

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Nutritional and chemical characterization of fruits and stems of *Lycium barbarum* L.

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The consumption of red berries has increased considerably in recent years. The fruits of *Lycium barbarum* L., traditionally known as goji are associated with health benefits in the liver, kidney, vision, and immune functions, but also in the circulatory system and longevity [1].

In the present study, the fruits and stems of *L. barbarum* were characterized for their nutritional profile (AOAC procedures), free sugars (HPLC-RI), fatty acids (GC-FID), organic acids (UFLC-PDA), tocopherols (HPLC-FP) and phenolic compounds (LC-DAD-ESI/MS).

Carbohydrates were the most abundant macronutrient found in fruits and stems (87 and 78.1 g/100 g dw, respectively). The stems also presented the highest levels of ash, protein and fat (9.9, 7.4 and 4.6 g/100 g dw, respectively), while the fruits had protein as the second main macronutrient (5.3 g/100 g dw), followed by fat and ash (4.1 and 3.21 g/100 g dry weight, respectively).

Glucose was the most abundant sugar found in both samples, followed by fructose and sucrose. As expected, the fruits had higher content in sugars (27.9 g/100 g dw) than the stems (1.08 g/100 g dw).

Regarding organic acids, the samples showed different profiles, while fruits revealed citric, succinic and oxalic acids (1.29, 0.77 and 0.010 g/100 g dw, respectively) as the main compounds, malic, oxalic and quinic acids (0.899, 0.65 and 0.53 g/100 g dw, respectively) were the major ones found in stems. Oxalic acid was the only common organic acid found in both samples.

Polyunsaturated fatty acids (PUFA) predominated in the fruit samples due to the presence of high levels of linoleic acid (53.4%), while in the stems saturated fatty acids (SFA) predominated with very similar percentages of palmitic (15.94%) and lignoceric (15.3%) acids.

The highest tocopherols content was determined in the stems (3.59 mg/100 g dw), mainly due to the presence of α-tocopherol (3.37 mg/100g dw).

Sixteen phenolic compounds were identified in goji fruits, while eleven compounds were detected in the stems. Quercetin-3-*O*-rutinoside was the major phenolic compound in stems (48 mg/g dw) and fruits (16.6 mg/g dw), followed in these latter case by *p*-coumaric acid (12.3 mg/g extract).

This study demonstrates the high potential of goji stems and fruits as sources of bioactive compounds, which could be used in nutritional formulations, or incorporated into foods with functional properties.

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Influência de ambientes lipídicos na interação de polifenois em modelos de membranas: impacto na adstrigência oral

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É sabido que os polifenóis presentes em frutos e vegetais são responsáveis por propriedades sensoriais de cor e sabor [1,2]. Sob o ponto de vista do consumidor, a cor confere uma característica apelativa aos alimentos incentivando o seu consumo, por outro lado o sabor adstringente associado a alguns alimentos condiciona o consumo de certos alimentos e bebidas. Na tentativa de desenvolver alimentos funcionais a indústria alimentar tem tido alguns desafios em reduzir ou eliminar a adstringência de alimentos e ao mesmo tempo manter as propriedades benéficas à saúde associadas aos polifenóis.

No sentido de melhorar a nossa compreensão acerca dos mecanismos moleculares responsáveis pela modulação da adstringência na mucosa oral, foram realizadas experiências de interação de polifenóis em modelos de membrana celular por fluorescência. As medições de fluorescência foram realizadas utilizando os polifenóis epicatequina-galato (ECG), a epigalocatequina galato (EGCG), a procianidina B4 e a pentagalloil-glucose (PGG) em condições de pH e temperatura que mimetizam as condições orais aquando da ingestão de bebidas. Os modelos de membrana celular foram construídos com variações de teor de colesterol ($0.34<\chi_{chol}<0.74$) mimetizando deste modo a composição lipídica das diferentes regiões da mucosa oral.

Os resultados de fluorescência obtidos mostram que a interação de polifenois com lípidos em modelos de membrana é influenciada pela estrutura (hidrofobicidade) e concentração do polifenol, e ainda pelo teor de colesterol que compõe a membrana lipidica. Com base no cálculo das constantes de partição (Kp) estimadas a partir dos dados de fluorescência, verifica-se uma menor interação do polifenol com um aumento no teor de colesterol (χ_{chol}). Estes dados sugerem que durante a ingestão de polifenóis adstringentes estes são percecionados de maneira distinta nas diferentes regiões da mucosa oral.

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Homogeneous and heterogeneous photocatalytic activation of PMS and PS for wastewater disinfection

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Advanced Oxidation Processes (AOPs) are emerging as effective alternative water treatments, for disinfection or oxidation of pollutants. Sulfate radical based-AOPs (SR-AOPs) involve the application of chemical oxidants as persulfate (PS) and peroxymonosulfate (PMS) anions. These substances alone do not present disinfectant activity at low dosages, but their action is significantly increased by: i) heat; ii) UV-radiation; and/or iii) the addition of a transition metal [1].

The goal of this study is the assessment of the efficiency of different homogeneous and heterogeneous iron species [Fe(II), Fe-citrate, Fe_2O_3 and Zero-valent iron (ZVI)] as activators of PS and PMS in the inactivation of wild strains of *E.coli* and *Enterococcus sp.* Figure 1 shows the inactivation of *E.coli* and *Enterococcus sp.* using Fe(III)-citrate as activator. This iron complex enhances the efficiency of photolytic activation of PMS and PS. The structural differences between both bacteria lead to dissimilar resistance to the treatments, being *E.coli* more easily removed than *Enterococcus sp*. In nearly all cases, the synergies between the different agents allow to maximize the bacteria inactivation with the minimum addition of reagents. However, coupling of nZVI with PMS and PS improved the inactivation of *E.coli, but not* of *Enterococcus sp.*

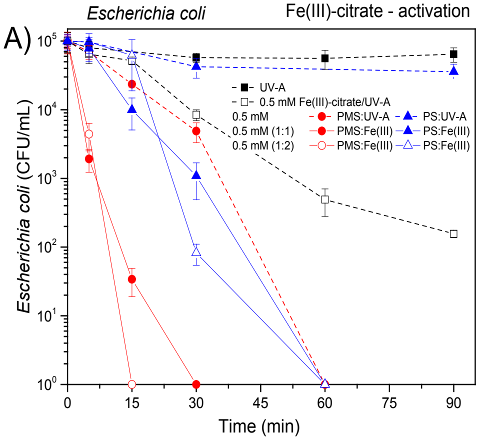

Figure 1. Fe(III)-citrate catalytic activation of PMS and PS coupled with UV-A radiation for A) *Escherichia coli* and B) *Enterococcus sp.* inactivation.

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Atividade neuro-protetora e anti-inflamatória produzida por extratos de C. *ficifolia*

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A *Cucurbita ficifolia* Bouché (Abóbora chila) é originária do méxico, contudo hoje encontra-se dispersa por vários pontos do globo, entre eles Portugal. Nos países de onde é originária, tem sido utilizada para fins medicinais, no tratamento de diabetes tipo 2, de feridas e no tratamento de febre, sendo também utilizada na alimentação humana principalmente na preparação de doces cristalizados e de sobremesas. Verificamos que os extratos hidro-etanólicos e respetiva fração metanólica e aquosa desta abóbora são ricos em compostos polifenólicos e em açúcares. Contendo os extratos da casca maior teor em compostos fenólicos que os extratos da polpa.

O nosso objetivo foi a verificação de diferentes bioatividades destes extratos a concentrações não citotóxicas, através de ensaios de inibição enzimática in vitro, das enzimas: α-Amilase, Acetilcolinesterase e Elastase, cujas atividades podem ser correlacionadas com propriedades anti-diabéticas, neuro-protetores e anti-envelhecimento, respetivamente. Foi ainda objetivo deste trabalho, a quantificação de óxido nítrico (NO), pelo método de Griesse, avaliando-se a atividade anti-inflamatória destes extratos pela exposiçao da linha celular Raw 264.7 (linha derivada de macrófagos de murganho), na presença de lipopolissacarídeo (LPS).

A ação inibitória dos extratos nas diferentes enzimas, foi feita usando os extratos hidro-etanólicos (polpa e casca) e respetivas frações (aquosa e metanólica), a várias concentrações entre 37,5 μg/mL a 300 μg/mL. Na avaliação da atividade anti-inflamatória, fez-se a avaliação citotóxica nas células Raw 264.7 e usaram-se concentrações não citotóxicas (20 μg/mL a 200 μg/mL), que foram expostas durante 24 horas.

Verificamos que há um efeito dose-resposta da inibição das enzimas acetilcolinestase e elastase, o que não se verificou na inibição da enzima α-amilase, onde praticamente não há inibição. Na atividade anti-inflamatória, também verificamos efeito dose-resposta dos extratos, havendo uma diminuição da produção de NO.

Os resultados permitem concluir que estes extratos possuem propriedades neuroprotetoras e anti-inflamatórias, dando crédito a este alimento como alimento funcional.

Volatiles and α- and β-acids: comparative analysis of hops clones, spontaneous and cultivars, in Bragança region

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Humulus lupulus L. is a member of the family Cannabaceae. Hop, as it is commonly known, is a perennial, dioecious and diploid herbaceous plant. It is in brewing that reveal its greatest economic value[1].

The demand for new aromas has increased, driven by the expansion of artisanal beer production in Portugal. **α** and **β**-Acids are responsible for the bitter aromas of beer[2]. Volatiles and acids,from spontaneous hops in the Bragança area were analyzed and compared with commercial varieties (Nugget, Cascade and Chinook).

The samples were collected in different areas of Bragança. Volatiles were extracted from the female cones, using a Likens-Nickerson system, and analyzed by GC and GC-MS. The **α** and **β**-acids, from varieties and from spontaneous, were extracted and analyzed by HPLC.

Nugget (bitter) and spontaneous clone showed similarities in the monoterpene component, with **β**-myrcene as the major compound (75 and 64%, respectively in the Nugget and spontaneous) and significant differences in the sesquiterpene component (12% cultivar, 0.2% spontaneous) and trans-**β**-farnesene (not detected in the Nugget, and 9% in the spontaneous). Noteworthy is the greater richness of the sesquiterpene fraction of the spontaneous clone, in particular in the oxygenated compounds. Regarding HPLC analyses samples of the cultivar (Nugget), were compared with samples from spontaneous. The cultivars showed values of 12.12% and 14.33% of **α**-acids and 3.31% and 3.99% of **β** acids, respectively, while the spontaneous has 5.35% of **α**-acids and 4.3% of **β**-acids.

Comparing the tested Cultivars from the range of aromas with the spontaneous,we found that the values of monoterpenes are maintained as well as the majority compound that remains the **β**-myrcene (67.5% for Cascade and 61.3% for Chinook), but in the sesquiterpene component (8.5% in the spontaneous and 6.4% in Cascade and not detected in Chinook) and **α**-humulene (12.5% in Chinook, 4.9% in Cascade and 0.2% in spontaneous), maintaining the great difference between the cultivars and the clone in the oxygenated sesquiterpene component (0.9% in Chinook, zero in Cascade and 2.4 % in the clone)

The higher values, in the cultivars, of the **α** and **β**-acids component is expected since the Nugget cultivar is characterized by a bitter taste, due to acids, whereas the aroma cultivars, which are more required by the artisan brewers, are valued for their richness in aromas (essential oils), the richness of the spontaneous in trans-**β**-farnesene being determinant to the stability of the beer.

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Evaluation of antioxidant fuction at renal level in response to chronic exercise and age

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Aging and sedentary lifestyle cause a depletion of the endogenous antioxidants, causing an increase in oxidative damage due to the stress generated by the reactive oxygen species (ROS). The increase of ROS leads to cellular oxidative stress that is linked to numerous diseases. Physical exercise attenuates the decrease in antioxidant defenses that normally occurs with aging. Thus, moderate intensity exercise may have a significant benefit in older populations by delaying the loss of antioxidants, which are required to cope with the daily production of reactive oxygen species [1].

In addition to beneficial effects to oxidative stress, physical activity has shown effects on cardiorespiratory and immunological functions, insulin regulation and metabolic syndrome [2] and has a great influence on chronic diseases, including diabetes mellitus, cancer, obesity, bone and articular diseases [3]. To date, no study has evaluated the impact of lifelong physical activity and only a limited number of studies have focused on the molecular mechanisms regulated by physical activity.

This study aims to analise the function of the renal antioxidant system in response to a daily exercise plan in young rats (32 weeks of life) and middle age (62 weeks of life) through the evaluation of oxidative stress parameters. We used kidney samples from 28 male Wistar rats randomly assigned to two non-exercised or exercised groups submitted to a treadmill running exercise plan (5 days / week, 60 min / day at a rate in cm / m defined at the beginning of each month by performing a stress test) for 24 or 54 weeks.

The results obtained for the antioxidant enzymes show that catalase had a significant decrease in activity in older animals whereas glutathione peroxidase had an increase in these animals. On the other hand, superoxide dismutase and glutathione reductase had a significant decrease in middle age animals that were not exercised. Regarding lipid peroxidation, we have observed that there is a significant decrease in the older animals. For thiols content there is a decrease in the concentration of GSH over time even in the exercised animals, but the same does not happen in the concentration of GSSG, with an increase in oxidized glutathione over time.

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Evaluation of the bactericide and bacteriostatic activity of biosurfactant obtained from corn steep water on *Escherichia Coli.*

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In recent years, the increasing demand by consumers of the utilization of biodegradable and biocompatible ingredients and additives in food formulations has led the food industry to improve in the search of more natural compounds. Among them, biosurfactants, which are obtained by microbial production, are gaining interest as natural detergents. In comparison to surfactants produced by chemical synthesis, biosurfactants have the advantage to be more biocompatible due to their polymeric structure composed of lipids, proteins and/or sugars. Moreover, agroindustrial wastes have proven to be an important source for the extraction of biosurfactants, such as corn steep liquor (CSL), an aqueous stream from the corn-milling industry [1], where *Bacillus* species are responsible for the production of biosurfactants. In addition, previous studies [2,3] have shown the antimicrobial ability of biosurfactants against pathogens, an important area of interest in the food industry, in order to avoid microbial contaminations [4].

In the present study, a biosurfactant extract obtained from CSL has been used to assess its bactericide and bacteriostatic capacity against *Escherichia coli*, a bacterial food pathogen that can produce adverse effects on humans. A liquid-liquid extraction with ethyl acetate, an organic solvent which utilization is allowed in the food industry by the European Union (EU) [5], was carried out to obtain the biosurfactant extract.

Results showed that concentrations of biosurfactant lower that 1 g/L were able to inhibit the growth of *E.coli* around 100 % after 24 h, thus proving its antimicrobial capacity. Therefore, this biosurfactant extract obtained from CSL can be used in several applications in the food, cosmetic and pharmaceutical industries.

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Estudio de interacción de gliadinas con la procianidina B3 y proteasas digestivas. Efecto sobre la inmunogenicidad y digestibilidad del gluten

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La modificación enzimática de proteínas de trigo durante la digestión humana está estrechamente relacionada con la inmunogenicidad del gluten[1]. De hecho, las proteínas del gluten son ricas en residuos de prolina y glutamina y esta característica las hace resistentes a la proteólisis[1]. Como consecuencia, grandes péptidos promueven reacciones de estrés oxidativo en las células epiteliales del intestino concluyendo en el desarrollo de lesiones en la mucosa intestinal. Además, la interacción con otros componentes de la dieta, como los polifenoles de los alimentos, podría cambiar las propiedades fisicoquímicas e inmunológicas de las proteínas del gluten. De hecho, los cambios inducidos en la estructura espacial de las proteínas después de la unión con polifenoles y su posterior hidrólisis pueden conducir a un enmascaramiento o degradación de péptidos inmunorreactivos. Del mismo modo, los polifenoles también podrían interferir en la actividad proteolítica y también en los sitios de corte después de la unión de polifenoles del gluten. Por lo tanto, el objetivo principal de este estudio fue dilucidar el efecto de un tanino alimentario comúnmente encontrado en frutas (fresa, cereza) o bebidas como el vino o la cerveza, la procianidina B3, para su posterior evaluación en la digestión de diferentes proteínas del gluten y su consecuente inmunorreactividad. Estudios previos destacaron que los polifenoles son capaces de unirse a las enzimas digestivas[2] y también a las gliadinas a través de interacciones hidrofóbicas, van der walls o puentes de hidrógeno[3]. Si los polifenoles de los alimentos se unen a la enzima digestiva pueden influir en la actividad enzimática y, por otro lado, si los polifenoles de los alimentos son capaces de unirse a las gliadinas, la división enzimática podría ser diferente y concluir en la formación de péptidos distintos. Así, con el objetivo de evaluar en profundidad el efecto global de este sistema ternario de interacción: (1) se realizaron estudios de interacción entre procianidina B3, proteínas de gluten y / o enzimas digestivas por SDS-PAGE, (2) se estudió el efecto en la actividad enzimática a través de espectrometría de extinción de fluorescencia, y (3) se caracterizaron los péptidos inmunogénicos mediante nano-LC-MS / MS y ELISA. En general, se observó una disminución significativa en la inmunogenicidad después de la digestión con procianidina B3. Paralelamente, se demostró que la actividad enzimática no se veía afectada después de la interacción gluten-procianidina B3. Cabe destacar que a pesar de haberse demostrado con anterioridad un efecto inhibitorio de los polifenoles en la actividad enzimática de proteasas. Cuando se trata de una interacción ternaria, el polifenol se une primeramente a las proteínas del gluten permaneciendo bloqueados los lugares de unión posterior a las enzimas digestivas. Del mismo modo, se puede concluir que esta interacción molecular de la procianidina B3 con las proteínas del gluten indujo cambios en los lugares de anclaje de las proteasas digestivas. Estas diferencias promovieron la formación de menor cantidad de péptidos inmunológicos y, por lo tanto, se puede concluir diciendo que la procianidina B3 disminuye el potencial inmunológico de estas proteínas durante la digestión gastrointestinal.

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Gastrointestinal absorption of anthocyanins: a molecular approach

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Anthocyanins are naturally occurring bioactive compounds that are extensively distributed in plant-derived foodstuffs and, consequently, largely consumed by humans. Their consumption is related to decreased risks of developing cardiovascular disease and cancer (1). From polyphenols classes, anthocyanins are the ones considered to have the lowest bioavailability. However recent developments suggest an undervaluation of the real bioavailability of these compounds.

An early appearance of anthocyanins in blood and urine after consumption of anthocyanin-rich foods, is not compatible with an exclusive absorption at an intestinal level, as initially accepted (2).

Bioavailability is highly dependent on the interactions between food components when ingested together (3).

However, only limited scientific evidences exist to provide information on the bioavailability of anthocyanins in the gut.

Thus, this study aimed to better understand the influence of food matrix components on anthocyanin absorption and molecular mechanisms potentially involved on their bioavailability.

The kinetics of absorption both at gastric and intestinal level using MKN-28 and caco-2 cancer cell lines, was evaluated for complex anthocyanins from purple sweet potato, which revealed higher absorption values than previously reported for other anthocyanins.

Food matrix evaluation using anthocyanin-rich extracts from purple sweet potato showed a decreased efficiency of anthocyanin absorption in the presence of glucose and proteins but not starch.

Recent evidence suggested the involvement of glucose transporters at gastric level on anthocyanins absorption (4). Thus, the molecular mechanism of absorption of anthocyanins on the stomach was evaluated using gene silencing with nano-technology approach. The results, for different anthocyanins with particular structural features, extracted from both wine and purple sweet potato, suggested the involvement of GLUT1 and GLUT3. Although the transport mechanism was not exclusive to these transport systems.

Also a simulation of gastrointestinal enzymatic action was performed to evaluate the first line of anthocyanin degradation.

These results elucidate new insights on the comprehension of anthocyanins bioavailability.

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Analysis of the extracts of two medicinal wild mushrooms from Northern Morocco: *Ganoderma lucidum* and *Macrolepiota procera*

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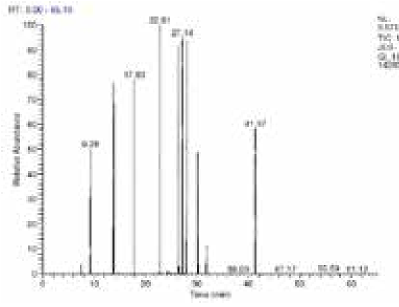
The region of M'Diq-Fnideq of Northern Morocco includes a diversified mycological heritage. From about fifty mushroom species harvested in the very degraded Quercus suber forest formation and reforested by the Pinus halepensis, and identified during the year 2018 [1,2], we conducted a study of Ganoderma lucidum and Macrolepiota procera, two Basidiomycetes mushroom from the family Polyporaceae and Agaricaceae, respectively. Ganoderma lucidum and Macrolepiota procera are mushrooms that have antioxidant, antimicrobial and anti-cancer properties.
Both mushrooms cultivation and purification were successfully carried out on PDA growing medium at 25°C. These cultures are well preserved for future use.
The fruiting body of each species was dried, crushed (20 mesh) and extracted with methanol [3]. The extract was derivatized and analyzed by GC-MS.
The chemical analysis of mushroom alcoholic extracts allowed the identification of the main constituents present in the extracts that will be subject of further research. This communication will present the results obtained



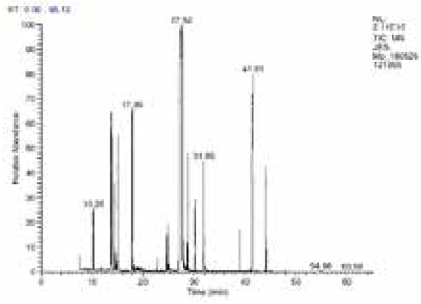


Figure 1: GC-MS analyses of Methanol extract *G. lucidum*
Figure 2: GC-MS analyses of Methanol extract *M. procera*

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Mesoporous metal-organic frameworks as nucleating agents in protein crystallography

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Mesoporous Metal-Organic Frameworks (mesoMOFs) have gained some attention as protein immobilization agents. Herein, and for the first time, three model proteins (lysozyme, trypsin and albumin) were used to show that crystallization is effectively induced when the protein is immobilized inside a terbium-based mesoMOF, with this occurring for lysozyme, while trypsin and albumin were size-excluded (Fig.1).

It is shown that heterogeneous nucleation is truly remarkable in the case of lysozyme, occurring through a gradual transition from the MOFs to the protein crystal lattices. These findings suggest that the ability to fix the target protein with a molecular-scale periodicity constitutes a significant advantage of mesoMOFs over other nucleating agents.

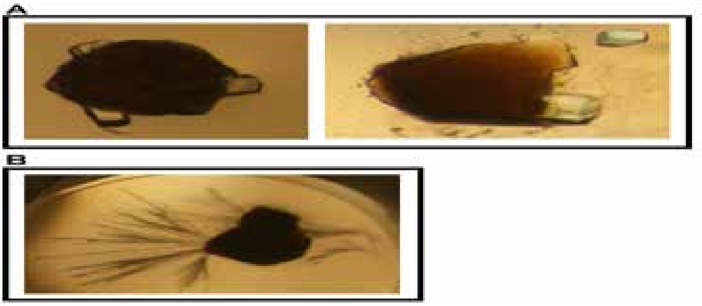

Fig.1. Lysozyme crystals grow abundantly at the surface of milimeter-size Tb-mesoMOF crystals

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Influence of the organic solvent during the extraction of biosurfactants from corn steep liquor

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Chemical surfactants are nowadays used in several areas like environmental, food cosmetic and pharmaceutical industries [1]. A structure consisting of a hydrophobic tail and hydrophilic head allows them to reduce surface tension and to be used as emulsifiers or solubilizers [2]. However, in the last years has increased the interest for obtaining more ecofriendly detergents, namely biosurfactants, which are produced by microorganisms, and composed by proteins, sugars, and/or lipids. For that, they are considered to be more biocompatible, and less toxic than their chemical counterparts [3]. The aim of this work is to compare the properties and composition of a biosurfactant extract (BS) obtained from an agroindustrial residue, corn steep liquor (CSL), using chloroform or ethyl acetate as solvents. The conditions of extractions are reflected in **Table 1**, as well as the results obtained in terms of critical micellar concentration (CMC), and surface tension reduction. In addition, FTIR analyses were performed to evaluate their compositions showing to be very alike. **Figure 1** represents in red the BS extracted with chloroform and in blue the one with ethyl acetate.

	Chloroform	Ethyl acetate
Rate water/solvent	1:2	1:3
Temperature (ºC)	56	25
RPM	200	200
Agitation time (h)	1	1
Critical Micellar Concentration (g/L)	0.120	0.176
Minima Surface Tension (mN/m)	40.40	38.05

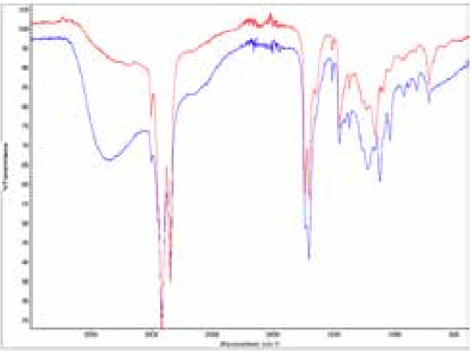

Table 1: Conditions and properties of both biosurfactant extracts.
Figure 1. FTIR spectra of the BS [4].

Both solvents were able to extract the biosurfactants contained in CSL, opening the door to their use in a wide range of applications in the cosmetic, pharmaceutical and also in the food industry, where ethyl acetate is allowed to be used in the EU [4].

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Enzymatic activity of extra- and intracellular extract from yeast isolated from textile wastewater

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Textile industry generates a large amount of effluents, mostly composed by synthetic dyes, that are discharged in the environment [1]. Although wastewaters are usually treated before discharge some dyes are not properly degraded and can cause serious problems in aquatic ecosystems [2]. The existent chemical treatments are very costly and generate large quantities of sludge [3]. Thus it is important to find alternatives such as biological treatments to aid the decolorization of dyes in textile wastewaters.

This work aims to detect the activity of specific enzymes from a yeast previously isolated from a textile wastewater that is capable of decolorization of dyes. The enzyme activity assays were chosen regarding the enzymes described as capable of dye decolorization such as laccase, tyrosinase and oxidoreductase [4]. The intracellular extraction was achieved by cellular disruption of the pellet using glass beads, whereas the extracellular extract was the supernatant resulting from 1 day of growth in liquid media. The enzymatic activities were determined spectrophotometrically and protein and molecular weights were also evaluated by Bradford and FPLC respectively.

The results show that the intracellular extract presented activity for oxidoreductase and tyrosinase. Extracellular enzyme activities were not detected. This work might suggest the involvement of these enzymes in the decolorization capacity of the yeast. The application of this yeast in the bioremediation of textile wastewaters is promising when used along with established methods, being environmentally friendly and cost-effective.

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Quantifying the polarity of pure and mixed lipid bilayers: the importance of cautiously using the pyrene Ham Effect

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Chemical and biochemical reactions that take place within amphiphilic aggregates such as micelles and lipid bilayers occur in media that are inherently heterogeneous. For instance, a fluid lipid bilayer is a highly stratified structure with a distinct trans-bilayer molecular profile, e.g. the so-called fluidity and polarity gradients, which in turn may influence or determine the roles of biological membranes as selective barriers, as functional arrays or as therapeutic targets [1]. However, the analysis of electron transfer reaction in cellular bioenergetics and redox processes occurring in membranes is based in a theoretical formalism assuming the solvent as a continuum whose dielectric constant value is well defined [2]. Also, the analysis of domain formation in lipid bilayers also presumes dielectric constant values analogous to those of apolar methylenic solvents [3].

There have been diverse attempts, both theoretical (calculations and molecular dynamics) and experimental (mostly EPR and fluorescence), to estimate the dielectric constant of lipid bilayers [4]. We present here the measurement of equivalent dielectric constants, and their thermal behavior, of fluid lipid bilayers composed of 1-palmitoyl-2-oleoyl-sn-glycero-3-phosphocholine (POPC) and its binary mixtures with cholesterol using the pyrene Ham Effect (I_1/I_3) [4]. The physical-chemical properties of pyrene (Py) settle its location in the ordered section of the methylenic palisade stating the values of dielectric constants as being averaged transversally in space (the longest axis of Py, 9.2 Å) and laterally in time (due to lateral diffusion of Py during its fluorescence lifetime in aerated samples, ~150 ns) [5]. To do so, the fluorescence spectra must be adequately corrected for the turbidity and Raman band from the aqueous liposome suspensions that fatally affects the I_1/I_3 measurements. Analogous procedure is adopted (only for Raman band) to settle a reference plot for I_1/I_3 in isotropic alcohols of known dielectric constants at 20 °C. Henceforth, POPC bilayers exhibits higher dielectric constant at 20 °C than the mixtures at high cholesterol proportions, pointing to features observed in the available thermal phase diagrams [6]. It is worth to emphasize that POPC bilayers display equivalent dielectric constant values analogous to 1-propanol which is much higher than those of apolar methylenic solvents such as hexadecane at 20 °C.

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Tracer diffusion coefficients of electrolytes and non-electrolytes in biological systems

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Some studies have been carried out on the thermodynamics behavior of electrolytes and non-electrolytes (e.g., sodium chloride, drugs, urea and amino acids) in biological systems. However, data on the transport behaviour of these systems are more limited, particularly in what concerns tracer diffusion coefficients in aqueous solutions (e.g. [1]).

The present work intends to fill this gap with the experimental determination of tracer diffusion coefficients, D measured by the Taylor dispersion method, for aqueous solutions of referred compounds (e.g., salts and urea) at 25 ºC.

From these data, we have estimated some structural and transport parameters, that is, the hydrodynamic radii, the limiting diffusion coefficient and ionic conductance, thus contributing for a better understanding of the structure of these systems (e.g., interactions ion-solvent) and their thermodynamic behaviour in aqueous solution. These studies have provided a comprehensive information – both kinetic and thermodynamic – for the design and operation of these systems and consequently, a better understanding of the physical chemistry of transport phenomena in multicomponent biological systems.

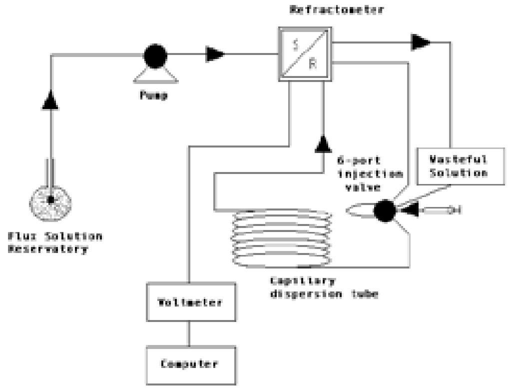

Figure 1: Diagram of the Taylor technique

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Interaction of *amphiphilic* molecules with model membranes followed by DSC and ITC

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Many drugs are not recognized by active transporters and thus passive permeation through the membrane is a significant route. [1]

Model membranes provide a simple model of biological membranes, as we can control their properties and modulate their composition as needed. Their use is thus an excellent experimental method to evaluate passive permeation.

In this work we used model membranes of DMPC, POPC and their binary mixtures with POPS and a model drug, chlorpromazine. The experimental technique used to characterize the membranes' phase behavior and their perturbation by the partition of the drug was DSC [2], and ITC [3] was used to obtain the thermodynamic parameters that characterize the partition of the drug to the membranes.

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Production of soap from waste organic seeds of the amazon

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Seeds of mango (Mangifera indica L.), bacuri (Platonia insignus Mart. Family clusiaceae) and cupuaçu (Theobroma grandiflorum) being studied are part of the diet of amapaense, its pulps are used in the food industry , in the form of ice cream, sweets and juices, while their seeds are discarded into the environment. This research allows the noble use of these residues for the production of soap. The seeds were supplied by rural producers of Amapá, after cleaning and asepsis, were dried and about 500 grams of each of the crushed seeds were placed in Soxlhlet extractors for the extraction of lipids, using acetone as the solvent. The amounts of lipids extracted were mango (26 grams), cupuaçu (32 grams) and bacuri (40 grams). In reflux apparatus, 10 grams of each extracted lipid was saponified with 20% NaOH and ethanol for three hours. The warm reaction system was added in molten sucrose, sodium dodecylsulfonate and glycerin. The mixture was placed in a small form and after 24 hours the pH was detected within the range 7-7.5. The sulfonation index (mg KOH / g) for the triglycerides extracted from the cupuaçu seeds was found using the AOCS method, with the reagents 0.5N alcoholic potassium hydroxide and 0.5N hydrochloric acid. , bacuri and mango: 250, 108, 178 respectively. The composition of the fatty acids was carried out at the Federal University of Pará, through the obtaining of fatty acid methyl esters, using the gas-liquid chromatograph Varian model Star 3400. The fatty acid found in good quantity in all the seeds studied was acid followed by palmitic acid.

Keywords: Seeds.Lipids. IV

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Novel eco-friendly method to extract keratin from hair

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Pig farming is a major worldwide industry that generates many by-products that can cause environmental problems [1]. Nonetheless, it is possible to have a management towards the re-use and valorization of these by-products. One opportunity focusses on the extraction of keratin present in the pig hair, since it is composed by 80% keratin [2]. There are some methods for keratin extraction from human hair, and other sources as wool and feathers, but they bring many problems as pollution, time-consumption and high costs [3].

This work uses a commercial detergent belonging to the category of degreasers, capable of fast and efficient dissolution of pig hair, followed by a simple filtration to remove residues from skin trimmings with fat and lard. The resulting solution is submitted to an ultrafiltration process to obtain a solution with higher protein content and purity, both at laboratory scale and pilot scale-up. Use of this keratin green extraction method allows to obtain a keratin product with protein purity up to 70% and yield extraction of ca. 50%, which although lower than the previous methods allow protein integrity and cleaner technology.

This method allows a relevant valorization of pig hair, using for the first time a simpler, cost-effective and environmental friendly approach

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Structural and functional study of the synuclein linked to native lipids nanodiscs

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The aggregation of specific proteins is related to the clinical progression of neurodegenerative diseases resulting in irreversible neuromotor degeneration and cognitive impairment. Parkinson disease (PD) has multifactorial causes, but studies indicate a causal relationship between the accumulation and aggregation of α-synuclein and the various forms of neuronal degeneration. Synuclein has also been identified in senile plaques of Alzheimer's disease and is involved in Lewy body dementia [1-3]. Lipids play a key role in PD because they act as modulators of α-synuclein functions and of α-synuclein-membrane interaction. They are responsible for inducing a helical structure in α-synuclein, thereby inhibiting its aggregation. Disorder of membrane cellular trafficking favors the protein aggregation [4].

Recently, a new experimental approach proposed the use of styrene-maleic acid (SMA) copolymer to extract lipid-associated proteins. SMA has amphiphilic characteristics that render it capable of permeabilizing and solubilizing biological membranes to form SMA-lipid nanodiscs (SMALPS). These nanodiscs retaining the native microenvironment to the protein keeping its structure and function [5].

We have prepared SMALPS using different lipids composition. The experimental approach involves biophysical techniques to study the structural, physicochemical and thermodynamic characteristics of synucleins family linked to native lipids nanodiscs as well as to assess the molecular parameters of protein aggregation in synucleinopathies. In present work results of the obtained SMAs with different lipid compositions will be presented, together with their characterization by DLS and DSC.

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Rose petals as a source of anthocyanins to develop dairy products with new sensorial and bioactive characteristics

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Natural additives are generally considered as producing no harmful effects on consumers' health, contrarily to some artificial compounds [1].

Rose petals might be an important source of anthocyanins with potential use as a natural colorant in the food industry [2].

In this study, an aqueous extract from rose was tested as an alternative to E163 to be incorporated into yogurts. Besides comparing the coloring capacity, the potential occurrence of changes in the proximate composition (AOAC methods), free sugars (HPLC-RI) and fatty acids (GC-FID) was also assessed.

Yogurts were evaluated immediately after incorporating the rose extract and once again after 7 days of storage. Furthermore, the prepared yogurts were compared with a "blank" (free of any additive) yogurt formulation.

Two anthocyanins were detected in rose petals, being cyanidin-3,5-di-*O*-glucoside the major compound (13.19±0.01 μg/g extract).

The yogurts prepared with the aqueous extract of rose, presented similar proximate composition and free sugars profile to those prepared with E163 and to the "blank" yogurt. Thus, the rose extract might be an effective alternative to E163, considering the main purpose of its coloring effect in the yellow-orange series. In addition to the provided color, yogurts incorporated with E163 and yogurts incorporated with rose extract showed very similar proximate composition, free sugars and fatty acids composition.

Therefore, rose petals have great potential to be used as natural colorants, being an excellent source of anthocyanins to develop innovative products with new sensorial and improved bioactive characteristics.

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Garcinia brasiliensis leaves: Bioactive properties and phytochemical assessment

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The Amazon rainforest is the home to several medicinal plant species popularly used for the treatment of a wide range of diseases. Despite the rich biodiversity of this region, there is still a lack of comprehensive studies regarding the uses, bioactivities, chemical composition and pharmacological properties of many of these medicinal plants [1]. In the present work, *Garcinia brasiliensis* Mart., a green plant native to the Amazon region, cultivated for its edible fruit, popularly referred to as "bacupari-anão" or "guapomo" was studied. Some of its well reported bioactive properties include antioxidant, antidiabetic, anti-inflammatory, antispasmodic and antiprotozoal activities but very little studies have been conducted describing the phytochemical profile and establishing compounds-bioactivity relationships of the extracts obtained from its vegetative organs [2]. In view of these pharmaceutical potentials, leaves of *G. brasilienses* were collected at São Cristóvão site, Parana, Brazil. They were then submitted to a cold methanol extraction, and further liquid-liquid partitioned to obtain hexane, dichloromethane and ethyl acetate fractions. The antioxidant, anti-inflammatory, antimicrobial and cytotoxic activities of each fraction were tested, and the most bioactive fraction was submitted to phenolic characterization using HPLC-DAD–ESI/MSn. The results showed that the ethyl acetate fraction showed the highest antioxidant activity which was comparable to Trolox, the positive control. This fraction also showed a broad spectrum antimicrobial activity against Gram-positive and Gram-negative bacteria, and *Candida albicans*. The phenolic profile of the ethyl acetate fraction presented twelve flavonoids, being morelloflavone-7"-*O*-glucoside (52.1±0.4 mg/g) and gardinia biflavonoid 2a glucoside (27.5±0.2mg/g) the major compounds identified. These results indicate that leaves of *G. brasiliensis* might be a potential source of natural biomolecules for pharmaceutical and medicinal applications.

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Removal of phenol from aqueous solutions by combined adsorption and catalytic processes

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By increasing of the industrial wastewaters, the demand for removal of organic compounds, including phenol, has grown rapidly due to the environmental and health issues such as high toxicity of these compounds even at very low concentration.
The objective of the present work was to study the impact of varied surface chemistries (acidic or basic) of functionalized carbon xerogels (CXs) applied as carbocatalyst for removal of phenol via combined adsorption and hydrogen peroxide-assisted oxidation reactions. For this purpose, modifications of the surface of CXs with: nitric acid (hydrothermal treatment at varied temperatures) or diluted gaseous ammonia and oxygen were applied. The presence of various oxygen functionalities on the surface of the CXs was confirmed by TPD (Figure 1) and XPS results. The catalytic tests for phenol conversion carried out at 35 °C in a batch mode reactor showed that both sorption and catalytic properties of CXs depended clearly on their chemical composition and acid-base properties and were significantly superior for the samples demonstrating higher basicity. The best CX carbocatalyst removed over 60% of phenol, in the presence of H_2O_2 in less than one hour.

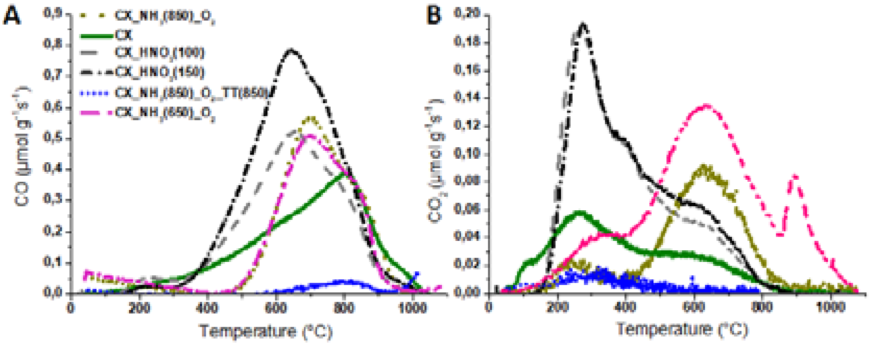

Figure 1: TPD-MS spectra of functionalized CXs, A) CO, B) CO_2

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Estudo mecanístico da conversão de CO_2 em carbonatos heterocíclicos através de organocatálise

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Apesar dos seus efeitos nocivos, o CO_2 pode ser considerado uma fonte abundante, renovável, barata e não tóxica de C1. Nomeadamente, o CO_2 pode reagir com epóxidos para dar origem a carbonatos heterocíclicos, os quais são úteis como matérias primas na síntese de fármacos, polímeros, eletrólitos e outros químicos. O desenvolvimento de processos de síntese eficientes que permitam explorar o CO_2 como uma fonte renovável de carbono pode levar a uma redução da nossa dependência de combustíveis fósseis para obter matéria-prima [1,2]

Tem havido um grande esforço no desenvolvimento de organocatalisadores para facilitar este processo [1,2]. Nestes sistemas a conversão de CO_2 ocorre do seguinte modo: a abertura do anel do epóxido ocorre através de um ataque nucleófilo, dando origem a um oxianião. De seguida ocorre a cicloadição do CO_2 ao oxianião, dando origem ao carbonato heterocíclico. No entanto, estes catalisadores não permitem ainda uma catálise suficientemente eficiente, necessitando de altas temperaturas [1,2]. Dadores de pontes de hidrogénio (HBDs) tem emergido como uma solução em sistemas catalíticos de dois componentes, com o racional que estes compostos interagem com o dador-O do epóxido por pontes de hidrogénio, o que facilita a abertura do anel do epóxido pelo nucleófilo [1-3]. Apesar de alguns avanços com o uso de HBDs, ainda existem poucos organocatalisadores verdadeiramente eficientes. Isto deriva do facto da maioria dos estudos existentes não separarem os fatores relevantes para os dois passos da conversão de CO_2. Deste modo, é difícil perceber qual o verdadeiro efeito catalítico dos HBDs e de que modo se pode melhorar a sua atividade catalítica.

O objetivo deste trabalho é obter informação mecanística relativa ao potencial efeito catalítico de HBDs na conversão de CO_2, com enfase no passo de abertura do anel do epóxido. Deste modo, a atividade catalítica de diferentes HBDs (baseados em carboidrato e ácidos orgânicos) é avaliada relativa à abertura de anel de um epóxido modelo (óxido de propileno) na presença de um nucleófilo co catalisador (piridina). A cinética e rendimentos destas reações são obtidos usando uma abordagem espectroscópica UV-Vis e cromatográfica (HPLC-DAD).

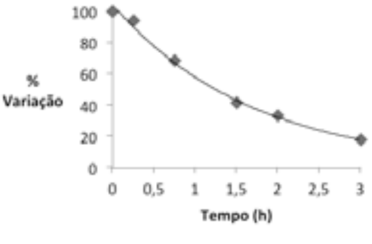

Fig.1. Monitorização da reação de abertura do anel de epóxido em função do tempo (em horas).

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Solketal, a new fuel additive for biodiesel mixtures

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With the depletion of fossil fuel reserves and aiming towards the reduction of greenhouse gases, such as CO_2 and $NO_{x,}$ more ecological and renewable sources have been sought, with the most attractive and wanted to be the use of used frying oils, in the production of biodiesel. Biodiesel is produced by transesterification of those vegetable oils with an alcohol, like methanol, and can be used after blending with fossil-based diesel. [1]

Glycerol, a by-product of the transesterification process, is produced on a large scale with little market value, which has led to the search for alternatives in using this by-product. This means that new applications for this polyol are being developed, such as, its ketalization, producing glycerol ketals as bio-based diesel additives, like solketal. Solketal can be used as a fuel additive to reduce the NO_x emissions and to improve the cold flow properties of liquid transportation fuels.

The aim of this experimental work is the study of the solketal's production by catalytic reaction of glycerol with acetone, under heterogeneous catalysis, such as zeolite Y, montmorillonite K10 and K30. With this reaction (fig. 1a), 2 enantiomers are formed, one of them being solketal (98%). In this process several reaction conditions, types of solid catalysts and amount of catalyst were tested. [2]

Solketal produced was quantified by refractometry and, solid catalysts were characterized by SEM-EDS (fig. 1b), FTIR-ATR, XRD, BET and basicity, by semi-quantitative Hammet's indicator method. It was also studied, catalytic activity and stability of these heterogeneous catalysts and, it was also performed, a significative kinetic study of this process, with these catalysts, under temperature gradient, where it was quantified the activation energy. [3]

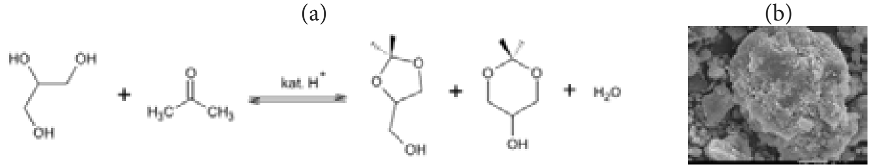
(a) (b)

Fig. 1: (a) - Reaction between acetone and glycerol; (b) – SEM image of MMK10 after 1st Batch

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Development of heterogeneous nanostructured catalysts for biodiesel production

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Studies have shown that the transesterification reaction used in the production of biodiesel can be catalyzed with great efficiency using heterogeneous catalysts based on calcium oxide. CaO can be obtained from waste materials from the food industry, such as mollusk shells, whose constitution is mostly calcium carbonate, which is easily converted to calcium oxide. However, during successive uses some problems related to the gradual loss of catalyst activity appear, so it is necessary to improve and optimize the procedural variables.[1,2] In the present work, in order to overcome some of the current limitations, the application of nanostructured composites as catalysts is being investigated.[3] The dispersed catalysts were prepared by a simple and solvent-free mechanochemical method, i.e., ballmilling,[4] and using cheap and non-hazardous starting materials. Several milling parameters such as size, type and number of milling balls beaker dimension, reaction time (milling time) as well as mode of operation (rotation/oscillation frequency) and calcination temperature were tested towards the optimization of the catalyst performance.
Until now, the catalysts that showed the best catalytic activity were CaO, CaO-SiO2, CaO-Al2O3 and CaO-CNT (carbon nanotubes).

Fig.1. Left: Planetary Ball Mill; Right: SEM image of CaO Catalyst before reaction

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Waste oils valorization through biodiesel synthesis using [HMIM] HSO$_4$ ionic liquid as catalyst

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Historically, economic growth was always dependent on energy generation, causing pressure on fossil energy sources. In this context, alternative renewable energy sources have been extensively studied. Hence, biodiesel, a biofuel obtained from renewable biomass for internal combustion engines or energy generation, exhibits potential to replace partially or totally fossil fuels. Biodiesel is chemically composed of FAME (fatty acid methyl esters), that can be obtained from the chemical reaction of triglycerides with an alcohol, in the presence of a catalyst. Different raw materials can be used to produce biodiesel, such as edible vegetable oils (soybean oil, rapeseed oil) or inedible oils (jatropha oil, castor oil), animal fats, waste cooking oils and oils extracted from algae [1]. Acid and basic catalysts are applied to increase the reaction rate. For transesterification reactions, basic catalysts (NaOH or KOH) are the most commonly used. Alternative options for these catalysts are ionic liquids (ILs), which are being studied since they enable a more environmentally sustainable biodiesel production process. Such compounds have potential for recyclability, high catalytic activity, simple operating conditions and high conversion rates with short reaction times [2].

The objective of this work is to study the influence of applying 1-methylimidazolium hydrogen sulfate [HMIM]HSO$_4$ IL on the catalysis of esterification/transesterification reactions of a highly acidic waste vegetable oil (WVO), in order to assess the viability of the use of acidic imidazolium based ILs as catalysts in biodiesel production processes. Therefore, samples of simulated oils with variable acidity were used as raw material. These samples were prepared by the incorporation of different contents of oleic acid (tech. 90%) in a previously qualitatively and quantitatively characterized WVO. For the reaction, methanol was used and IL [HMIMHSO$_4$ was applied as the catalyst. An experimental design based on a total factorial was generated with three parameters at two levels (2^3) in duplicate: incorporated oleic acid, methanol/simulated oil molar ratio, and reaction time. Table 1 describes the three parameters chosen, the code applied, and the two levels used. Two responses were evaluated: the conversion of the simulated oil, measured according to the procedure described in the European Standard EN14104/2008, and the produced biodiesel FAME content, estimated by GC-FID, according to the procedure established in the European Standard EN 14103/2003. The fixed reaction parameters were: temperature, 90°C, and catalyst charge, 10% wt, and the statistical analysis was carried out with Design Expert 11 software.

The influence of the factors for the conversion response was C>B>A, and the optimal conditions were: 20% (factor A), 1:40 (B), and 8h (C), reaching a maximum conversion of 96.6%. On the other hand, regarding the FAME content response, the influence of factors was A>C>B, and the optimal conditions were, 40% (A), 1:20 (B), and 8h (C), for a maximum FAME content of 36.5%. It is concluded that the studied IL promoted mainly the esterification of the free fatty acids in the WVO samples, and apparently had little influence in promoting transesterification reactions.

Parameter	Code	-1	1
Oleic Acid incorporated (%)	A	20	40
Molar ratio oil/methanol (mol/mol)	B	1:20	1:40
Time (h)	C	4	8

Table 1. Levels applied in the experimental design.

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Kinetic study of the esterification process catalyzed by ionic liquids for fatty acid methyl esters production

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Due to the massive use of energy from non-renewable sources, as well as to environmental problems, it is important to find green alternatives to energy production. In this context, biodiesel arises as a possible diesel substitute which can be produced using basic or acid catalysts. Despite these traditional catalysts allow high production yields, problems related to its use and the environmental impacts associated, result in the need to search for more sustainable alternatives. Ionic liquids (ILs), used as possible catalysts, represent an interesting alternative because they can be recovered and reused, being environmentally friendly.
The kinetics of the esterification of free fatty acids (FFA) using oleic acid and methanol, and 1-buthyl-3-methylimidazolium methyl sulfate, [BMIM][$MeSO_4$], IL as catalyst is presented. All kinetics measurements were carried out for 8 hours, with a catalyst quantity of 10% w/w, and a molar ratio oleic acid/methanol of 1:10, using four different reaction temperatures (60, 80, 100 and 110°C), under stirring, temperature control and reflux. Throughout the reaction, and at predetermined times (0, 15, 30, 60, 90, 120, 180, 240, 300, 360, 420 and 480 min), 1 mL of sample was collected from the reaction vessel. The acidity value, expressed in mg KOH/g biodiesel, was determined immediately after the sampling using the experimental procedure according to European Standard EN 14104 [1]. The conversion of oleic acid, in percentage, was estimated by comparing the initial and final acidity values. It was considered for the calculation of the initial acidity value, the sample collected at time 0 min. The integral method was applied considering 0th, 1st, 2nd and 3rd order kinetics relating to oleic acid, for all temperatures. Therefore, the coefficients of determination (R^2) were compared and the order of reaction was selected taking into account the highest value attained. Finally, the Arrhenius theory was used to predict the activation energy value (see Fig. 1).

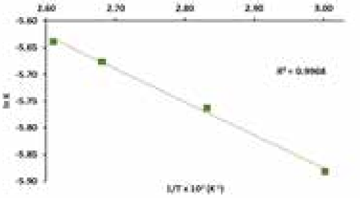

Fig. 1. Arrhenius plot of the rate constant (ln k) versus the inverse of temperature ($1/T \times 10^3$) for the esterification of oleic acid with methanol catalyzed by [BMIM][$MeSO_4$] ionic liquid.

The results showed that the coefficient of determination ($R^2=0.998$) was obtained considering a 2nd order kinetics for all temperatures. Therefore, the activation energy (E_a) and the pre-exponential factor (A) were predicted assuming the kinetic order referred above. The activation energy (E_a) was determined as 5.16 kJ/mol and the pre-exponential factor (A) as 0.0624 $L^2.mol^{-1}.min^{-1}$. The relative low value found for the activation energy, indicates that [BMIM][$MeSO_4$] IL may be a promising catalyst for this type of reactions, showing a relative low sensitivity to temperature changes for the studied temperature range.

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New potential heterogeneous catalysts based on cobalt(II) coordination polymers

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Coordination polymers (CPs) are in general extended materials with a high level of organization and their structural features are extremely dependent of the linker functionalities, as well as of the metal coordination environments, among other parameters [1]. The development of this type of materials is of great importance in the progress of materials science and modern chemistry, due to their potential in diverse technological and industrial applications [2].

Considering the enormous interest in the development of new CPs to be of use in heterogeneous catalysis with relative low cost, we selected 5-aminoisophthalic acid (H_2aip) as ligand and cobalt(II) acetate salt to prepare new materials. According to this intent, two CPs were prepared, using hydrothermal (HT) and microwave-assisted synthesis (MWAS) Their structures were determined by single-crystal X-ray diffraction (XRD) and formulated as $[Co(aip)(bpy)1/2(H_2O)].2H_2O$ (Co-aip1) and $[Co(aip)(phen)]$ (Coaip2), where phen and bpy correspond to 1,10-phenanthroline and 4,4'-bipyridine, respectively (Figure 1). The CPs were further characterized by FT-IR spectroscopy, powder XRD, SEMEDS and ICP. Both CPs revealed 2D extended structures, but while the Co-aip1 shows a denser arrangement the Co-aip2 contains 1D channels partially occupied by lattice water molecules.

The application of both Co-aip1 and Co-aip2 CPs as efficient heterogeneous catalysts in olefin oxidation reactions was studied and compared. Two different oxidative agents, H_2O_2 (hydrogen peroxide) and TBHP (*tert*-butyl hydroperoxide), were applied and *cis*cyclooctene and styrene were used as substrates. Comparative results between the CPs will be discussed.

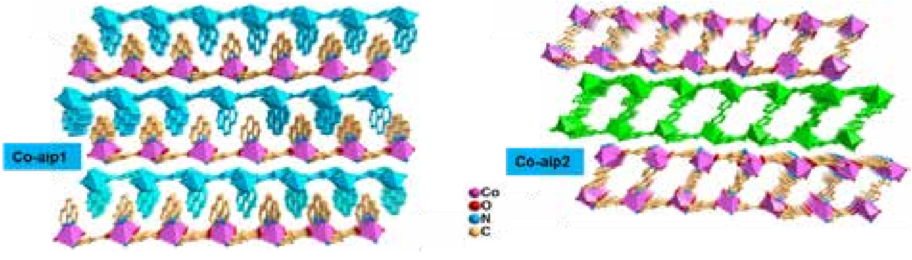

Fig.1. Extended crystalline structures for Co-aip1 (left) and Co-aip2 (right), where different layers are distinguished by different coloration schemes.

ACKNOWLEDGMENTS: This work received financial support from the European Union (FEDER funds through COMPETE), National Funds (FCT), PT2020 (UID/QUI/50006/2013-POCI/01/0145/FEDER/007265), M-ERA-NET/0005/2014; ON.2-O Novo Norte under QREN; Feder (NORTE-01-0145-FEDER-000024); LAPSEN (MAT2014-57652-C2-1/2-R) and PTDC/CTM-CTM/31983/2017. LCS thanks the FCT for the Post-Doctoral fellowship (SFRH/BPD/111899/2015).

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Treatment of oily streams contaminated with lipophilic pollutants by peroxide oxidation using catalysts developed from compost derived from municipal solid waste

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Nowadays, waste management through mechanical biological treatment (MTB) consists on the use of the separated organic fraction of municipal solid waste (MSW) to feed anaerobic digestion processes, resulting therein a solid stream, further processed to compost, which can be used in agriculture. Currently, the production of compost is higher when compared to its demand and expected developments on coming directives under "End-of-waste" criteria are leading to barriers on the use of fertilizers resulting from waste [1]. Within this context, the current work proposes an alternative strategy to the valorisation of compost, through the production of low-cost materials to be used in catalytic processes. Thus, several materials were prepared from compost obtained from a MTB plant for MSW. The compost was first mixed and washed with water, in order to homogenise and remove soluble compounds and suspend solids. Then, two different materials were prepared by carbonization at 400 (C-400) and 800 ºC (C-800). In addition, following the procedure previously described [2], two materials were prepared with H_2SO_4 before and after the carbonization at 800 ºC (C-S-800 and C-800-S, respectively). The materials were assessed in H_2O_2 decomposition and peroxide oxidation of three model pollutants with different lipophilic character, Sudan-IV (S-IV), 2-nitrophenol (2-NP) and 4nitrophenol (4-NP) in cyclohexane and water in order to simulate oily wastewater (Fig.1). The materials show catalytic activity in both H_2O_2 decomposition and peroxidation of the pollutants when compared to the non-catalytic runs. The most significant difference was found when C-800-S was used, since low conversions of H_2O_2 and 4-NP was achieved. However, the acidification of the sample resulted favourable in the oxidation of S-IV, leading to the highest conversion of this pollutant.

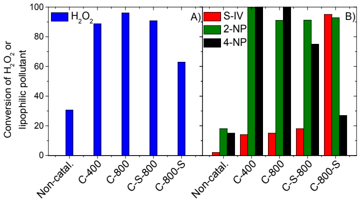

Fig.1. Conversion of (A) H_2O_2 in its respective decomposition runs and of (B) the lipophilic pollutants in the peroxidation runs.

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Extraction of laccase from *Trametes versicolor* growth media using aqueous biphasic systems

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Laccases are copper-containing oxidases that are produced by plants, bacteria, insects, and especially by white-rot fungus, such as *Trametes versicolor*. Due to that, this fungus has been widely used in wood delignification [1], bioremediation [2], decolorization of dyes [2] and other applications [3] the potential of several aqueous two-phase systems (ATPS. Nevertheless, the purification of laccase from the fermentation medium is still considered a laborious step, requiring expensive techniques such as precipitation, flocculation, immobilization, gel filtration, chromatography, among others [4]. Moreover, some of the applied techniques also require time consuming sample pretreatment. Therefore, there is a crucial need on the development of cost-effective techniques to recover and preserve laccase from fermentation media. To attain this aim, aqueous biphasic systems (ABS) can be used. ABS are considered a valid technique for the extraction, concentration and purification of proteins mainly due to their high-water content [5]. In this work we studied ABS as effective platforms for the extraction, concentration and purification of laccase from *T. versicolor* fermented medium, followed by the use of the ABS coexisting phases as preservation media.

Nowadays, laccase from microorganisms such as filamentous fungus *Aspergillus oryzae* (Novozym ® 51003) is preserved in a mixture containing water (66%), Propylene glycol (PPG) (25%), Sucrose/Glucose (4%) and Glycine (2%). That way, ABS composed of ILs or amino acids and polymers, such as polypropylene glycol 400 (PPG 400) and polyethylene glycol (PEG)400 and 600 were investigated. The first step consisted in the screening of the best components that could form ABS in presence of a commercial laccase solution. After that, the best systems were characterized by the determination of the respective phase diagrams, comprising the respective tie-lines and tie-lines lengths. Thenceforth, the theorical biomolecule concentration factor was calculated through the lever rule. As previously referred, after the screening of the best ABS components, the systems were applied in the partition of a commercial laccase, where the activity of the enzyme was evaluated and the best systems (ABS formed by betaine + PEG600 and glycine + PPG400) were identified. The formed ABS allowed to calculate two parameters: top or bottom phase yield (Y) and the top or bottom concentration factor (CF), depending of the enzyme partition. The Y variable represents the fraction of enzymatic activity recovered in a specified phase in relation to the total activity introduced into the system. The CF denotes the *T. versicolor* fermented media enrichment when compared to the ABS total volume [6]. The higher these parameters, the more successful the enzyme concentration process.

The previous systems were then tested as new platforms for extraction of laccase directly from the *T. versicolor* growth media. The glycine and PPG400 ABS allowed to form an ABS with a reduced bottom phase (glycine rich phase) but protein precipitation occurred. This system was very promising, since the bottom phase yield (YBP) was 0.7, average value using different mixture points. Moreover, the bottom CF was 18.7, double the registered values in the literature [6]. However, Betaine and PEG600 ABS was chosen and obtained a Y>0.8 and CF of 8, but without precipitation. Then, the enzyme activity in the betaine phase was measured for 2 weeks, at 4ºC and 25ºC, registering an enzyme activity loss of 80% only after 21 days at 4ºC. Although other preservation alternatives should be explored to preserve the laccase activity, this preliminary study shows that properly designed ABS can act as simultaneous extraction, concentration and preservation media.

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Redução de bromato em água na presença de catalisadores metálicos suportados em nanotubos de carbono modificados

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O ião bromato é detetado frequentemente em estações de tratamento de água para consumo humano em concentrações que representam um risco significativo de cancro para exposições ao longo da vida. A sua presença deve-se à ozonização do ião brometo durante o tratamento da água [1]. A redução catalítica com hidrogénio tem sido vista como um dos métodos mais promissores de remoção de bromato de águas destinadas ao consumo humano, dado que não apresenta as desvantagens dos tratamentos tradicionais [2].

Neste trabalho pretende-se avaliar a influência das propriedades texturais e da química superficial de nanotubos de carbono de paredes múltiplas (NTC) no desempenho de catalisadores de Pd, Cu e Pd-Cu suportados em NTC para a redução de bromato a brometo. Assim, os nanotubos de carbono comerciais (amostra NTC-O) foram submetidos aos seguintes tratamentos: i) oxidação em fase líquida com ácido nítrico (NTC-HNO3), seguida de tratamentos térmicos em atmosfera inerte (N_2) para remoção seletiva de grupos oxigenados superficiais (NTC-400 e NTC-900); ii) tratamento mecânico por moagem num moinho de bolas (NTC-MB); e iii) dopagem com azoto utilizando dois precursores (melamina ou ureia, NTC-MB-M e NTC-MB-U, respetivamente). Os suportes e catalisadores foram caraterizados com recurso a diferentes técnicas, incluindo adsorção de N_2 a -196 °C, dessorção a temperatura programada, análise elementar, microscopia eletrónica de transmissão e espectroscopia de fotoeletrões de raios-X. Os ensaios catalíticos foram realizados num reator semi-fechado **à** temperatura ambiente e à pressão atmosférica.

Os resultados obtidos revelam que a presença de catalisadores de Pd e Pd-Cu melhora significativamente a redução de bromato a brometo em água na presença de hidrogénio, enquanto o catalisador monometálico de Cu não é ativo para a reação. Os nanotubos de carbono demonstraram ser um bom suporte para a reação catalítica do bromato a brometo em água. O desempenho dos diferentes catalisadores metálicos suportados é altamente influenciado pelas propriedades texturais e pela química superficial dos suportes. Os nanotubos de carbono dopados com azoto são os melhores suportes para este processo catalítico, enquanto os suportes com grandes quantidades de grupos oxigenados na superfície desfavorecem o desempenho catalítico das fases metálicas para a redução de bromato.

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Biomimetic oxygenation of benzofuran derivatives under environmentally benign conditions

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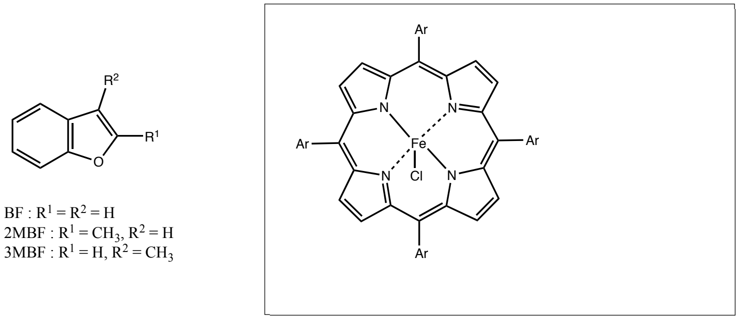
The chemistry of natural occurring and synthetic benzofurans has attracted much attention due to their broad spectrum of pharmacological activities.[1] Besides their antimicrobial or anticancer activities, particular attention has been paid to their action as antioxidants, and to their efficacy in the treatment of Alzheimer's disease. Thus, the development of biomimetic eco-sustainable oxidation procedures allowing the synthesis of novel and potentially biologically active compounds is of relevance. Iron(III) and manganese(III) porphyrins are known as important models of CYP450 monooxygenases. These complexes have been widely used as efficient catalysts for several oxidation reactions.[2]

In this communication, the results of the catalytic oxygenation using BF, 2MBF and 3MBF as substrates, the well-known Fe(TF$_5$PP)Cl as catalyst and H_2O_2 as oxidant under mild conditions will be presented. It is noteworthy that different reaction pathways could be selected by small changes in the reaction conditions.



BF : $R^1 = R^2 = H$
2MBF : $R^1 = CH_3$, $R^2 = H$
3MBF : $R^1 = H$, $R^2 = CH_3$

Figure 1: Structures of the benzofuran derivatives and the metalloporphyrin catalyst used in the catalytic assays

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Materiais de carbono isentos de metais para o tratamento fotocatalítico de compostos fenólicos

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Os processos avançados de oxidação são baseados na produção de espécies altamente reativas capazes de oxidar moléculas orgânicas. Entre estes processos, a fotocatálise heterogénea consiste na ativação de um material semicondutor com radiação (e.g., ultravioleta e/ou visível), gerando-se pares eletrãoburaco altamente reativos. O nitreto de carbono grafítico (g-C_3N_4) tem sido utilizado para uma larga gama de aplicações fotocatalíticas por ser facilmente sintetizado, isento de metais e ativado por incidência de luz visível [1]. Neste trabalho, foi utilizado como fotocatalisador um material de nitreto de carbono exfoliado termicamente [2]. Estudou-se a degradação de dez compostos aromáticos comummente encontrados em efluentes líquidos da indústria do azeite, incluindo derivados do fenol com diferentes grupos substituintes. O sistema fotocatalítico em estudo permite a produção de H_2O_2, o qual é simultaneamente decomposto aumentando a degradação e mineralização dos poluentes. As concentrações dos compostos aromáticos, do peróxido de hidrogénio (H_2O_2) e o carbono orgânico total foram seguidas durante as experiências fotocatalíticas, com recurso a diversas técnicas analíticas. Foi demonstrado que o H_2O_2 é formado unicamente na presença de material fotoativado, oxigénio dissolvido e do composto aromático, este último atuando como dador de protões. Verifica-se também que a concentração de H_2O_2 aumenta até **à** remoção completa do composto aromático, como exemplificado na Figura 1. Os valores máximos para a quantidade de H_2O_2 gerada para os vários compostos em estudo **são** semelhantes aos reportados na literatura, no entanto os tempos de irradiação no presente trabalho são bastante inferiores [3, 4].

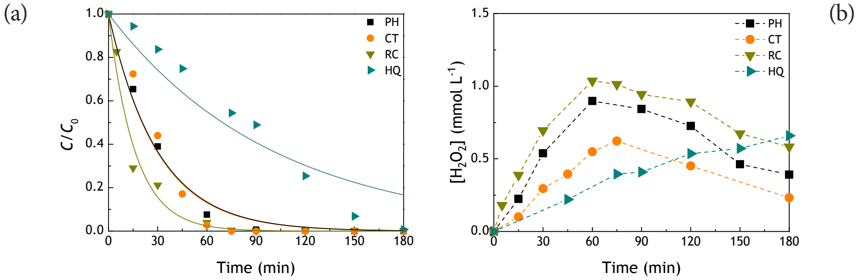

Fig.1. (a) Concentração normalizada (C/C0) de fenol (PH), catecol (CT), resorcinol (RC) e hidroquinona (HQ) e (b) concentração de H2O2 produzido durante as experiências fotocatalíticas (concentração inicial de poluente: 0.640 mmol L-1, carga de catalisador: 0.50 g L-1 e saturação contínua de ar).

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Efficient Polyoxomolybdate Catalyst Supported in Mesoporous Silica Nanoparticles for Oxidative Desulfurization Processes

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The presence of sulfur compounds in fuels even after the refining process results in the harmful emission of SO_x during combustion [1,2]. These compounds are still very hard to remove [3] but one of the most promising approaches to the conventional method (hydrodesulfurization) is the extraction process combined with the catalytic oxidative desulfurization system (ECODS) [4]. A novel composite materials were prepared by immobilization of an active but unstable homogeneous polyoxomolybdate catalyst $[PMo_{12}O_{40}]^{3-}$ (PMo_{12}) on a strategic functionalized mesoporous silica nanoparticles (MSNs). The materials were tested as heterogeneous catalysts in ECODS process of a multicomponent model diesel and their desulfurization performance compared with the homogeneous catalyst. The prepared PMo_{12}@TBA-MSN composite demonstrates to confer a high stability and an increase of oxidative desulfurization efficiency to the polyoxomolybdate catalytic center. This work proposes a highly efficient system for desulfurization of diesel under sustainable conditions (using H_2O_2 oxidant and an ionic liquid solvent $[BMIM][PF_6]$). Continuous reusing the catalyst and ionic liquid solvent for consecutive oxidative desulfurization cycles was successfully performed avoiding the production of residual wastes. The reuse of PMo_{12}@TBA-MSN catalyst has led to a faster performance reaching complete desulfurization just after 1 h of catalytic stage. Moreover, the composite showed a remarkable robustness by retaining its structural and chemical integrity as suggested by several characterization techniques after catalytic use.

ACKNOWLEDGMENTS: This work was partly funded through the project REQUIMTE-LAQV, POCI-01-0145-FEDER-007265 [FCT (Fundação para a Ciência e a Tecnologia) Ref. UID/QUI/50006/2013] financed by national funds through the FCT/MEC and when appropriate co-financed by FEDER (Fundo Europeu de Desenvolvimento Regional) under the PT2020 Partnership Agreement and the project PTDC/CTM-CTM/31983/2017.

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Desenvolvimento de processos de produção de aldeídos aromáticos baseados em fotocatalisadores de nitreto de carbono

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Os materiais laminados à base de nitreto de carbono com propriedades semiconductoras apresentam uma eficiência relevante em diversas aplicações fotocatalíticas. A sua fácil preparação, a partir de precursores de baixo custo, e a sua estabilidade térmica e química conferem-lhes propriedades bastante promissoras na síntese fotocatalítica de compostos aromatizantes com elevado valor acrescentado [1, 2].

Neste trabalho, sintetizou-se um nitreto de carbono laminado (designado por gCN) a partir da decomposição térmica da dicianodiamina. O material resultante apresentou uma morfologia bastante compacta, constituído por folhas de nitreto de carbono, e consequentemente uma baixa área superficial. Este material foi submetido a um tratamento térmico, o que conduziu à separação das placas do material original, promovendo um aumento da área superficial. A eficiência fotocatalítica do material resultante deste pós-tratamento (gCN-T) foi avaliada na oxidação seletiva de diferentes álcoois aromáticos nos respetivos aldeídos, nomeadamente anisaldeído (AAD), benzaldeído (BAD), tolualdeído (TAD), vanilina (VAD) e piperonal (PAD). O processo fotocatalítico de síntese de AAD apresentou-se como o mais eficiente, tendo-se atingido valores de rendimento e seletividade superiores a 99% (Fig.1).

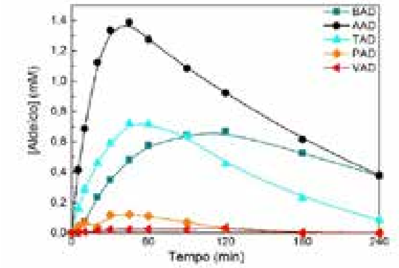

Fig. 1.Perfil de concentrações dos aldeídos aromáticos durante a síntese fotocatalítica utilizando gCNT.

De modo aumentar a eficiência na síntese fotocatalítica do AAD, submeteu-se o material gCN-T, a um tratamento por ultrassons, tendo-se obtido uma suspensão aquosa coloidal (gCN-TS) com uma carga de catalisador de 0.2 g/L, cuja eficiência é comparável aos resultados obtidos com 1 g/L de gCN-T.

No sentido de se eliminar a etapa de separação do catalisador no final da reação e de se poder operar em modo contínuo, imobilizou-se o catalisador gCN-TS em anéis de vidro, tendo-se testado este sistema para a produção fotocatalítica de AAD.

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Preparation and characterization of natural and pillared clays for catalytic wet peroxide oxidation of 4nitrophenol

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This work deals with the evaluation of two natural clays (NCs) extracted from Karatau (KNC) and Akzhar (ANC) deposits (located in the Zhambyl region of Kazakhstan) to prepare pillared clays (PILCs) for catalytic wet peroxide oxidation (CWPO) of 4-nitrophenol (4-NP), used as model pollutant. NCs were washed with HCl 1 M and then pillared using a solution containing Fe, Cu and Zr. NCs and PILCs were characterized by Electron Microprobe (EMP), X-Ray Diffraction (XRD), Fourier Transform Infrared Spectroscopy (FTIR) and Transmission Electron Microscopy (TEM), as detailed elsewhere [1,2]. EMP confirms the cation exchange of the Ca contained in the NCs (Ca > 15%) in the form of calcite (according to DRX and FTIR), by polycations of the pillaring solution (Ca < 2% for the PILCs). TEM reveals that the impregnation of polycations on the washed NCs also take place, coupling with its pillarization. CWPO runs were performed following the methodology and operational conditions described in previous works [1,2]. All materials show catalytic activity, since the H_2O_2 is consumed (Fig. 1A) to oxidize the 4-NP. Both KPILC and APILC, prepared from KNC and ANC, respectively, allow the complete removal of 4-NP after 4 h, whereas the conversion of 4-NP was less than 20% with the NCs (Fig. 1B). TOC conversions higher than 60 % were achieved with PILCs after 8 h. The subtraction of the theoretical TOC contribution of 4-NP from experimental TOC allowed to observe the formation of oxidazable intermediate compounds (maximum value of $TOC_{experimental}-TOC_{4\text{-}NP}$ at 1 h of reaction), which are oxidized to form refractory products (Fig. 1C). Based on these contributions of the TOC, a kinetic model based on TOC lumping into three blocks ($TOC_A \rightarrow TOC_B \rightarrow TOC_C$, corresponding to the initial TOC of 4-NP, oxidazable intermediates and refractory products, respectively) was developed for the NCs and PILCs, predicting suitably the evolution of 4-NP, H_2O_2 and TOC in the CWPO of 4-NP (Fig. 1).

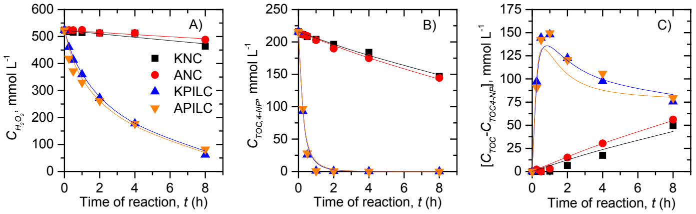

Fig.1. Evolution of (A) H_2O_2, (B) theoretical TOC contribution of 4-NP and (C) the sum of TOC_B + TOC_C (symbols as experimental data and curves as predicted values by the developed kinetic model)

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Titanate nanotubes/Carbon dots nanocomposites: Advanced materials for photodegradation of organic pollutants

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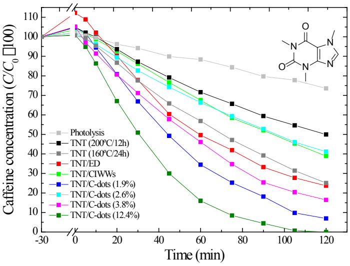
Advanced nanomaterials with enhanced optical and photocatalytic properties for the photodegradation of organic pollutants, in particular pharmaceuticals and personal care products (PPCPs), were successfully prepared by a swift one-pot synthesis. The nanostructured materials were synthesized through an integrated hydrothermal procedure which generates simultaneously titanate nanotubes (TNTs) with *N*-doped carbon dots (C-dots) embedded onto them, from an amorphous Ti source [1,2], cork industry wastewaters (CIWWs) as the carbon source [3], and ethylenediamine (ED) as additive. The structural, microstructural, morphological, and optical properties of the new nanocomposites were studied by XRD, TEM, UV-Vis diffuse reflectance spectroscopy and fluorescence spectroscopy, being their specific surface areas measured by the B.E.T. method. As aimed, the new materials extend their light absorption toward the red in comparison to pristine TNTs, prompting for a more efficient use of visible light irradiation in photocatalysis. A series of as-synthesized TNT/C-dots nanocomposites varying their content of C-dots were tested in the degradation of caffeine as a pollutant model for PPCPs. Rewarding results were obtained. Fig. 1 depicts the overall results obtained so far, clearly showing the enhanced photocatalytic ability of the nanocomposites [*e.g.* TNT/C-dots (12.4%)] toward caffeine degradation in comparison to TNTs used alone or modified with ED [4]. Possible mechanisms underpinning the observed results will be presented and discussed.



Photodegradation experiments were conducted in a refrigerated photo-reactor using a 450 W Hanovia medium-pressure mercury-vapour lamp as radiation source (40–48% in UV range and 40–43% in visible region).

Fig.1. Degradation of caffeine in the presence of various photocatalysts and under photolysis.

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Michael addition of indole to α,β-unsaturated steroidal ketones as a synthetic route to new bioactive compounds

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A classical and efficient method for the construction of C-C or C-heteroatom bonds in organic synthesis which is extremely useful in the preparation of bioactive molecules, including drugs, involves the Michael addition reaction [1]. Over the years, several improvements in this type of transformation were observed, including comprising the applications of the principles of Green Chemistry, predominantly including the use of catalysts. Structural modifications of steroids, including by means of nucleophilic additions, have been performed aiming to develop bioactive compounds, including with antitumor effects.

In this work, Michael addition reactions were explored intending to develop more environmentally friendly procedures to obtain functionalized steroids with potential therapeutic interest. For this and using progesterone as Michael acceptor and indole as nucleophile (Figure 1) the use of $Bi(OTf)_3.xH_2O$ as catalyst was explored. Interestingly, faster reactions and higher yields of the 5α-indolepregnan-3,20-dione were observed when compared with the previously described use of $RuCl_3$ as catalyst [2]. In addition, the use of microwaves to accelerate the reaction was also studied and after 10 minutes of reaction a 90% yield of the product was achieved. However, when applied to other steroidal enones, different reactivities were observed. Furthermore, it was performed 3-(4,5-dimethylthiazol-2-yl)-2,5-diphenyltetrazolium bromide assays in several cell lines after exposition to the substrates and indolyl steroids during 48 h and interesting results were observed for the functionalized steroids.

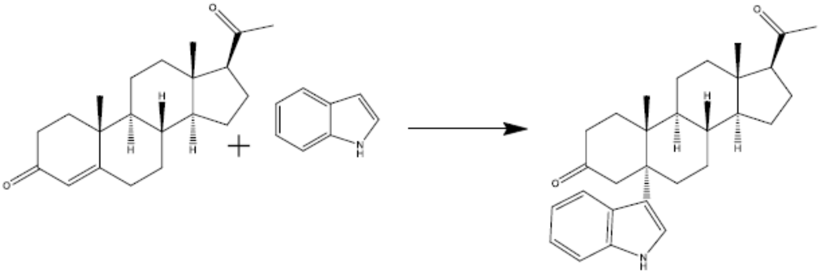

Fig.1. Michael addition of indole to progesterone

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Materiales de carbono derivados de biomasa implicados en la síntesis de quinoxalinas. Consideraciones mecanísticas

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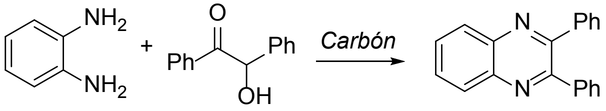
La utilización de biomasa juega un papel fundamental en el desarrollo de sistemas renovables y sostenibles en lo que hoy en día se conoce como economía circular. La biomasa vegetal, compuesta principalmente por C, H y O, se puede transformar fácilmente en materiales carbonosos de bajo coste [1] que pueden servir como catalizadores en procesos de interés. En esta comunicación se presentan diferentes carbones sintetizados por activación química de la especie invasora *Hedychium gardnerianum*, procedente de las Islas Azores, así como dos series de carbones activados con diferentes composiciones, texturas y morfologías, para su comparación como catalizadores en procesos de Química Fina (QF), en particular en la síntesis de quinoxalinas **1** (Esquema 1), un tipo de sistemas heterocíclicos de interés por sus propiedades terapéuticas. Así, se prepararon tres series diferentes de materiales carbonosos: i) materiales procedentes de la biomasa por activación con distintas proporciones de H_3PO_4 (RCB2), ii) xerogeles mesoporosos, obtenidos por polimerización resorcinol-formaldehido [2] y posterior tratamiento con HNO_3 (XN) y H_2SO_4 (XNS) y, finalmente, iii) carbones mesoordenados preparados por el método descrito por Deng et al [3] y posterior tratamiento con HNO_3 (CZN).



2 **3** **1**

Esquema 1. Síntesis de quinoxalinas 1 a partir de o-fenilendiamina 2 y benzoina 3, en tolueno, a 100 °C, catalizada por los materiales de carbón investigados.

Nuestros resultados demuestran que todos los catalizadores ensayados condujeron a valores de conversión de **2** altos, en torno al 80% en tan solo 60 min de tiempo de reacción, a excepción de CZN que dio lugar a valores de conversión considerablemente inferiores (50%), lo que indica que la porosidad y la química superficial de los materiales investigados tiene gran influencia en la reacción. Es importante destacar que los materiales RCB, procedentes de la biomasa, son materiales competitivos y reutilizables en la síntesis de quinoxalinas, lo que supone la valorización tecnológica de los residuos biomásicos.

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Overview on Calcium diglyceroxide Biodiesel Catalyst

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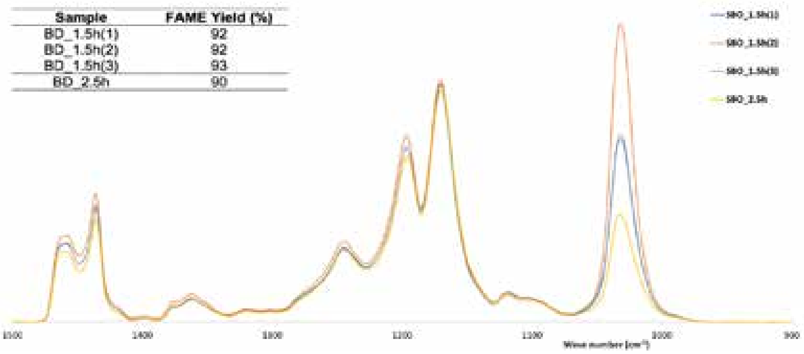
Biodiesel is viewed as a feasible renewable substitute for fossil diesel, which can contribute to mitigate issues related with energy security and global warming [1]. In order to reduce the biodiesel production costs, the currently in use homogeneous basic catalyzed process must be replaced by a heterogeneous one. Lime is an inexpensive and environmental benign material that presents high catalytic activity towards the methanolysis of vegetable oils but is less active than the homogeneous basic catalysts [2]. Some researchers reported an improved catalytic behavior of Ca based catalysts obtained by contacting CaO with glycerin. Such findings allowed them to attribute high catalytic activity to Ca-diglyceroxide crystalline phase [3]. Other researchers ascribe the high catalytic activity to calcium diglyceroxide but through a homogeneous catalyzed process, which leads to deactivation by Ca leaching into the reaction medium [4].

In order to improve the knowledge on the calcium diglyceroxide catalyst for the transesterification reaction CaO, obtained by calcination of mollusks and crustaceans shells, and eggshells at 900 °C for 3 h, was contacted with a glycerin and methanol mixture (1:1, volumetric ratio) for 2 h. The so-obtained catalyst, after dried, was used to transesterify alimentary grade soybean oil in standard conditions for 1.5 and 2.5 h (more details on the procedure are given elsewhere [1]). After reaction time, the catalyst was recovered by vacuum filtration and the biodiesel and glycerin phases were separated by gravity settling. Both phases were characterized by ATR-FTIR and TGA without further purification. FAME yield was assessed by ATR-FTIR based on the biodiesel reference band centered around 1436 cm^{-1}.

Calcium diglyceroxide presented itself as a highly active catalysts, with all FAME yields around 90 % (Fig. 1), however, regarding the TGA characterization, it was possible to check that the residual mass, a measure of the leached catalyst, was 12.5 % and 2.5 % for the biodiesel and glycerin, respectively, thereby proving a high leaching of the catalyst.



Sample	FAME Yield (%)
BD_1.5h(1)	92
BD_1.5h(2)	92
BD_1.5h(3)	93
BD_2.5h	90

Fig.1. FTIR spectra of the biodiesel FAME and assessed FAME yield.

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Acidic waste cooking oil valorization by biodiesel synthesis catalyzed by hydrogen sulfate 1-butyl-3-methylimidazolium

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Biodiesel is a fuel that shows growing demand as a promising alternative to petroleum-derived fuels. It is produced by esterification or transesterification reactions from renewable raw materials such as animal fats and vegetable oils , where the presence of catalysts is used for an effective conversion. The basic catalysts are very sensitive to the presence of water and FFAs, promoting saponification reactions. On the other hand, the use of acid catalysts means reaction times up to 4000 times higher, higher alcohol/oil molar ratios and higher reaction temperatures. In this context, Ionic Liquids (ILs) used as catalysts, come as a viable alternative to overcome these problems in biodiesel production processes [1,2]. Imidazolium-based ILs, have been extensively studied, mainly due to their specific characteristics such as, low pressure and ability for self-organization in different states. Hydrogen sulfate 1-butyl-3-methylimidazolium [BMIM]HSO_4 has been showing promising results in this type of applications. Table 1 presents a summary of some published results obtained for biodiesel production using [BMIM]HSO_4 IL as catalyst.

Table 1. Summary of the reaction conditions for biodiesel production found in the literature.

Reaction	Feedstock	Molar Ratio alcohol/oil	Catalyst Dosage	Temp. (°C)	Reaction Time (h)	Conversion (%)	REF.
Trans.	crude palm oil	12:1	4.4 wt%	160	2	91.2	[3]
Esterif.	oleic acid	9:1	3.4 wt%	90	4	84.4	[4]
Esterif.	oleic acid	9:1	0.06 mol	87	5.2	81.8 and 80.4[a]	[5]
Trans.	Camptotheca acuminata seed oil	6:1	5 wt%	60	0.5	38.5	[6]
Esterif./ Trans.	palm oil	15:1	5 wt%	160	1	95.6[b]	[7]
Esterif.	oleic acid	10:1	10 wt%	90	4	89.7	[8]
Esterif.	oleic acid	10:1	20 wt%	90	6	84.8	[9]

a 81.8% e 80.4% for methyl oleate yield and conversion of oleic acid, respectively;
b after esterification with LI and transesterification with KOH.

Therefore, the objective of this work is to study the application of the [BMIM]HSO_4 IL in the catalysis of esterification/transesterification reactions of triglycerides mixtures with high free fatty acid contents coming from waste cooking oils samples, with further characterization of the quality of the biodiesel produced. The present work includes also the assessment of the catalyst potential for recovery and recycling.

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Photoinduced water splitting with a Mn(III) supramolecular box

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The catalytical center in water oxidation, called oxygen evolving complex (OEC), may be modelled by artificial inorganic complexes. We have previously reported that a number of manganese model compounds are catalysts for water photolysis [1-2]. In this sense, manganese-Schiff base μ-aqua dimers were found to be active systems under light irradiation and in the presence of p-benzoquinone, which acts as a hydrogen acceptor. In our search for more efficient catalysts, we are looking for systems with higher nuclearity, different topologies, and other donor atoms beyond the iminic nitrogen or the phenoxy oxygen atoms. We are also interested in checking the hypothesis of the ease of coordination of the water molecules to achieve active catalysts. In order to address some of these issues, in this communication, we report on a new potential biomimetic model of the OEC (**1**, see Figure 1), synthesized using a bisamido-bisphenoxy ligand (H_4L_1), and thoroughly characterised.

The ability of Ba_2Mn_2 supramolecular box **1** to split water has been studied by means of water photolysis experiments. DFT calculations show that **1** can follow a mechanism with successive hydrogen abstractions from water molecules bound to the metal ion by optically excited p-benzoquinone.

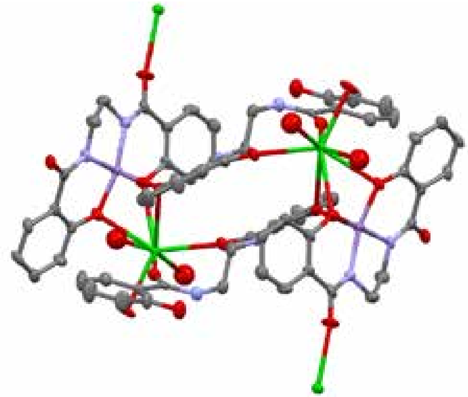

Fig. 1. X-ray crystal structure for 1.

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Optimization and kinetic study of esterification reaction of oleic acid using $[HMIM]HSO_4$ as catalyst

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Biodiesel is a promising fuel, since its similarity to petrodiesel allows the application in regular diesel engines without major changes, while still promoting a reduction in environmental impacts caused by fossil diesel [1]. Meanwhile, the employment of high quality feedstock, for instance the usual edible oils, has disadvantages, such as competition with the food market. The replacement of those oils by waste cooking oils (WCO) brings major advantages, amongst them, the reduction of the costs associated to the feedstock and the value added to a material usually considered as waste [2].

The current work, proposes an optimization study using a Response Surface Methodology (RSM), focusing on two responses: (i) the conversion of oleic acid (OA), used as a model compound to simulate the FFAs present in the WCO, estimated on the acid value drop between initial OA and the biodiesel samples produced, determined according to EN 14104 [3] and (ii) the FAME content, measured according to EN 14103 [4]. The chosen design was Box-Behnken Design (BBD), with 4 variables (time, temperature, molar ratio methanol/oleic acid, and catalyst dosage) and 3 levels, leading to 27 experimental runs. The optimization was followed by a kinetics study, where time, molar ratio and catalyst dosage remained constant and set to optimal conditions, and the temperature was varied from 70 to 110°C. The acid value of the samples collected throughout the reaction was measured, and the conversion was calculated, allowing the establishment of the reaction evolution with time, which was used to predict the respective activation energy and the pre-exponential factor, according to Arrhenius theory.

Table 1 presents the optimal conditions estimated for each response and Fig. 1 shows the evolution of the OA conversion for each temperature. As OA was the limiting reactant, the reaction order was predicted using the integral method. The experimental results were best described by a third-order reaction model. The activation energy was estimated as 6.8 kJ/mol and the pre-exponential factor as $0.0765\ L^2 \cdot mol^{-2} \cdot min^{-1}$, with a coefficient of determination of $R^2 = 0.965$.

Table 1. Optimal conditions estimated by the RSM design.

Variable	Responses	
	Conversion of OA	FAME content
Time (h)	8	8
Temperature (°C)	110	110
Molar ratio (mol/mol)	15:1	14:1
Catalystdosage(wt%)	15	13.5
Optimal value	95%	90%

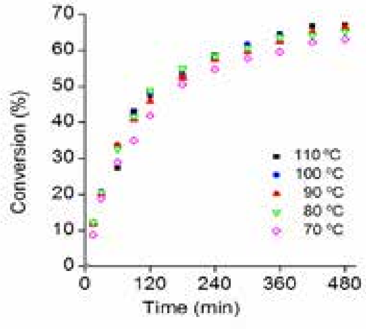

Fig.1. Conversion evolution with reaction time for each temperature

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Synthesis, Characterization of TiO_2 modified by (P, Mo) (P, W) and (Si, W) co-doping and its visible light photodegradation

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In the present study, TiO_2 nanoparticles prepared by the sol-gel method were successfully modified with (P,Mo), (P,W) and (Si,W). Various analytical and spectroscopic techniques were carried out to determine the physicochemical properties of the prepared samples, including XRD, SEM-EDX, and FTIR, XPS, and UV-Vis diffuse reflectance spectroscopy.

The photocatalytic activities of the prepared samples were evaluated by photodegradation of methyl orange (MO) as model pollutants under visible light irradiation.

The results showed that, using (P,Mo) to modify TiO_2 nanoparticles, affect the electronic transition energies by shifting the optical band gap to below the band gap energy of TiO_2 anatase [1]–[3], indicating a high ability to absorb visible light and a potential improvement in photocatalytic activity of TiO_2 nanoparticles under visible light. The results showed also that, using (Si,W) to modify the TiO_2 nanoparticles has no effect on the band gap of TiO_2, While doping TiO_2 with (P,W) increases its band gap energy.

The results of methyl orange (MO) photodegradation, showed an improvement in the photocatalytic activity under visible light for all the synthesized nanomaterials, compared to that of the bare TiO_2 pure. In fact, modifying TiO_2 with (P,Mo) improve its removal efficiency toward methyl orange (MO) by 11.6%.

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NiCeAl-LDH/g-C_3N_4 as photocatalyst for light-driven hydrogen production

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Driven by decreasing fossil fuel consumption, increasing energy demand and environmental pollution, the search for clean and sustainable energy is attracting massive research interest. The photocatalytic hydrogen production from water is regarded as one of the most promising technologies to convert solar energy into hydrogen (H_2) [1]. However, the demand for catalysts capable of producing H_2 with high yields is still a challenge to make the process industrially viable and economical.

In this context, the aim of this study was to develop new 2D layered nanomaterials composed of polymeric carbon nitride (g-C_3N_4) and layered double hydroxides (LDH) for the efficient photocatalytic H_2 generation through water splitting. g-C_3N_4 is a metal-free semiconductor with a band gap of 2.7 eV and suitable electronic band structure for photocatalytic H_2 evolution [2,3]. However, the limited absorption in the visible region and the fast recombination of the charge carriers still limits its photocatalytic performance. Consequently, the layered structure, compositional flexibility (type of metals and its ratio; type of anion) and the structural morphology of LDH materials make it attractive as semiconductor photocatalysts [4] to couple with g-C_3N_4 [5].

In this work we report the synthesis of the 2D composite NiCeAl-LDH/g-C_3N_4 for the photocatalytic H_2 production. The 2D composite was prepared through a facile impregnation method and characterized by different physicochemical techniques. The photocatalytic performance of the composite NiCeAl-LDH/g-C_3N_4 was evaluated in aqueous media under UV-vis irradiation, in the presence of an electron donor and Pt as co-catalyst. Experimental results reveal that the photocatalytic activity of the composite NiCeAl-LDH/g-C_3N_4 is dependent on the type of sacrificial electron donor used, EDTA or TEOA. In fact, the composite NiCeAl-LDH/g-C_3N_4 produces higher amount of H_2 when irradiated in presence of EDTA than with TEOA. The enhancement of the photocatalytic activity of the composite over the individual semiconductors might be ascribed to improved separation and transfer of the charge carriers.

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Materiales híbridos de carbono/ZnO en la síntesis verde de heterociclos nitrogenados

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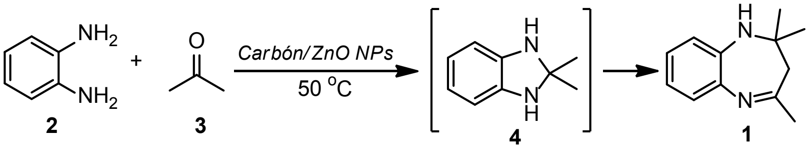
Las nanopartículas de ZnO (NPs) tienen gran aplicación en la industria cosmética, eléctrica y óptica. Además, ZnO en forma de NPs se ha investigado muy extensamente, en las últimas décadas, como catalizador eficiente en gran variedad de transformaciones orgánicas de interés; se caracteriza por ser un catalizador heterogéneo comercial, eficiente y reusable y lo que es más importante, no tóxico y de bajo coste. En este sentido ZnO se ha utilizado en la síntesis de diversos sistemas heterocíclicos [1]. Por otra parte, recientemente se han investigado diferentes materiales de carbono híbridos compuestos por nanocarbones - entre ellos los nanotubos de carbono, láminas de grafeno y nanofibras de carbono - con NPs de metales nobles y óxidos semiconductores actuando como sensores en la detección de gases en procesos de producción y fabricación industriales [2].

En esta comunicación se presentan diferentes nanocarbones con NPs de ZnO soportadas, con diferentes composiciones, texturas y morfologías, para su comparación como catalizadores en procesos de Química Fina (QF), en particular en la síntesis de benzodiacepinas (Esquema 1), sistemas heterocíclicos de interés por sus propiedades terapéuticas. Así, se prepararon dos series diferentes de nanocarbones sintetizados por el método de impregnación húmeda incipiente, empleando disoluciones acuosas de $ZnNO_3$ de concentración 1 y 3% (wt % en Zn), a partir de: i) un carbón activado comercial, Norit RX3, y iii) nanotubos de carbono de pared múltiple comerciales (MWCNTs, Aldrich) y iii) un aerogel de carbono preparado por polimerización resorcinol-formaldehído.



Esquema 1. Síntesis de la benzodiacepina **1** a partir de o-fenilendiamina **2** y acetona **3**, en ausencia de disolvente, a 50 °C, catalizada por los materiales de carbón investigados.

Todos los catalizadores ensayados son activos en la síntesis de la benzodiacepina **1** con buenas conversiones y selectividades, observándose en todos los casos la formación del intermedio **4** que evoluciona con el tiempo hacia la formación de **1**. Se trata de materiales de carbono modificados con NPs de ZnO como catalizadores eficientes y reutilizables durante al menos tres ciclos consecutivos sin pérdida de actividad, alternativos a la sílice mesoporosa SBA-15/3Zn análoga.

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Desarrollo de materiales multimedia como recurso didáctico en la enseñanza universitaria de la Química Analítica Instrumental

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El conocimiento y empleo de la instrumentación es fundamental en el análisis químico. Los avances tecnológicos hacen posible el desarrollo de nuevas técnicas instrumentales y amplían el uso de las ya existentes. Esto hace que las enseñanzas de la instrumentación analítica y sus múltiples aplicaciones para la resolución de problemas reales sea cada día más complejo.

Por otra parte, los estudiantes universitarios demandan cada vez más materiales que hagan posible un aprendizaje activo y autónomo y faciliten la adquisición de conocimientos y el desarrollo de competencias en la resolución de problemas prácticos y profesionales.

Las tecnologías de la información y la comunicación (TIC) han revolucionado el concepto tradicional de la enseñanza y están propiciando el desarrollo y aplicación de recursos innovadores y facilitando el proceso de enseñanza-aprendizaje.

Esta comunicación presenta detalladamente un Proyecto de Innovación Educativa (PIE) que está desarrollando un Grupo de Innovación Docente (GIDOCA) de la Universidad Nacional de Educación a Distancia de España. El proyecto persigue el desarrollo y la implementación de material multimedia que combina teoría y ejemplos prácticos y permite al estudiante adquirir los conocimientos y las habilidades necesarias para resolver problemas prácticos relacionados con la asignatura universitaria de Química Analítica Instrumental.

La metodología de este proyecto se basa en los esquemas clásicos de aprendizaje en los estudios de ciencias (conceptos teóricos, resolución de problemas, y, finalmente, ejercicios de autoevaluación) apoyados por herramientas multimedia digitales.

El material enriquecido desarrollado consiste en una parte teórica concisa, que tiene incorporado videos explicativos con presentación de imágenes, audio, gráficas, hiperenlaces y animaciones, para la resolución pormenorizada de problemas representativos de Química Analítica Instrumental. Los problemas quedan explicados exactamente igual como lo haría un profesor en una clase presencial. Este material multimedia desarrollado es una herramienta de enseñanza que permite un aprendizaje autónomo y en cualquier lugar ya que puede instalarse en dispositivos móviles y está dentro del contexto de la adaptación de las metodologías al Espacio Europeo de Educación Superior.

En la comunicación también se presenta un ejemplo de material desarrollado, que explica la calibración y el método de la adición estándar con la técnica electroanalítica, voltamperometría diferencial de impulsos, en la determinación de un estimulante en orina.

AGRADECIMIENTOS: Al Instituto Universitario de Educación a Distancia (IUED) de la UNED por la financiación del proyecto GID2016-40

¿Cuánta ciencia puedes aprender con 20 minutos de Los Simpsons? Una propuesta constructivista para la mejora de la comprensión y transmisión del conocimiento científico en el aula

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A la hora de hablar de la educación actual, observamos como la memorización sistemática de contenidos y su aplicación directa a problemas modelo es uno de los métodos más empleados tanto en educación secundaria como en educación superior. Sin embargo, existe poca vinculación entre la formación teórica que recibe el alumnado y la capacidad que poseen al finalizar sus estudios, para la aplicación de estos conceptos en situaciones desconocidas y en la vida cotidiana. Otra de las dificultades que muestra una gran parte del alumnado es la de transmisión del conocimiento adquirido de manera comprensible y divulgativa para el público en general. En esta propuesta educativa de carácter constructivista [1] en la que el docente actuará como guía, se pretende dar solución a ambas cuestiones, facilitando en primer lugar que los alumnos identifiquen diversos aspectos científicos relacionados directamente con su formación previa, como otros contenidos transversales con los que estén menos familiarizados y posteriormente, los comuniquen a un público no especializado empleado formatos novedosos que mejoren la capacidad de transmisión del contenido científico.

Con el fin de motivar al alumnado e introducirlo paulatinamente en la interconexión de conocimientos teóricos con la vida cotidiana, se visualizará un capítulo de la archiconocida serie televisiva Los Simpsons, en donde tendrán que identificar que contenido científico se encuentra oculto. Después de una sesión de debate y reflexión, se les mostrarán otros aspectos científicos que han pasado desapercibidos y escogerán dos temas en los que trabajar. El desarrollo dirigido en grupos de diferentes aspectos relacionados con los temas científicos escogidos les permite refrescar o adquirir conceptos clave para facilitar posteriormente la transmisión de esos contenidos. Posteriormente, una sesión interactiva en línea empleando Kahoot! permite conocer el grado de comprensión de los diferentes conceptos teóricos. Para obtener un aprendizaje significativo y duradero en el tiempo, se propone vincular el conocimiento teórico con la realización diversas sesiones de laboratorio trabajando por estaciones. En cada una de ellas, se realizarán diferentes experiencias prácticas relacionadas con los temas científicos identificados en la visualización del capítulo como la radiación, la creación de híbridos vegetales o termodinámica de alimentos, sirven como punto previo a la creación de una presentación didáctica por los alumnos, favoreciendo así, la transmisión de esos conceptos complejos de una manera original, divulgativa y comprensible para público no especializado. La evaluación de los propios alumnos del material presentado por sus compañeros realizando propuestas de mejora retroalimenta el proceso.

Fig.1. Algunos de los fotogramas empleados en la identificación de contenido científico inicial.

AGRADECIMIENTOS: A Barbara D. C. por las fructíferas discusiones sobre la pedagogía de esta propuesta educativa.

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Uso de la gamificación en el aula para desarrollar la resolución creativa de problemas y otras competencias transversales

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La competencia puede ser definida como una combinación de habilidades prácticas, conocimientos, motivación, valores éticos, actitudes, emociones, y otros componentes sociales y de comportamiento que se movilizan conjuntamente para lograr una acción eficaz. Actualmente, existen numerosos currículos educativos que apuestan por el aprendizaje basado en competencias. A parte de las siete competencias clave, existen también otras transversales igualmente importantes para el desarrollo de los estudiantes, como la capacidad de relacionar conceptos, de resolver problemas, de tomar decisiones, la gestión del tiempo, etc. El desarrollo de competencias está directamente relacionado con una actuación exitosa en el ámbito laboral futuro, ya que le permitirán al alumnado poseer la capacidad de comprender situaciones y resolver problemas identificando los modelos o conexiones entre situaciones y aspectos claves subyacentes en asuntos complejos.

Actualmente, muchos alumnos realizan un pensamiento restrictivo, lógico y rígido ante la necesidad de resolver un problema lo cual conlleva que en numerosas ocasiones no puedan llegar a una solución, ya que cada vez es más común que se necesite hacer uso del pensamiento creativo. La no consecución de los objetivos suele conllevar la frustración de los estudiantes y una bajada generalizada en el rendimiento académico. Con el fin de motivar al alumnado, en esta propuesta educativa constructivista [1] se busca que los estudiantes trabajen distintos tipos de competencias clave como la competencia matemática, la competencia digital y la competencia de aprender a aprender pero también otras transversales en un ambiente gamificado en el cual deberán resolver diferentes retos semanales de manera creativa. Estos retos consisten en jeroglíficos moleculares, pequeños juegos de pistas, textos que incluyen información oculta o retos numéricos sencillos que los estudiantes deben resolver semanalmente. Un sistema de puntuación determina un ranking de los estudiantes, clasificación fundamental para la segunda parte del proyecto, el apadrinamiento de una estructura química. Los estudiantes con puntuaciones más bajas son los que escogen en primer lugar a que molécula de las que descubrieron en los retos quieren apadrinar para investigar sobre ellas y crear una pequeña infografía o póster que resuma los principales hallazgos, para fomentar de esta forma la implicación del alumnado. Una sesión de exposición pública de los resultados de los apadrinamientos a modo sesión de póster de un congreso, permite a los estudiantes interactuar y adquirir conocimiento de otras moléculas que son de interés para su formación. Posteriormente, la redacción por cada estudiante de diversas preguntas acerca de sus moléculas apadrinadas permite crear una gran base de preguntas para la última fase del proyecto, el juego al quimitrivial [2]. Para ello se dividen preguntas por áreas y como en el tradicional juego de preguntas y respuestas, los alumnos deben avanzar por el tablero respondiendo correctamente a las preguntas para alzarse con los seis quesitos que te otorgan la victoria.

AGRADECIMIENTOS: A Barbara D. C. por las fructíferas discusiones sobre la pedagogía de esta propuesta educativa.

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Determinación del calor de fusión del hielo mediante una práctica virtual de laboratorio de química

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Nuestra experiencia como docentes nos indica que, debido a la disminución de horas asignadas a la Química en los estudios de los Grados de Ingeniería, el tiempo que se dedica a las prácticas es pequeño, quedando muy reducida la presencia del alumno en el laboratorio. En consecuencia, la presentación de videos descriptivos sobre prácticas virtuales en clase, permite al profesor explicar la práctica y promover el debate con los estudiantes, favoreciendo la comprensión de los conceptos expuestos.

Las consideraciones anteriores nos llevaron a realizar un estudio sobre prácticas virtuales complementarias con las del laboratorio, sin pretender que lleguen a sustituirlas, ya que es imprescindible que el estudiante realice trabajo experimental en el laboratorio. Para ello se realizaron prácticas relativas a la preparación de disoluciones y calor de reacción [1,2] e identificación de iones a partir de sus mezclas en disolución [3], usando el programa virtual ChemLab, General Chemistry Laboratories, v.2.5, anexo al texto de Pearson Educación [4].

Esta comunicación describe una práctica con el objeto de determinar el calor de fusión del hielo, mediante datos obtenidos en un experimento realizado en un laboratorio virtual de Química. El programa informático usado permite elaborar un video, a visualizar por los alumnos, en el que se describen las etapas del experimento, debiendo anotar los valores de los parámetros necesarios para el cálculo del calor de fusión, obteniéndose un resultado muy concordante con el valor de referencia [5]. Finalizada la práctica, con el fin de verificar la comprensión y asimilación de los conocimientos presentados, el profesor propondrá unas cuestiones sencillas sobre la práctica, que deberán ser resueltas por los estudiantes en la misma sesión de clase.

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Temperature-switch nanomagnetic logic gates for cellular hyperthermia

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The quest of temperature monitoring at micro and nanoscales has been a path of interest in many research contexts, such as cellular hyperthermia. In this case the answer to the question “did the system locally exceed a certain threshold temperature?” can be more accurate and useful than a continuous temperature monitoring. Following this question, we developed a system based on iron selenide (Fe_3Se_4) magnetic nanoplatelets that are capable of behaving both as an actuator and as a sensor, simultaneously, while recording temperature fluctuations above a defined threshold. Such nanoplatelets are considered hard magnets, which means that they retain a magnetic moment even in the absence of an applied magnetic field. Additionally, they present a magnetic phase transition that occurs at a defined temperature (T_C), which is slightly above room temperature and can be easily modulated by tuning their size. Therefore, below T_C, we can set a well-defined magnetization that will remain unchanged until TC is crossed. Adapting methods from literature, new iron selenide nanoplatelets were developed with great control over size and, consequently, T_C – between 0 and 60 ºC. Nanoplatelets with T_C tuned to 42 ºC were applied in a cellular hyperthermia assay using prostate cancer cells and different thermal doses (induced by a Near-Infrared LED). It was observed that for low thermal doses, the threshold of 42 ºC was not crossed and most cells appeared to be viable, whilst in the case of high thermal doses, the results show the opposite. This shows the potential of such materials to behave as logic gates having temperature and magnetic field as inputs and as the output a Yes/No answer to the question “was the 42 ºC barrier crossed?”. This proof of concept was a pioneer assay using hard nanomagnets in a biological application, opening the pathway to other note-worthy applications.

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Targeting and killing the ever-challenging ulcer bug

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Helicobacter pylori (*H. pylori*) is the main cause of chronic gastritis and peptic ulcers. The importance of the eradication of these bacteria at the first clinical symptoms is well-recognized. In fact, persistent infections can evolve into gastric cancer, which underlies their classification as human carcinogenic bacteria by the International Agency for Research on Cancer [1]. Nevertheless, the treatment of *H. pylori* infections is hindered by several limitations, such as the pharmacokinetic properties of the commonly used antibiotics and their degradation under acidic pH [2].

This work aimed to design and produce amoxicillin-loaded lipid nanoparticles to protect the drug from the acidic pH of the stomach lumen. A targeting agent was also incorporated to increase the affinity of the nanoparticles to the bacterium, hindering their adhesion to gastric cells. Furthermore, a polyunsaturated fatty acid known for its antibacterial properties was added as a therapeutic adjuvant.

The nanoparticles showed suitable physico-chemical features for being henceforward used by the oral route, with high potential for being retained at the stomach. The lipid nanoparticles killed *H. pylori* through the detachment of the bacterial membrane and the release of the cytoplasmic content. Moreover, due to the targeting agent, the lipid nanoparticles were bound to the bacteria within the first 15 min, which decreased the adhesion of the bacteria to gastric cells. These lipid nanoparticles were successfully used to load amoxicillin and protect it from the acidic pH. An *in vitro* infection model was developed once a complex system composed of a gastric epithelial barrier, mucins, and acidic pH protects *H. pylori in vivo.* Contrary to the observed with plain amoxicillin, amoxicillin-loaded lipid nanoparticles were effective in the *in vitro* infection model.

Overall, the amoxicillin-loaded lipid nanoparticles have shown promising features to be used in the treatment of *H. pylori* infections, showing a higher efficacy than plain amoxicillin on an *in vitro* infection model. Furthermore, the developed *in vitro* model can be used by other researchers for the evaluation of antimicrobial compounds on a more realistic model than planktonic bacteria.

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Carbon nanodots from olive mill wastewater as sensors for nitroanilines and nitrophenols

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We have recently unveiled that fluorescent carbon nanodots (CNDs) can be obtained directly from olive mill wastewaters (OMWWs) in excellent yields following expedite and sustainable hydrothermal processes with minimum post-processing [1]. CNDs are a very recent class of spherical-shaped nanosized carbon materials that are being used in a diversity of applications ranging from bioimaging and nanomedicine, chemo/biosensing, photocatalysis and optoelectronics, owing to their unique photoluminescence, outstanding photostability and negligible cytotoxicity [2].

Herein we report our most recent findings regarding the CNDs synthesis from a two-phase centrifugation system OMWW and their behaviour as chemical sensors for nitroanilines (NAs) and nitrophenols (NPhOHs) by a fluorimetric method. The synthesized CNDs have a quite high quantum yield (ca. 0.35-0.4) and exhibit an outstanding performance toward the detection of NAs and NPhOHs. On the other hand, a negligible sensitivity was attained for nitroaromatic compounds (NACs) used as explosives or explosive taggants (e.g. TNT, 2,4-DNT), as found from their corresponding apparent Stern-Volmer constants (K_{SV}). The highest sensitivity and selectivity was found for p-NA ($K_{SV} = 4.0 \text{ x } 10^4 \text{ M}^{-1}$; $\lambda_{exc} = 380$ nm) in aqueous solutions, which are several times (3-4.5) higher the other reported values for NAs detection by CNDs [3]. Fig. 1 shows the changes in the emission intensity of CNDs upon addition of several analytes. The rational underlying the observed results will be discussed.

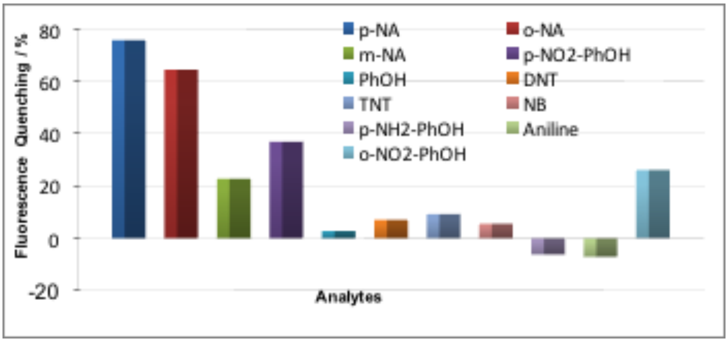

Fig.1. Quenching of CNDs emission by NAs, NPhOHs, NACs, aniline and phenol at a fixed concentration of 7.5 x 10-5 M; [CNDs] = 0.01 mg/mL; lexc = 380 nm.

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Fighting bacterial resistance: a novel nanosystem for N-acetyl-cysteine (NAC) delivery

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Bacterial resistance is an increasing concern worldwide due to the loss of antibiotic efficacy and the lack of new antibiotics in the market. Consequently, bacterial infections represent an economical burden for Healthcare Systems. Thus, novel effective therapies are necessary to overcome these limitations.

Lipid nanoparticles are useful for delivery purposes, once they protect encapsulated compounds against *in vivo* degradation [1]. Furthermore, these nanoparticles may exhibit a controlled drug release at the target site, reducing systemic side effects while increasing therapeutic compliance and efficiency [1].

In this work, lipid nanoparticles (LNPs) loading N-acetyl-cysteine (NAC) were developed to increase its bioavailability. NAC is a mucolytic agent with antibacterial activity against a variety of bacteria [2]. The LNPs were optimized by a response surface design, revealing a low polydispersity index with a mean size diameter around 220 nm and a zeta potential superior to |30| mV. Additionally, the loading capacity was satisfactorily high, around 11% (w/w). The optimal formulation was stable in suspension at 4°C during at least 1 month. Methylthiazolydiphenyl-tetratozium bromide (MTT) assay revealed that the optimal formulation does not have cytotoxic effects in fibroblasts (L929 cell line) at higher concentrations than the NAC plasmatic concentration reported in the literature.

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Hybrid Supercapacitors: Textiles with Energy

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In an Era that is increasingly focused on sustainable technologies and energy, several efforts have been made to develop more sophisticated, intelligent, minimalist and useful electronic devices capable of acting in different strands [1]. There are several examples of their applications, such as tools for remote monitoring of patients with heart diseases or as wearable technologies (devices such as bracelets or watches that facilitate access to data like cardiac levels and travelled distances) [2]. For each of these devices, an energy storage system that can charge faster and store energy for a long period of time is highly desired. For that, several types of energy storage technologies have been developed and optimized, such as batteries and supercapacitors (SCs).

This work is focused on the development of hybrid supercapacitors (hy) based on transition metal oxides and carbon nanomaterials (NC) incorporated on textile substrates, in order to obtain improved energy storage properties. These devices capable of storing energy and releasing it when necessary (Fig. 1) are characterized by being based on textile substrates, while maintaining the fabrics intrinsic characteristics such as comfort, safety and flexibility [3].

Various characterization techniques, such as X-ray diffraction, Fourier transform infrared spectroscopy and scanning electron microscopy-energy dispersive spectroscopy, confirmed the successful preparation of the nano-hybrids.The production of an asymmetric SC device hy@NC//NC was verified through electrochemical measurements with high values of specific capacitance (88.79 F g^{-1}), energy density (125.30 W s g^{-1}) and power density (0.122 W g^{-1}). The device showed a behavior characteristic of a hybrid SC with simultaneous occurrence of oxidation-reduction reactions and a non-Faradaic type charge storage mechanism.

This type of energy storage device is a revolutionary promise for the technological world.

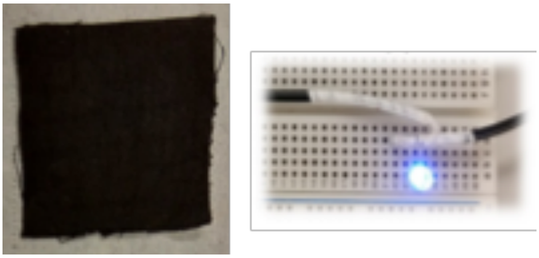

Fig.1. LED lighting resulting from energy stored on textile SCs.

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Nanoagents with CO-releasing molecules to treat rheumatoid arthritis

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Rheumatoid arthritis (RA) is a chronic, systemic, inflammatory and autoimmune disorder of the joints characterized by synovial inflammation that can lead to cartilage and bone destruction [1,2]. Although notable advances have been made in the treatment of RA, long-term administration of anti-rheumatic drugs still has some disadvantages, including high dose and high frequency of administration, as well as dysfunctions in the heart, liver, kidneys, and so on [3]. Due to the above problems, new drugs continue to be needed and investigated. Nowadays, carbon monoxide (CO) is known to have anti-inflammatory effects *in situ*, however, the administration of this molecule represents a challenge and the development of a technology that controls the delivery of CO under different physiological conditions represent a major step in the use of CO-releasing molecules (CORMs) [4,5]. Nanobased delivery systems are being developed to avert non-specific binding and upregulate the efficacy by improving the accumulation of drugs in lesion tissues [3] and can thus represent an effective approach. In this project, we intend to develop a nanosystem that is capable of releasing CORMs in a controlled and targeted way to be further used in the treatment of rheumatoid arthritis.

Customized lipid nanoparticles loaded with CORM-2 and surface functionalized, in order to direct the nanoparticles to the desired therapeutic target, have been developed. The formulations have been physic-chemically characterized regarding their size, zeta potential, payload and surface modification efficiency. Release studies were performed in order to assess whether a controlled release of the drug was achieved with the purpose of overcoming some of the drawbacks of conventional treatments. Franz cell diffusion assay with pig ear skin as a model barrier was also performed to assess the ability of the formulations to permeate the skin barrier. Additionally, *in vitro* cell toxicity studies were conducted using cell line THP1.

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Nanoestruturas híbrido-magnéticas para remediação *in situ*

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Atualmente, a atividade humana não é a única causa de poluição presente em todo o mundo, toxicidade biogênicas sazonais *são também* encontradas amplamente difundidas nos recursos hídricos, solos e por ultimo na cadeia alimentar, provocando doenças em animais e humanos, produzindo assim inúmeras perdas econômicas.

Uma grande variedade de contaminantes com um amplo perfil químico (nanopartículas, toxinas, hidrocarbonetos aromáticos policíclicos (HAPs), corantes, fármacos, disruptores endócrinos, metais pesados etc) podem ser encontrados em água doce e com tamanhos que se situam na faixa nanométrica sendo assim um desafio técnico para seu monitoramento e remoção.

Métodos convencionais de limpeza de águas residuais como a coagulação e filtração são ineficazes para poluentes nanométricos, e métodos alternativos usados, como a inativação de toxinas por agentes químicos sequestrantes e de biotransformação tendo como resultado a acumulação de produtos químicos dentro da matriz alimentar afetando assim a saúde humana e animal. Agentes magnéticos nanoestruturados com propriedades catalíticas especificas e afinidades químicas com capacidades de remediação, fornecem uma nova geração de agentes de limpeza de toxinas e poluentes, sendo posteriormente separados do material de matriz por extração magnética.

Neste estudo, é apresentado um conjunto de materiais magnéticos nanoestruturados com diferentes revestimentos para extração magnética de metais pesados e toxinas, que podem ser usados em águas, bebidas ou matrizes alimentares. Estes materiais com tamanhos na faixa do milimetro incluem nanopartículas de magnetita, compostos inorgânicos e biopolímeros (Fig.1A) que foram testados para a extração magnética de metais pesados (Ce, Cu, Sr, Hg, Cd) e várias toxinas (Deoxinivalenol, Fumonisina B1, Zearalenona, Aflatoxina) com capacidades de extração que variam entre 50% e 80%. A reutilização destes materiais ainda está em curso.

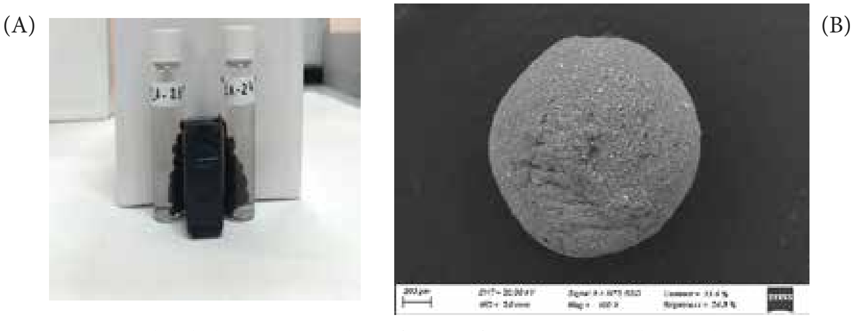

Fig.1. Suscetibilidade magnética das esferas na forma seca e molhada sob um campo magnético externo (A) e micrograma SEM de uma esfera magnética (B).

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Topical delivery of cyclosporine A using lipid nanoparticles

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Skin diseases affect around one-quarter to one-third of the world population. The current treatment of severe topical diseases focus on immunosuppression with oral corticosteroids or cyclosporine, but associated side effects on prolonged systemic therapy compromises the treatments' effectiveness. These limitations justify the need for reliable and efficient topical therapies, aiming the design of affordable treatments to be implemented in routine healthcare.

Cyclosporine A (CsA), an immunosuppressant drug used to treat many dermatological diseases, was used to be encapsulated in Solid Lipid Nanoparticles (SLNs) to overcome its high molecular weight, hydrophobic nature and low permeability through skin barriers. In the nanotechnology field, SLNs have been reported as biocompatible, capable of delivery hydrophobic drugs to the main target and easily produced enabling simple scale-up methods.

SLNs were prepared by hot emulsification using Tween 80® and Softisan®, a non-animal derived semisolid lanolin substitute with high water-binding capacity and good adhesion to the skin, widely used in the cosmetic industry.

The nanoparticles presented nanometric sizes and were characterized in terms of surface potential, morphology, storage stability during 8 weeks. Fourier-transformed infrared spectroscopy and differential scanning calorimetry were used to understand the interactions between the SLNs components. SLNs loaded with CsA permeated the pig ear skin at a higher extent than free CsA, possibly due to the characteristics of Softisan®. Cellular viability and uptake assays were performed in fibroblast and keratinocyte cell lines and confirmed SLNs biocompatibility. The obtained results suggest that CsA-SLNs may present a key-treatment for skin-related disorders.

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Metal-free nanomaterials for the oxygen reduction reaction

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In an effort to improve the sluggish kinetics of the oxygen reduction reaction (ORR) in fuel cells, research efforts have led to the development of a wide range of electrocatalysts. These can be classified in three categories: noble metal (e.g. Pt and Pd alloys), non-noble metal, and metal-free based catalysts. Tremendous attention has been given to carbon nanomaterials, as metal-free catalysts, due to their long-term stability, environmental friendliness and low cost production. However, their efficiency to convert oxygen into water is often low, leading mainly to the formation of hydrogen peroxide.

In this work, Electrogenerated Hydrophilic Carbon (EHC) nanomaterial, recently developed in our group [1], was used to evaluate its suitability to overcome the mentioned constraint. For this purpose, EHC prepared at different galvanostatic conditions (different applied current and polarization time) were used. The resulting nanomaterials were drop cast onto a glassy carbon electrode and were electrochemically characterized using $Fe(CN)_6^{3-/4-}$ redox probe. In addition, their physical and chemical properties were investigated by Raman, XPS, and AFM. It was found that the EHC nanomaterials prepared by long polarization time show very high catalytic activity and high efficiency for the ORR in an alkaline medium, providing an alternative to metal-based catalysts.

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Hydrophilic carbon nanomaterials -a novel insight into antioxidant therapeutic applications?

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Numerous benefits for human health can be provided by carbon nanomaterials. However, their intrinsic therapeutic potential, coming from their antioxidant and radical scavenging capability in biological systems, remains almost unexplored. Despite recent studies have shown that some carbon-based nanomaterials, like fullerenes, carbon nanotubes, graphene and graphene oxide, own antioxidant properties [1-5], the application of these nanomaterials in the biomedical field is limited due to their toxicity, water solubility and low bioavailability.

Electrogenerated Hydrophilic Carbon (EHC) nanomaterial, recently developed in our group, may emerge as a potential material to overcome the above mentioned constraints [6]. Hence, motivated by the challenge of developing affordable health-care strategies for diseases associated with oxidative stress, it was investigated the physical-chemical properties of EHC nanomaterial, assessed by several characterization techniques, as well as its antioxidant and cell protective activities.

In a first stage of this work, it was demonstrated that the redox ability of the hydrophilic material could be selectively tuned by simply modifying the nature of the electrolyte used in the electrochemical synthesis. In this way, it was prepared two pools of nanomaterials, one was prepared in an organic buffer (EHC-o) and another in an inorganic buffer (EHC-i). Evaluation of the redox properties was provided by the cyclic voltammetry technique. Characterization of their crystallinity and surface functional groups were accomplished by TEM, HRTEM, AFM and XPS techniques.

It was demonstrated by antioxidant tests (e.g. DPPH, ABTS, Folin-Ciocalteau) that EHC-o exhibit a very high radical scavenging activity. In view of these results, the EHC-o solution was chosen to pursue the studies. Subsequently, it was evaluated the ability of EHC-o to modulate the redox state of biological systems under stress conditions. The results revealed that the EHC-o have the capacity to protect the membrane lipids and the intracellular thiol groups from the oxidation promoted by external oxidant agents (e.g. *tert*-butyl-hydroperoxide and ascorbate/Fe^{+2}). Cell assays also revealed that the nanomaterial has ability to protect, at non-cytotoxic concentrations, the neuronal cells against oxidative damage and toxicity promoted by *tert*-butyl hydroperoxide and amyloid-β_{1-42} peptide.

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Rational optimization of the microwave-assisted synthesis of bright ternary $AgInS_2/ZnS$ quantum dots

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Ternary I–III–VI quantum dots (QDs) have emerged as potential alternatives to Cd-based QDs [1]. The interest on this class of nanocrystals derives from the absence of heavy metals on their composition, in opposition to CdX QDs, and from their good optical properties such as, high absorption coefficients, high photoluminescence (PL) quantum yields (QY), and high PL lifetimes [2]. I–III–VI QDs can be synthetized either by organometallic and by aqueous based route [3-4]. On this behalf, aqueous based route yields the formation of the QDs on a truly environment friendly pathway [3]. However, the absence of rigorous synthetic methodologies, particularly for the not so well-known $AgInS_2/ZnS$ QDs, impedes the suitable control of their PL properties.
In this work, we report the optimization of aqueous-based and microwave-assisted synthesis of MPA-capped $AgInS_2/ZnS$ QDs. Exploiting Design of Experiment methodologies, models were established in order to guide the optimization. The mathematical models were used to identify the most important reaction parameters, and to predict the optimum conditions. The predicted and the experimental outcomes were in accordance highlighting the accuracy of our methodology. This way, the reported methodology provides an accurate and reproducible synthetic pathway for the synthesis of $AgInS_2/ZnS$ QDs with a wide tunable PL emission and bright PL emission (PL QY up to 60%).

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Limpeza e branqueamento de têxteis de algodão em cru usando nanopartículas fotossensíveis

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O dióxido de titânio (TiO_2) tem vindo a ser amplamente utilizado em aplicações fotocatalíticas, devido ao seu baixo custo, à sua estabilidade química e não-toxicidade. Além disso, apresenta elevada fotoatividade quando exposto a radiação ultravioleta (UV) [1]. Assim sendo, este trabalho teve como objetivo o desenvolvimento de uma alternativa aos métodos convencionais de processamento têxtil (fervura, mercerização e branqueamento). Este estudo surgiu na necessidade de reduzir o impacto ambiental e os gastos associados a estes processos. Para tal, nanopartículas de TiO_2 comercial (Aeroxide® TiO_2 P25) foram impregnadas em algodão cru e algodão pré-tratado (por fervura e mercerização). Diferentes parâmetros foram testados, incluindo estudo da carga de catalisador e o tempo de exposição a radiação, utilizando diferentes fontes de irradiação (lâmpada na gama do UV-Vis e LED com $l_{\text{máx}}$ a 390 nm).
Por microscopia eletrónica de varrimento (SEM) verificou-se que as nanopartículas de TiO_2 encontramse distribuídas de forma homogénea no algodão (Fig. 1).

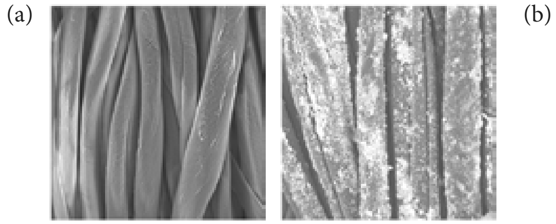

Fig.1. Exemplo de imagens SEM do algodão antes (a) e após (b) impregnação do TiO2.

Os resultados fotocatalíticos mostraram que na presença de água e utilizando como fonte de radiação o LED, o branqueamento do algodão cru apresentou valores de *Berger* (classificação do grau de branco) bastantes promissores. Com uma concentração de TiO_2 de 0,5 g/L, após 5 h de exposição foi possível obter uma brancura de *Berger* de 37,2 ± 2,7, aproximadamente 25 unidades mais branco que o algodão cru sem tratamento. No caso do algodão com pré-tratamento (fervido e mercerizado), com a mesma concentração de TiO_2 (0,5 g/L) e o mesmo sistema de radiação, foi possível obter uma brancura de *Berger* de 52,1 ± 2,6 após 5 h de exposição. Este valor *é* muito próximo do obtido utilizando os *método*s de branqueamento industrial (brancura de *Berger* de 58,7 ± 0,1).
Desta forma, este trabalho permitiu demonstrar que a tecnologia fotocatalítica apresenta-se como uma alternativa promissora ao método de branqueamento industrial. Isto porque é possível reduzir na utilização produtos químicos e de recursos energéticos, e, deste modo, diminuir também os resíduos gerados durante o processo de branqueamento convencional.

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Synthesis and antibiotic functionalized blue silver triangular nanoplates

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It is well known that silver spherical nanoparticles have antibacterial action by the release of silver ions which is strongly toxic to micro-organisms. [1] Moreover, silver nanoparticles exhibit a shape-dependent activity, indeed, anisotropic nanoparticles like triangular or rods shaped silver nanoparticles have high atomic density facets which promote the reactivity of silver and the etching of nanoparticles. In addition, anisotropic nanoparticles have the advantage of having a tunable LSPR band ranging from the visible spectrum to the near IR, becoming good candidates as SERS substrates, sensitive plasmonic sensors among others [2]. Continuing with our scientific interest in the synthesis and application of noble metal nanomaterials [3], we have designed triangular silver nanoplates to study their antibacterial properties, evaluating the release of silver ions by passivation of silver nanoplates surface. Their action will be compared with passivated surface triangular nanoplates and functionalized with innocent molecule.

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Silver nanoparticles as colorimetric tools for ofloxacin antibiotic detection and bactericidal properties

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Antibiotics are certainly one of the most important breakthroughs in modern medicine, because of their great contribution in reducing the mortality and morbidity determined by infectious diseases. However, a massive and often indiscriminate use of antibiotics, , has led to a dramatic increase in manifestations of antibiotic resistance,[1][2] and to severe accumulation of antibiotic and parent compounds in soil and acqueous envirnments[3]. Both antibiotic resistance and accumulation in the environment can be fought by reducing the amounts of antibiotics used in therapies. Silver nanoparticles as tools for antibiotic colorimetric detection[4] and drug delivery [5]has already been proved with success.
In the present communication, we report how silver nanoparticles (*AgNPs*) can serve both as an efficient colorimetric system for the detection and, when combined with silica, as nanocarriers, for the synthetic antibiotic Ofloxacin.

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Microfluidic Biofuel Cell Integrated With Nanostructured Paper-like Electrodes

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In the development of point-of-care diagnostic or *in-situ* analytic systems, the flexibility, portability and reduced dimensions are usually crucial requirements. For instance, electrochemical sensors for this purpose must integrate robust, flexible and miniaturized electrodes. Paper-like electrodes based on nanostructured carbon materials are good examples, passible to be miniaturized at any dimensions. A simple method of vacuum filtration is used for the fabrication of the electrodes similar to the process of buckypaper production [1]. A surfactant is used to aid the dispersion of the carbon allotrope avoiding aggregation and the filtration produces a homogeneous, thin conductive film. Lately, carbon derived materials such as graphene and nanotubes have been used as components or primary electrode materials enabling the substitution of noble metals as catalysts in electrochemical reactions. However their relatively high cost may be a drawback in cheap and disposable applications. Although carbon blacks such as Vulcan XC72 have inferior electrical properties compared with nanotubes, their availability and reduced cost makes them a practical alternative. Besides the common use of carbon blacks in fuel cells, their applicability as electronic enhancer and "wiring" of enzymes to the electrode surface has already been demonstrated.

In the present work the fabrication of a self-powered microfluidic biofuel cell is proposed. Paper-like electrodes of carbon black Vulcan XC72 are the conductive support for the glucose oxidase bioanode and the bilirubin oxidase biocathode. First, carbon black is compared through cyclic voltammetry with other nanostructured materials for conductivity assessment. Then each enzymatic bio-electrode is characterized individually by CV and amperometry registering responses to their respective substrates. Finally, bioanode and biocathode are integrated in a single-compartment cell of the microfluidic device to register the maximum power obtained from the fuel solution containing glucose and oxygen.

The process of construction starts with the dispersion of carbon black Vulcan XC72 in a 1% sodium dodecyl sulphate solution in an ultrasonic bath for 1h. Larger particles and aggregates are separated by centrifugation and the supernatant is vacuum-filtered in a 0.22 **μm** nylon membrane. After air drying, the electrodes shape are done in laser patterning machine. Bioanode is made by deposition of a mixture of MWCNT crosslinked GOx and nafion [2]. BOx enzyme is linked through succinimide bonds to a pyrene compound previously attached to the electrode surface [3], producing this way the biocathode. The microfluidic device was made by bonding PDMS to a channel-engraved acrylic sheet using plasma etching.

Electrical properties of Vulcan XC72 were inferior when compared with graphene and SWCNT by CV of the ferrocyanide redox system. Nevertheless, due to its lower cost, Vulcan XC72 was selected as carbon material for paper-like electrode construction due to its availability and comparable performance. Bioanode was characterized by CV to assess the successful immobilization of GOx which is attested by the higher oxidation peak of glucose when compared in the absence of it. Sucessive additions of glucose lead to an increase in current in a Michaelis-Menten amperometric response, with a calculated sensitivity to glucose of about 1 **μA**/mM. The same was performed for biocathode with catalytic reduction response in the presence of oxygen by CV. Amperometric response to successive additions of oxygen saturated solutions was registered by the decrease in current, obtaining a sensitivity to oxygen of about 37 **μA**/mM. When bioanode and biocathode were assembled in a microfluidic device, the biofuel cell produced a maximum power density of about 30 **μW**/cm^2.

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Metodologia mecanotérmica para a incorporação de heteroátomos em nanotubos de carbono: preparação, caracterização e desempenho catalítico na oxidação húmida

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A incorporação de diferentes heteroátomos (O, N, S, B, P) na superfície dos materiais de carbono veio abrir uma janela de novas oportunidades a esta classe de materiais, cuja principal aplicação foi durante largas décadas limitada ao seu uso como suportes em catálise [1,2]. Apesar do elevado número de estudos dedicados à modificação da química superficial de materiais de carbono, a maioria dos métodos envolve sínteses complexas, com solventes, aumentando o custo de produção e limitando a aplicação destes catalisadores. Neste contexto, é necessário desenvolver metodologias menos dispendiosas para a incorporação de heteroátomos em materiais de carbono.

A química superficial dos nanotubos de carbono (CNT) foi modificada recorrendo a uma metodologia sem solvente, que envolve tratamentos mecânicos e térmicos na presença de precursores de diferentes heteroátomos (S, B, P), promovendo alterações significativas das propriedades texturais e de química superficial originais. A moagem no moinho de bolas (tratamento mecânico) revelou-se um método promissor para a modificação dos CNTs, permitindo ajustar o comprimento dos tubos, promover a sua abertura e dopar a estrutura grafítica (Fig. 1).

O efeito dos diferentes heteroátomos no desempenho catalítico dos materiais foi avaliado na oxidação húmida de compostos orgânicos, como alternativa aos catalisadores tradicionais de metais nobres ou óxidos de terras raras.

1 **TRATAMENTO MECÂNICO**
Quebra dos CNTs, abertura das extremidades
Promoção das misturas físicas CNTs/precursores

2 **TRATAMENTO TÉRMICO (TT)**
Decomposição térmica dos precursores
Incorporação de grupos funcionais

Fig.1. Ilustração esquemática da metodologia mecanotérmica para a incorporação de heteroátomos em nanotubos de carbono.

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Green-synthesis of starch capped silver nanoparticles

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In the proposed work, silver nanoparticles were synthesized in a single step and by exploiting an environmentally friendly approach. The redundant agent was soluble starch, which also acted as the capping agent. Additionally, the reduction efficiency of soluble starch over silver ions, in alkaline medium, was enhanced using microwave energy [1]. The adopted method was facile, straightforward and biocompatible making it more convenient than most of other available procedures. Moreover, the synthesis procedure was expeditious considering the average time for the synthesis of AgNPs was about 2 minutes.

Using the above procedure, the yield synthesis of AgNPs was tunable, depending on the timing of the nucleation and growth periods. Some of the variables tuned in the chemical synthesis process in order to control the size and shape of AgNPs were temperature, time of synthesis, pH of the medium and molar ratio between silver ions and reducing/capping agent.

The chemical and physical parameters involved in the synthesis procedure were optimized using a factorial and central composite experimental model designs. The optimized synthesis conditions aiming at the highest synthesis yield, monitored through the maximum absorbance obtained after the synthesis, were Ag^+/OH^- molar ratio fixed at 1.61, starch concentration at 1.46 %(w/v), temperature at 138 ºC and time of synthesis at 77 seconds.

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Aplicação de nanomateriais na desinfeção de água para consumo humano

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São vários os fatores associados **à** escassez de água potável no mundo fazendo com que o processo de desinfeção se revele de extrema importância. A utilização de nanomateriais surge como uma ideia inovadora para o processo de desinfeção de água para consumo humano pois estes apresentam uma grande área superficial específica, fazendo com que sejam bastante eficientes na adsorção de diferentes compostos orgânicos, inorgânicos e biológicos, apresentando, para além disso, uma forte ação antibacteriana [1,2]. Com este trabalho pretende-se desenvolver uma tecnologia de desinfeção de água para consumo humano através da aplicação de nanopartículas magnéticas (NPM's) para a remoção de diferentes microrganismos.

Para tal foram sintetizados vários tipos de nanopartículas magnéticas (NPM's) através de diferentes processos: FeO, CuFeO, FeO/CNT, CuFeO/CNT, 5% Ag/FeO, 5% Ag/CNT, C-FeO@CVD750 e N-C-FeO@CVD750. Todas as nanopartículas foram devidamente caracterizadas recorrendo a diferentes técnicas e foram estudadas em ensaios em reator fechado (ensaios cinéticos e de influência de concentração das NPM's) utilizando suspensões bacterianas de *Escherichia coli* (gram-negativa) e de *Staphylococcus aureus* (gram-positiva) com densidade bacteriana de 10^6 UFC's/ml.

As NPM's consideradas mais eficientes foram as de CuFeO/CNT, C-FeO@CVD750 e de 5% Ag/FeO pois apresentaram maiores eficiências de remoção bacteriana para tempos de contacto mais curtos com a suspensão. De uma forma geral, para tempos de contacto mais longos e maior concentração de NPM's as eficiências de remoção bacteriana estabilizavam próximo do valor de 100%. No entanto, o valor máximo de redução logarítmica de células bacterianas foi 3. As condições consideradas mais apropriadas para a remoção bacteriana foram tempo de contacto de 1 min e concentração de NPM's de 50 mg/L. Quando utilizadas estas condições para o tratamento de uma suspensão bacteriana de *S. aureus* foi possível verificar que existe uma pequena perda de eficiência em relação aos resultados obtidos para a suspensão de *E. coli*. No entanto, esta perda é praticamente insignificante pelo que se pode concluir que as NPM's estudadas são eficientes na remoção dos dois tipos de bactérias.

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Silver-silica core@shell nanoparticles synthesis as potential antibacterial agents

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During the last twodecades researchers have been debated the mechanisms by AgNPs exert toxicity towards bacteria and other microorganisms. It has been proven the role of Ag+ release in the action mechanism in numerous studies [1]. To this respect the release of Ag+ ions in Ag-Si Core@shell NPs has been vaguely studied, although oxidation of silver core has been shown to occur even in silica-coated systems [2]. In addition, the coating with silica offer a wide range of functionalization possibilities based on silane chemistry, offering an attractive possibility modulate the terminal organic moieties grafted in the NPs surface. The surface charge and the molecular affinity of the NPs surface are therefore modified. Continuing with our interest in the synthesis, functionalization and application of metal NPs, we have synthesized news core@shell Ag@Si nanoparticles with different coating thickness between 10 to 30 nm. The hydroxyl ended (Ag@Si-OH) NPs can be easily converted into amine, thiol or aldehyde functionalized NPs. The aim of the present communication is to investigate if the antibacterial properties of our core@shell Ag/Si colloids can be controlled by the thickness of silica coating or different organic surface functionalities.

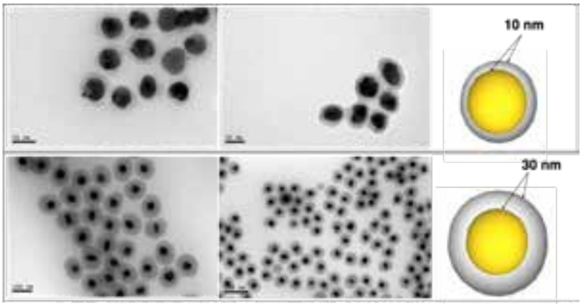

Figure 1: Low magnification TEM images core@shell NPs with different silica thickness synthetized for this studied.

ACKNOWLEDGEMENTS: H.M.S. thanks the IF contract to the FCT-MEC (Portugal). J.F.L. and E. O. acknowledge the post-doctoral grants from (FCT-MEC) (Portugal) SFRH/BPD/93982/2013, and SFRH/BPD/72557/2010 respectively. A.F.L. thanks the PhD grant from FCT-MEC (Portugal) SFRH/BD/52528/2014. J.D thanks the PhD grant associated to the FCT project PTDC/QEQ-MED/2118/2014. Financial support from PROTEOMASS Scientific Society (Portugal), the FCT-MEC grant (PTDC/QEQ-MED/2118/2014), LAQV/REQUIMTE (UID/QUI/50006/2013) are also acknowledged.

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Exploiting the size-tunable photoemission properties of cdte quantum dots in quantitative analysis of food colorants

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Quantum dots (QDs) are monodisperse crystalline clusters of inorganic semiconductor materials with dynamic dimensions in the range of 1-10 nm [1].
Amongst them, metal chalcogenide quantum dots are nanomaterials of large potential for analytical methodologies due to their size tunable photoemission and quantum confinement. Although QDs can be obtained through organic synthesis, aqueous synthesis proved to be less toxic and of low cost. And, more important the obtained QDs were water-soluble, being thus more compatible with most of the analytical methodologies [1,2].
Since the size of QDs can be controlled during synthesis, CdTe QDs capped and stabilized with thioglycolic acid (TGA) was undertaken through microwave radiation, aiming at a higher quantum yield and a narrower emission band. The resultant QDs obtained by aqueous synthesis were characterized recurring to spectrophotometric methods and by direct quantum yield measurements.
The synthesized QDs were later exploited for the development of a new analytical methodology, to allow the chemical control of the food colorant malachite green in foodstuffs. The interaction between malachite green and the TGA-CdTe QDs resulted in a quenching effect on the native fluorescence emission of the nanoparticles. A relation between the concentration of the food colorant and the quenching effect was ascertained, allowing the analytical determination of the analyte.

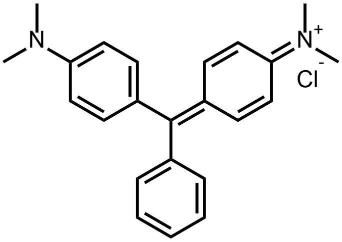

Figure 1: Malachite green chemical structure.

ACKNOWLEDGEMENTS: This work received financial support from the European Union (FEDER funds POCI/01/0145/FEDER/007265) and National Funds (FCT/MEC, Fundação para a Ciência e Tecnologia and Ministério da Educação e Ciência) under the Partnership Agreement PT2020 UID/QUI/50006/2013.

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Luminescent silica nanoparticles as novel *green* drug nanocarriers for cancer therapy and their toxicological evaluation

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The urge for novel anti-cancer drugs is an impending need for the emergence of revolutionary non-painful, non-degrading and highly target-specific cancer therapies. Nanomaterials have been reported as promising nanocarriers, of outstanding target-specificity and efficiency, for several drug systems [1,2]. CdTeQDs@MNs@PEG1, SiQDs@Isoc@MNs and SiQDs@Isoc@MNs@PEG2 luminescent mesoporous silica-based nanoparticles, were successfully synthetized and characterized by SEM, TEM, XRD, N_2 isotherms, ^{1}H NMR, IR and UV-Visspectroscopy. Cytotoxicity was assessed in relevant *in vitro* cell models of human hepatoma HepG2, human brain endothelial (hCMEC/D3) and human epithelial colorectal adenocarcinoma (Caco-2) cell lines [3,4]. No significant cytotoxicity was observed against the respective controls (solvents and/or coating) in any of the assays (MTT/NR/LDH). As expected, CdTeQDs@MNs@PEG1 nanoparticles were strongly toxic towards hCMEC/D3 cells. Moreover, SiQDs-based mesoporous silica nanoparticles, now loaded with doxorubicin (%EE of 80%), proved to be cytotoxic for HepG2 cell lines with pH-responsive drug release profiles. Both systems pose two promising building blocks for future integration in more efficient nano-vehicles for anti-cancer therapy.

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Lipid-based nanocarriers for oral administration of Lapatinib

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Lapatinib is an oral dual tyrosine kinase inhibitor targeting the epidermal growth factor receptor-2 (HER2) currently approved by FDA for treatment of HER-2 positive breast cancer. Although effective, the clinical use of lapatinib is compromised by its poor aqueous solubility, low oral bioavailability, high binding affinity to blood proteins and toxicity induced by its administration at high daily doses [1]. Entrapment of this drug into a suitable delivery vehicle is a promising strategy to increase its efficacy and accumulation in tumor tissues and reduce the administered doses and associated toxicity [1].

In this work, nanostructured lipid carriers (NLC) were designed, optimized and characterized for loading of lapatinib. To increase blood circulation time, and target the folate receptors, which are overexpressed in most tumor cells [2], the NLC produced were coated with a 1,2-distearoyl-sn-glycero-3-phosphoethanolamine-N-[carboxy(polyethylene glycol)-2000]-folic acid (DSPE-PEG-FA) conjugate. The NLC developed appeared homogeneous with a spherical morphology, presented adequate size for oral administration and highly negative surface charge, suggesting good stability. Furthermore, a high encapsulation efficiency (higher than 70%) of the drug was obtained. Taken together, these results suggest that the NLC developed is suitable for oral administration of lapatinib and can be further explored as a promising therapy for breast cancer.

POSTER

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Synthesis of hybrid nanoreactors for the fabrication of magnetic materials

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POSTER

Herein we report the fabrication of a novel catalytic nanoreactor consisting of a silica core functionalized with dendritic platinum nanoparticles (Pt_d NPs) and oxidized multiwalled carbon nanotubes (ox-MWCNTs). This nanocomposite has been assembled following a layer-by-layer strategy of the Pt_d NPs and the ox-MWCNTs onto mesoporous silica nanoparticles. The structural arrangement of this architecture opens up the possibility of promising applications in the field of nanocatalysis and nanofabrication. Along these lines, this reactor is endowed with the capability of reducing nickel ions (Ni^{2+}) to magnetic nickel (Ni^0) in the presence of a reducing agent. This process has been previously reported to occur on the surface of the Pt_d NPs, which would operate as catalysts of the reduction reaction [1]. In this case, the Pt_d NPs would act as nucleation point upon which the growth of additional materials would take place.

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Stimuli Luminescent Mesoporous Silica Nanoparticles for Imaging in Cancer Cells.

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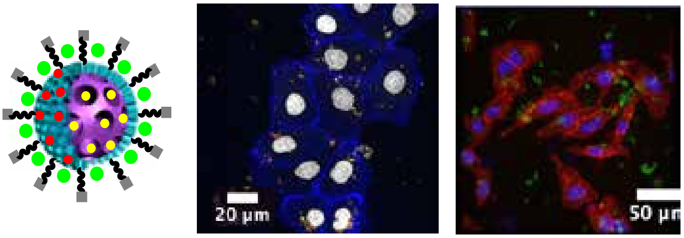
Despite the advances in Nanotechnology-based target delivery in preclinical models, the translation of these models to the clinic are still questionable, because of the enhanced permeability, retention effect, ligand recognition, the biodegradability, and toxicity of these systems. Based on such issues the development of nanocarriers sensitive to exogenous or endogenous stimuli may represent an attractive alternative to target drug delivery in chemotherapy [1]. From all nanoparticles systems that have been used as drug delivery agents, luminescent inorganic mesoporous silica nanoparticles and silicon nanocrystals emerged as a multifunctional new generation of nanocarriers acting as all-in-one diagnostic and therapeutic tools [2, 3]. In fact, silicon nanocrystals are new promising biocompatible emissive nanomaterials and are the most promising candidates as benign quantum dots [2, 3]. Herein it is presented the synthesis of new stimuli luminescent nanocarriers, combining silicon quantum dots and mesoporous silica nanoparticles with biodegradable materials for diagnosis and controlled drug (doxorubicin) release in cancer cells.



Nanocarrier **CACO cells** **Hela cells**

Figure 1: Schematic representation of a nanocarrier; Imaging of luminescent nanoparticles in CACO-2 and HELA cancer cells.

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Fucoidan-chitosan nanoparticles as vehicle for oral delivery of quercetin

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One of the most trending and promising areas in the medical industry is the nutraceuticals, especially due to adverse side effects of pharmaceuticals and the enlightenment associated to the importance of a balanced and healthy diet. The nutraceutical definition was first described in 1979 by Stephen DeFelice as "a food or parts of food that provide medical or health benefits, including the prevention and treatment of disease", so it is considered any food supplement that scientifically proves to have a bioactive outcome. Flavonoids are a class of phenolic bioactive compounds very explored in the nutraceuticals area. Among the best well known flavonoids there is quercetin, a nutraceutical ingredient abundant in a wide range of fruits and vegetables. The interest in quercetin has grown due to its great therapeutic potential, namely the anti-oxidant and anti-inflammatory activities, the strong anticancer profile and also its ability to decrease and prevent cardiovascular diseases. However, the stability and general characteristics of quercetin change according to the food processing and pharmaceutical handling such as the pH changes, temperature, oxidation and degradation. The major drawbacks of quercetin are related with its low water solubility and consequently the low bioavailability and instability in physiological medium. Having in mind the quercetin bioactivity, and considering its lipophilic behavior, the convenient oral administration might be improved through nanotechnology.

Drug delivery systems are formulations or devices that enable the process of administering a drug or active compound, increasing its bioavailability and target-site specific interactions for a therapeutic purpose. Nature, especially the marine biodiversity, can be a source of new, promising compounds which bioactivity and polymeric properties can be used to create stable drug delivery systems. In this case, chitosan (a polysaccharide derived from chitin, present in the exoskeleton of crustaceans) and fucoidan (a sulfated polysaccharide isolated from brown seaweed) were explored to produce polymeric nanoparticles for oral delivery.

To avoid the harsh acidic conditions of the stomach and to enhance the intestinal absorption of quercetin, different ratios of fucoidan and chitosan were combined, in order to search for pH responsive nanoparticles. The marine polysaccharides were mixed in ratios of 1:1, 3:1 and 5:1, (fucoidan : chitosan) to find the most suitable ratio for the intended purpose.

The fucoidan/chitosan nanoparticles were physicochemically characterized, the morphology was assessed by transmission electron microscopy and the pH sensitivity was tested under distinct conditions to search for gastric resistant nanoparticles. The quercetin release from fucoidan/chitosan nanoparticles was evaluated in biorelevant media for both gastric and intestinal conditions, and different release profiles were observed in a ratio dependent manner. The obtained results show that 3:1 and 5:1 ratios of fucoidan/chitosan nanoparticles may present a solution for oral delivery of quercetin.

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Reproducible and robust ultra-fast protein digestion for label-free quantitative mass-spectrometry

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Background: Protein digestion is a key step before mass spectrometry (MS)-based proteomics analysis. Although a wide array of enzymes can be used for protein digestion, trypsin is the most common due to its specificity and reproducibility. One problem observed in MS analysis of tryptic-digested proteomes is the presence of peptides resulting from trypsin auto-lysis [1-2]. To overcome this problem, immobilized trypsin has proven to be a highly effective method for protein digestion [3].

Methods: *E.Coli* proteome was digested using in-house made immobilized nano-trypsin, and for comparative purposes immobilized commercial micro-trypsin. Digestion was done with and without ultrasonic energy.

Results: nano-trypsin performs better than micro-trypsin in digesting complex proteomes. Ultrasonic energy helps to speed the protocol for digestion so 96 samples can be handled in two hours.

Conclusions: ultrasonic assisted digestion of complex proteomes using immobilized nano-trypsin allows high sample throughput in proteomics with a special focus on clinical proteomics.

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KEYWORDS: Proteomics, protein digestion, immobilized trypsin, ultra-fast digestion.

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Synthesis and studies of gold nanorods for drug delivery in cancer cells

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Metallic nanoparticles show a great variety of applications, since the first uses for a decorative purpose in stained glass (Lycurgus cup from the British museum, Sainte Chapelle in Paris)[1] until the most modern applications in photodynamic therapy, sensing and catalysis[2,3]. Nowadays a huge number of metallic nanomaterials are widely used. Here we report the synthesis, characterization and the surface modification of different gold nanorods. To avoid degradation of the nanorods, we have been introduced a thin mesoporous silica coating shell, making them, more stable, and enabling us to functionalize with different types of drugs, antibiotics or chromophores. Here we are communicating the functionalization of the surface and the drug loading using Doxorubicin, Methylene blue and Rose Bengal.

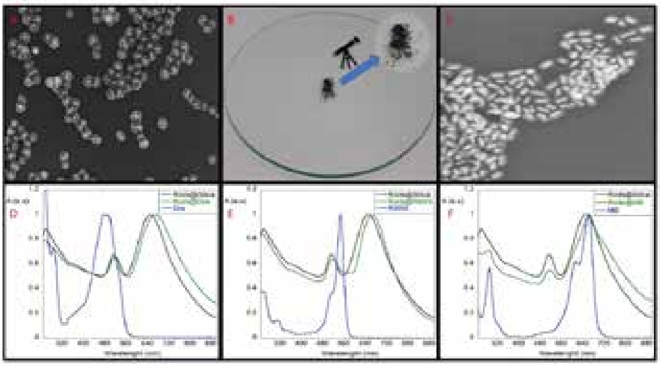

Figure 1: A) SEM image of the gold nanorods before the encapsulation, B), aspect of the gold nanorods after the encapsulation and lyophilization, C) SEM image of the gold nanorods after resuspension the solid powder D, E, F), absorption spectra of the drugs (blue), initial rods (black), and rods with the different drugs encapsulated (green).

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Autoclave sinthetised phenilboronic acid carbon dots for the glucose, frutose and h_2o_2 sensing

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Diabetes is a disease characterized by high blood glucose (Glc) levels, derived from defects in insulin secretion, insulin action, or both. Insulin is the hormone that regulates Glc levels in the blood when these reach high concentrations [1]. Glc has a vital role in the natural growth of cells and is the main energy source in cellular metabolism. Besides Glc there are other related chemical species such as fructose (Frc) and hydrogen peroxide (H_2O_2) that might offer benefits by having their blood concentrations quantified. Frc is a Glc related sugar with high sweetness and is a major component of added sugars. H_2O_2 is also a relevant chemical species for diabetic individuals as oxidative stress seems to play an important role in the pathogenesis of diabetes [2]. Thus, the rapid and accurate quantification of Glc, Frc and H_2O_2 in human blood is of high importance in controlling several biochemical processes, and in the diagnoses and management of diabetes.

Carbon Dots (CDs) are carbon based nanoparticles with very interesting optical and analytical properties with a great potential for the Glc, Frc and H_2O_2 fluorescence sensing [3]. The boronic acids due to their linked hydroxyl groups are ideal for binding the Glc and for is recognition. So, diol modified CDs probes with boronic acids could be synthetized for the fluorescence sensing of Glc [4]. Some boronic acids functionalized CDs have already been used for the direct fluorescence sensing of Glc [5-7].

In this communication, are presented the results found in the fluorescence detection of Glc, Frc and H_2O_2 by autoclave synthesized CDs functionalized with boronic acids. The evaluated boronic acids were the phenylboronic acid, 3 and 4-hydroxyphenylboronic acid (3-, 4-HPBA) and 3 and 4-aminophenylboronic acid (3-, 4-APBA). Different fluorescent response profiles were observed for the CDs prepared from the different phenylboronic acid precursors in the presence of Glc, Frc and H_2O_2.

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GC-MS analysis of *Spartina maritima* and *Puccinellia maritima*, two halophytic grasses from Aveiro saltmarshes

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Poaceae is considered the most important group of monocotyledonous crops [1], among which 65 genus and 148 species are halophytes [2]. Recently, halophytic grasses have been targeted as a possible solution to cope with the soil salinity increase observed worldwide [3]. Furthermore, from salt stress arises the accumulation of secondary metabolites, some of them relevant to pharmaceutical and food industries [4]. Nonetheless, studies regarding the phytochemistry of this group of plants are yet to be performed. *Spartina maritima* and *Puccinellia maritima*, found in Aveiro saltmarshes, are, as far as we know, examples of the unstudied plants. Therefore, the present study aims to elucidate these plants' lipophilic composition and identify similarities among the *taxa* that can be related to salt stress adaptations.

The hexane extracts of *S. maritima* and *P. maritima* were analyzed by GC-MS allowing the identification of 58 and 54 compounds, respectively. The achieved data revealed a high diversity of chemical families in which are included carboxylic acids, saturated and unsaturated fatty acids, terpenoids, carbohydrates, alkanes, akenes, alcohols and aldehydes.

This study allowed an in-depth knowledge regarding the lipophilic profile of *S. maritima* and *P. maritima*, with the first report on their chemical composition. It was evident the presence of diverse chemical families, rich in valuable compounds that could be exploited by pharmaceutical/nutritional sectors. Some of the similarities among the chemical profile of the studied *taxa* will be presented and discussed.

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QAMA2

Efeito da pectina no mecanismo de auto-associação da malvidina-3-*O*-glucósido

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As antocianinas constituem uma importante classe de pigmentos, responsáveis pela enorme diversidade de cores evidenciada pelas plantas, vegetais e frutos. No entanto, a cor que estes pigmentos exibem em solução é extremamente dependente do meio onde se encontram dissolvidas. Por exemplo, cor que das antocianinas exibem é dependente do pH, resultando de alterações entre as diferentes formas de equilíbrio presentes: o catião flavílio vermelho a pH ácido, o hemicetal incolor e as chalconas amarelas a pH ligeiramente ácido e a base quinoidal roxa a pH mais elevados [1]. Nas plantas, apesar do pH fisiológico no interior dos vacúolos ser mais propenso para estabilizar as formas incolores das antocianinas, estas estão maioritariamente presentes nas suas formas coradas, como resultado da ocorrência de mecanismos de estabilização das antocianinas, nomeadamente através de fenómenos de auto-asssociação [2]. No entanto, o impacto de polissacarídeos pécticos (que poderão interagir com as antocianinas durante o processamento alimentar [3]) no processo de auto-associação das antocianinas é ainda desconhecido.

Neste trabalho, a constante de auto-associação (K_a) do catião flavílio (pH 1) da malvidina-3-O-glucósido (mv3glc, antocianina mais abundante no vinho tinto) foi determinada por ^{1}H-RMN, avaliando a alteração dos desvios químicos dos protões da mv3glc em função da concentração do pigmento. A constante de auto-associação foi igualmente determinada na presença de um polissacarídeo péctico comercial (pectina) numa concentração de 10 e 20 mM. Adicionalmente, a associação antocianina-pectina e antocianina-antocianina foi também caracterizada por UV-Visível.

A pH ácido, a mv3glc e a pectina evidenciaram uma baixa afinidade de ligação. Por outro lado, as constantes de auto-associação determinadas por ^{1}H-RMN e por UV-Vis, revelaram um aumento sistemático da K_a da mv3glc, na presença de concentrações crescentes de pectin.

De um modo geral, estes resultados sugerem que os polissacarídeos pécticos poderão afetar o mecanismo de auto-associação das antocianinas, tornando-o mais favorável, o que constitui um aspeto fundamental para a estabilização da cor vermelha das antocianinas.

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Gunnera tinctoria: A preliminary study about an invasive plant

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Gunnera tinctoria (Nalca) is a native plant from South America that grows up in the São Miguel Island, Azores. It is a highly competitive plant, dominant in some pasture areas and able to successfully colonize and threaten the native Azorean flora [1]. This plant is used in Chile for various purposes: as wool and cotton dyeing; to treat diarrhea, genito-urinary infections, and circulatory system diseases, due to their pharmaceutical properties [3]; it is used in alternative therapies, due to their antibacterial activity against *Streptococcus pyogenes* and *Staphhylococcus aureus* [4] and high antioxidant and antifungal capacities [5]; the young leaves are ingredients of a typical Chilean food, the *curanto* [2]; the root is used in infusions.

This study aims to explore the valorization of this plant and, if possible, to help in its dissemination control.

Samples were collected in Sete Cidades, São Miguel, Azores, during the spring season. Flowers/stems and leaves were lyophilized individually and their nutritional characterization was assessed according to official methods [6]. Antioxidant capacity was evaluated by spectrophotometric methods, using an UV-Vis microplate reader [7]. Leaves presented the highest contents of total dietary fiber (45%), ash (14%) and protein (13%) and the lowest amounts of available carbohydrates (27%). In turn, flower/stems was the richest part in available carbohydrates (49%). As expected, both of them had low amounts of total fat (~1%). In what concerns to the antioxidant activity, flower/stems presented the highest values for phenolic compounds (180 mg gallic acid eq./g of sample), ferric reducing power (6806 µmol ferrous sulfate eq./g), and $DPPH^{\bullet}$ scavenging activity (2858 mg trolox eq./g).

Taking into account the obtained results, this plant can be seen as an interesting source of dietary fiber and antioxidants.

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Nanoparticulas de lenhina para a encapsulação de piranoantocianinas azuis. estabilidade em sistemas aquosos

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A procura de pigmentos azuis naturais, como alternativa aos corantes sintéticos tem despertado um elevado interesse por parte da comunidade científica.

Pigmentos derivados das antocianinas como os dímeros de piranoantocianina e as portisinas que apresentam cor azul, foram encontrados em vinhos do Porto envelhecidos. Contudo, estes compostos demonstraram uma falta de solubilidade em sistemas aquosos e lipofílicos, dificultando na sua aplicação em matrizes alimentares e cosméticas [1].

A fim de melhorar a solubilidade desses pigmentos em água foram produzidas nanopartículas de lenhina por diálise (LNP_D). Partículas com tamanho de cerca de 200 nm foram obtidas com uma estabilidade de pelo menos um mês à temperatura ambiente. A estabilidade das partículas a diferentes valores de pH (1 a 8) foi avaliada durante 7 dias através da determinação do tamanho médio da partícula (Z-average), do índice de polidispersão (PDI) e do potencial zeta médio (x) por DLS e ELS. A morfologia das nanopartículas de lenhina (LNPs) foi determinada pela análise de TEM, STEM e SEM e as imagens obtidas estão de acordo com o descrito por *Figueiredo*, et al. 2017 mostrando uma forma esférica uniforme e simétrica, e uma estrutura compacta [2].

Além disso, o efeito do pH na estabilidade da cor dos pigmentos livres e encapsulados foi também estudada e foi demonstrado que os pigmentos encapsulados apresentam uma maior estabilidade cromática quando comparados com os pigmentos livres.

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Ochratoxin A occurrence and risk assessment in the Portuguese wine market

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Ochratoxin A (OTA), a mycotoxin produced by different Aspergillus and Penicillium species, is considered to be the most toxic ochratoxin, being classified as a possible human carcinogenic (Group 2B) by the International Agency for Cancer Research (IARC) [1].
These fungi mainly contaminate cereals, however, wine and grape juice [1–3] are considered to be the second largest source of OTA daily intake [4], being present at concentration levels that depend upon both environmental and processing conditions [5]. Being one of the most consumed alcoholic drinks in Portugal and one of the main sources of human exposure to OTA, wine monitoring and exposure studies are essential.
In this study, the validated analytical methodology consisted in the direct injection of the filtered samples, into the liquid chromatographer with fluorescent detection system (LC/FD).The OTA linearity in both in mobile phase and in matrix-matched calibrations was good with R2 values higher than of 0.9974. The detection limits were 0.0757 and 0.3884 μg/L for white and red wine, respectively. The quantification limits of 0.23 μg/L and 1.18 μg/L for white and red wine, respectively, were below the maximum limit of 2 μg/L set by the European Commission [6]. Recoveries higher than 91.93% were obtained at fortification levels ranging between 0.5 and 3.0 μg/L.
In this study, 100 wine samples acquired in Portugal were investigated. In 5 samples the presence of OTA was found below the limit of quantification. Regarding the risk to human health it was observed that the EWI is considerably lower than the established tolerable weekly intake (TWI) of 120 ng/kg b.w./week [7].
The incidence of OTA and levels found in the present study was lower when compared to previous Portuguese studies. Dryer climate scenarios may contribute for these changes, on the other hand, improved grape treatments and wine making procedures, required in recent years for this important sector of the European economy, minimised exposure of European consumers. In fact, these low levels found do not imply risk of humans exposed to OTA through wine consumption. However, one should bear in mind that other OTA sources are available through food intake.

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Validation of a liquid chromatography coupled to tandem mass spectrometry (LC-MS / MS) methodology for the monitoring of emergent mycotoxins in plants

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The consumption of teas and infusions has gained increasing importance due to its richness in compounds beneficial to our health, in particular phenolic compounds endowed with antioxidant activity. These products, however, are not exempt from the possibility of the presence of chemical contaminants such as mycotoxins. Mycotoxins are secondary metabolites produced by certain species of filamentous fungi, belonging mainly to the genera Fusarium, Aspergillus, Penicillium and Alternaria. Within mycotoxins there is a group that is commonly classified as "emerging mycotoxins", since they are not routinely studied and are not yet covered by existing regulations. The most relevant examples are Enniatins, Beauvericin, Sterigmatocystin.

In this work an analytical methodology was developed and validated for the determination of several emerging mycotoxins in plants and infusions. The extraction of the compounds was based on the QuEChERS technique, optimized according to the specificities of this type of samples. The detection and quantification of the different mycotoxins was performed by liquid chromatography coupled to tandem mass spectrometry (LC-MS/MS). The method showed recoveries for all target substances near 100% with average Relative Standard Deviation (RSD) lower than 20.3%. LOQ and LOD were respectively 10 and 40 µg/kg, for the plants, and 2 and 2.5 µg/L for the infusions.

All the different 19 plants studied were contaminated with at least one of the emergent mycotoxins (Beauvericina, Eniatinas and Esterigmatocistina). The maximum levels detected were: 181.35; 81.47; 36.12; 313.61; 239.2 and 256.32 µg/kg (BEA, EN-A, EN-A$_1$, EN-B, EN-B$_1$ and STE, respectively) . In the case of infusions only 6 types of contaminated infusions were detected, with lower concentrations. STE was detected in 4 different types of infusions: Chamomile (6.23 µg/L), Lemongrass (5.95 µg/L), Bilberry (7.84 µg/L) and Carqueja (5.77 µg/L). BEA was detected in Passion Fruit infusion (4.62 µg/L) and Guaco (4.27 µg/L). At least EN-A$_1$ was detected in a sample of Lemongrass infusion (4.48 µg/L).

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Caracterização química e nutricional de gãos de *Chenopodium quinoa* Willd (quinoa): uma boa alternativa para produtos alimentares nutritivos

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O interesse da sociedade moderna pela prática de estilos de vida mais saudáveis tem vindo a aumentar gradualmente, nomeadamente no que concerne à mudança dos hábitos alimentares. Assim, tem sido evidente a preferência por alimentos que proporcionam benefícios para a saúde e bem-estar, além de satisfação nutricional [1]. Desta forma, as sementes de *Chenopodium quinoa* Wild (quinoa) têm mostrado possuir um elevado valor nutricional, substituindo os cereais comummente consumidos e apreciados [2]. Esta espécie, ao longo de vários séculos, foi cultivada nos países andinos como o Peru e a Bolívia, no entanto, hoje em dia, o seu cultivo estendeu-se a outros países, como Austrália, Canadá, China, Inglaterra, Índia, Itália, Paquistão, Estados Unidos, entre outros [3].

O objetivo deste estudo consistiu numa caracterização química e nutricional de 39 amostras pertencentes às variedades mais comuns de *C. quinoa* (vermelha, preta e branca), provenientes de diferentes origens (comerciais e não comerciais originárias do Peru e da Espanha).

Para tal, o perfil nutricional foi avaliado usando metodologias oficiais de análise de alimentos, os ácidos orgânicos através de um sistema UFLC-PDA, os açúcares livres por HPLC-RI, os tocoferóis por HPLC-fluorescência e os ácidos gordos por GC-FID.

Os resultados obtidos revelaram a presença de muitos compostos de interesse, tornando-se primordiais na promoção do consumo deste pseudocereal. O perfil nutricional evidenciou a predominância do teor em hidratos de carbono e proteínas, comparativamente com os restantes macronutrientes analisados. Por outro lado, na determinação dos compostos hidrofílicos foram identificados vários ácidos orgânicos, sendo os ácidos oxálico e cítrico os maioritários. Nos açúcares, verificou-se a presença de arabinose, frutose, glucose e sacarose, destacando-se este último como maioritário. Relativamente aos compostos lipofílicos, foi analisado o teor em tocoferóis, identificando-se as isoformas **α**-, **γ**- e δ-tocoferol, e o perfil em ácidos gordos, predominando os ácidos gordos insaturados, particularmente os ácidos oleico e linoleico. Tendo em conta as diferentes variedades analisadas (preta, branca e vermelha), não se verificaram alterações estatisticamente significativas na maioria dos parâmetros avaliados.

Assim, foi demonstrado que as sementes de quinoa são, claramente, uma excelente escolha para a dieta dos consumidores, exibindo compostos nutritivos mas também moléculas de elevado interesse, como tocoferóis e alguns ácidos orgânicos que promovem benefícios bioativos para o organismo. Deste modo, este pseudocereal assume uma posição de excelência, comparada a outros cereais consumidos com maior frequência, representando um ingrediente promissor para muitos usos na indústria de alimentos.

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Extração e quantificação de proantocianidinas totais da farinha da grainha da uva

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O setor vitivinícola gera uma grande quantidade de subprodutos, nomeadamente a grainha de uva. Estes subprodutos, que podem ser fontes de compostos bioativos de grande valor para a saúde humana, são por vezes subaproveitados [1].

A grainha de uva é utilizada para a extração do óleo de grainha de uva. Após o seu processamento, é gerado um subproduto secundário – a farinha de grainha de uva. Este subproduto é uma boa fonte de polifenóis, nomeadamente de uma grande variedade de proantocianidinas [2].

Este trabalho teve como objetivo determinar o teor de proantocianidinas totais de uma amostra de farinha de grainha de uva. Para isso, numa primeira etapa foram testados três diferentes métodos extrativos: extração a quente com refluxo, extração à temperatura ambiente e extração contínua a quente (Soxhlet) e quatro diferentes sistemas de solventes (metanol 80% em água, metanol 50% em água, acetona 80% em água e acetona 50% em água). Numa segunda etapa, após extração, procedeu-se à quantificação das proantocianidinas totais por dois ensaios espetrofotométricos: ensaio da vanilina e ensaio do butanol-ácido.

Os resultados mostraram que, dependendo do método extrativo, o teor de proantocianidinas totais variou entre 0,12 e 1,82 g de equivalentes de catequina/kg de farinha de grainha de uva (ensaio da vanilina) e entre 2,56 e 5,60 g de procianidina/kg (ensaio do butanol-ácido).

De um modo geral, verificou-se que a extração com acetona 80% pelo método extrativo a quente com refluxo apresentou teores de proantocianidinas totais significativamente superiores ($p<0,05$) aos outros métodos utilizados. O método extrativo que extraiu menor quantidade de proantocianidinas foi o método Soxhlet e o solvente extrator menos eficaz foi o metanol 50%.

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Sumo de sabugueiro como ingrediente alimentar com propriedades corantes e bioativas

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O sabugueiro é uma planta amplamente disseminada no território português, sendo o fruto (bagas pretas brilhantes) rico em compostos fenólicos (antocianinas), compostos naturais associados à prevenção de determinadas doenças mas, também, com um forte poder corante [1]. Neste sentido, e tirando partido da potencialidade corante e bioativa das bagas de sabugueiro, estas foram utilizadas para funcionalização de *croissants*, um alimento muito apreciado mas pobre em termos de promoção da saúde [2]. Foram preparadas diferentes formulações de *croissants*: com concentrações de sumo de sabugueiro distintas; sem adição de aditivos e, com corante comercial de cenoura preta. As formulações foram analisadas relativamente ao seu valor nutricional, perfil em ácidos gordos por GC-FID, perfil em açúcares por HPLC-RI, perfil em compostos fenólicos por HPLC-DAD-ESI/MS, e parâmetros físico-químicos de cor (L^* (luminosidade), a^* (intensidade da cor vermelha) e b^* (intensidade da cor amarela). Foi ainda avaliada a bioatividade relativamente à sua atividade antioxidante (atividade captadora de radicais livres DPPH, poder redutor e inibição da descoloração do β-caroteno), e citotoxicidade pelo método da sulforrodamina B em 4 linhas celulares tumorais humanas (HeLa: carcinoma cervical, MCF-7: adenocarcinoma de mama, NCI-H460: carcinoma de pulmão, HepG2: carcinoma hepatocelular) e numa linha não tumoral (PLP2: cultura primária de células de fígado de porco). Do ponto de vista nutricional, os *croissants* não apresentaram diferença relevante entre as diferentes formulações. A frutose foi o açúcar maioritário, o ácido oleico o ácido gordo mais abundante e a cianidina-3-*O*-sambubiósido a antocianina encontrada em maior quantidade. Em relação à intensidade da tonalidade vermelha (a^*), o aumento da concentração de sumo de sabugueiro causou um expectável aumento, da mesma forma que o parâmetro b^* apresentou os menores valores (cor menos amarela) também nos *croissants* com maior concentração de sumo, o que está de acordo com o tipo de pigmentos presentes. Em termos de bioatividade, a atividade antioxidante e a citotoxidade em linhas tumorais dos *croissants* diminuiu em comparação com a atividade demonstrada pelo sumo. No entanto, salienta-se que o sumo não apresentou citoxicidade para a linha de células não-tumorais. Assim, a incorporação de sumo de bagas de sabugueiro em *croissants* tornou possível funcionalizar um alimento vastamente consumido, adquirindo simultaneamente uma aparência inovadora e atrativa, e melhorando a sua funcionalidade fisiológica.

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Fracionamento do extrato de acetona das sumidades floridas de *Calluna vulgaris* (L.) Hull: perfil fenólico e potencial antibacteriano

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As plantas medicinais são uma importante fonte de moléculas bioativas, que têm vindo a demonstrar um elevado potencial terapêutico. Vários estudos científicos fazem referência à imensa diversidade de moléculas bioativas presentes nestas matrizes, como são exemplo os compostos fenólicos, as proteínas e os esteróis. Estas moléculas são responsáveis pelas atividades biológicas exibidas por estas matrizes, nomeadamente as atividades antioxidante, antibacteriana, anti-inflamatória e citotóxica [1]. *Calluna vulgaris* (L.) Hull, vulgarmente designada por urze ou torga, é um arbusto pertencente à família *Ericaceaes*, amplamente distribuído pela Europa e noroeste de África. É uma espécie utilizada na medicina tradicional devido às diferentes propriedades medicinais associadas: propriedades antissséticas, anti-inflamat**órias** e diuréticas; mas é sobretudo o seu potencial antimicrobiano que estimula o seu consumo na medicina tradicional [2].

Neste sentido, a atividade antimicrobiana de *C. vulgaris*, foi avaliada atrav**és da técnica de** microdiluição e do método colorimétrico de deteção rápida com cloreto de *p*-iodonitrotetrazóliio (INT). Devido ao elevado potencial antibacteriano demonstrado pelo extrato de acetona, este foi fracionado através de uma coluna cromatográfica de sílica gel com sistema de eluentes de grau de polaridade crescente, sendo o perfil fenólico das frações resultantes analisado por HPLC-DAD-ESI/MS. O potencial antibacteriano foi testado contra bactérias patogénicas, isolados clínicos, Gram-positivo: *Enterococcus faecalis*, *Listeria monocytogenes*, *Staphylococcus aureus* resistente à meticilina (MRSA), *Staphylococcus aureus* suscetível à meticilina (MSSA); e Gram-negativo: *Escherichia coli*, *Klebsiella pneumoniae*, *Proteus mirabilis*, *Morganella morganii*, *Pseudomonas aeruginosa* e *Neisseria gonorrhoeae*). Além disso, foi também analisado o efeito das frações em bactérias Gram-positivo: *Lactobacillus plantarum* (DSM 12028), *Lactobacillus delbrueckii* subs. *bulgaricus* (LMG 6901) e *Lactobacillus casei* (NCTC 6375)) e de Gram variável: *Gardnerella vaginallis,* pertencentes à microbiota vaginal.

Foram identificados quarenta e sete compostos fenólicos: um ácido fenólico, dezasseis fravan-3-óis, duas flavanonas e vinte e quatro flavonóis. Os compostos mais abundantes foram os flavan-3-óis, tais como dímeros do tipo B da (epi)catequina, (-)-epicatequina e (+)-catequina. Todas as frações revelaram atividade inibitória contra as bactérias patogénicas. No entanto, apenas algumas frações demostraram eficácia contra os microrganismos patogénicos testados, sem afetar as bactérias pertencentes à microflora vaginal, destacando-se as frações **Fr7** e **Fr8**, que revelaram CMI´s mais elevadas para os lactobacilos (2,5 e 1,25 mg/mL, respetivamente) e mais baixas para as bactérias patogénicas *L. monocytogenes* (0.625 mg/mL), *N. gonorrhoeae* (**Fr7** = 1,25 mg/mL; **Fr8** = 0,625 mg/mL). Desta forma, o fracionamento do extrato de acetona das sumidades de *C. vulgaris* mostrou-se benéfico, corroborando o uso tradicional deste arbusto.

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Deconstructing apple pomace chemistry

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Apple pomace is a byproduct from apple processing industries, frequently discarded despite its high organic load [1]. A very probable reason for this relies on gaps in the knowledge and potential of the apple pomace chemistry. Therefore, this work intends to make use of distinct currently available extraction (hot water, Microwave Assisted Extraction (MAE)), separation (solid-phase extraction) and analytical (GC-FID, GC-MS, HPLC-DAD-ESI-MS^n) techniques to elucidate the chemical deconstruction of apple pomace, allowing its deeper knowledge and global valuation.

Sugar analysis, after derivatization to their alditol acetates followed by GC-FID analysis, revealed that 620 g/kg of the dry apple pomace correspond to carbohydrates, comprising free sugars and polysaccharides of pectic, hemicellulosic and cellulosic nature. HPLC-DAD-ESI-MS^n allowed to identify flavanols, dihydrochalcones, hydroxycinnamic acids, flavonols and some of their oxidation products, the sum of which accounted for 6 g/kg of the pomace. Hot water allowed to extract about 50% of the polysaccharides and polyphenols in the pomace. By performing solid-phase extraction with C18 cartridges, this extract could be separated in three distinct fractions on C18 cartridges: F1 retained at pH 7, F2 retained at pH 3 and F3 not retained. All were rich in polysaccharides (400-900 g/kg). A further extraction with 60% acetone applied to the hot water extraction residue allowed to further recover 4% of the originally present phenolic compounds. As demonstrated by HPLC after thioacidolysis and alkaline fusion, procyanidins remained in the acetone extraction residue with an average degree of polymerization of 4.7, closely related with their oxidized structures. Along with these polyphenols, the acetone extraction residue still contained some residual pectin and hemicelluloses that were extractable by MAE, while cellulose remained as a final unextractable component.

Apple pomace chemistry could thus be deconstructed in components with distinct chemical features and potential applications in several fields.

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Recuperação otimizada de antocianinas de *Prunus spinosa* L. e *Ficus carica* L. para aplicação como corante alimentar

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Os corantes alimentares são amplamente utilizados em todo o mundo para melhorar as características dos alimentos, nomeadamente conferir uma nova coloração ou intensificar a cor natural do alimento. No entanto, a maioria destes compostos é de origem artificial e muitos deles têm revelado problemas de toxicidade para a organismo humano. Entre eles, destacam-se reações alérgicas, hiperatividade e défice de atenção em crianças, ou até mesmo propriedades cancerígenas [1]. Por outro lado, existem moléculas de origem natural com elevado poder corante que não revelam toxicidade, podendo assim ser aplicadas na indústria alimentar em detrimento das artificiais. O presente estudo surge no seguimento desta problemática e visa recuperar antocianinas, uma classe de compostos fenólicos com reconhecidas propriedades corantes, a partir de fontes naturais muito pouco exploradas. Assim, o epicarpo dos frutos de *Prunus spinosa* L. (abrunho), rico em cianidina 3-rutinósido e peonidina 3-rutinósido, e a casca dos frutos de *Ficus carica* L. (figo), rica em cianidina 3-rutinósido, foram utilizados para extração destes compostos. Para assegurar uma recuperação máxima, foram testadas duas técnicas de extração, assistida por maceração (EAM) e por ultrassons (EAU), às quais se aplicou uma metodologia de superfície de resposta usando o desenho composto central circunscrito com cinco níveis em cada uma das variáveis independentes estudadas (tempo, proporção de água-etanol como solvente e temperatura (EAM) ou potência (EAU)). O perfil antociânico dos diferentes extratos foi obtido por HPLC-DAD-ESI/MS e como respostas para o modelo foram utilizadas a concentração total de antocianinas (C) no resíduo de extração (R; mg C/g R) e na amostra desidratada (A; mg C/g A), bem como o rendimento de resíduo obtido (g R/g A).

Em ambas as matrizes, a técnica mais eficiente foi a extração assistida por ultrassons, obtendo-se condições ótimas de recuperação de compostos aos 5 min, 400 W e 48% de etanol no caso do epicarpo de abrunho, com um rendimento de extração de 0,69 g R/g A e um total de antocianinas de 18,17 mg C/g R e 11,76 mg C/g A. Por outro lado, a partir da casca de figo foi possível obter 17,0 mg C/g R e 3,11 mg C/g A, e um rendimento de 0,19 g R/g A, nas condições ideais de extração de 21 min, 310 W e 100% de etanol. Assim, a extração de antocianinas a partir de biorresíduos dos frutos de abrunho e figo, com recurso a técnicas de extração não convencionais, revelaram ser uma boa alternativa para recuperação destes compostos com vista à sua utilização na indústria alimentar.

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Optimized Acetonitrile Based-Extraction for Determination of Polycyclic Aromatic Hydrocarbons in Cooked Muscle Foods

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Smoked, grilled and barbecued muscle foods such as meat and fish have long been associated with increased risk of cancer, with polycyclic aromatic Hydrocarbons (PAHs) being one of the potential carcinogenic agents. The European Food Safety Authority concluded that the sum of 4 PAHs (benz[a]anthracene, chrysene, benzo[b] fluoranthene and benzo[a]pyrene), PAH4 is the most suitable indicator for the occurrence of these compounds in food and the European Commission established maximum levels for these compounds in foods [1] and also established criteria for their analysis[2]. Several analytical methods for PAHs detection and quantification have been proposed, along with pre-concentration and cleanup steps due to the complexity of muscle foods [3]. However there is currently an increasing demand for fast and reliable analytical methodologies, since in routine analytical applications; sample throughput is an important issue to consider in the choice of an analytical method.

The main goal of this work was to develop and validate a fast analytical methodology for 14 PAHs analyses, including the priority PAH4, on different types of grilled and smoked foods taking into account the simplicity, high recovery, quickness and low cost of process. For this propose, we developed an acetonitrile based-extraction followed by HPLC-FL detection with the aid of chemometrics.

The optimum amounts of magnesium sulfate and sodium chloride that promoted phase separation of acetonitrile extraction containing PAHs from matrix and aqueous phase were selected by Central Composite Design. Matrix-matched calibration curves were constructed by adding different concentrations of PAHs and then subjected to extraction followed by HPLC. An excellent linearity for all compounds applying weighed least squares linear regression procedure was achieved. LODs and LOQs were lower than 0.12 and 0.39 ng g $^{-1}$ respectively. Validation was done according to International Conference on Harmonization recommendations for 14 PAHs [4]. The criteria for 4 EU marker PAHs, PAH4, established by European Commission Regulation No. 836/2011 [2] was also accomplished. Repeatability and reproducibility were lower than 8 and 13.3%, and the most of recoveries fall in the range of 80–110% in different muscle foods. The proposed method is a robust tool for determination of PAHs in grilled and smoked muscle foods, being easy to perform in short time.

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In-house validation method for the determination of 24 pharmaceuticals in clams using QuEChERS-LC-MS/MS

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The pharmaceutical compounds (PhCs) are always biologically active and their presence – even in trace concentrations – raises the possibility of potentially significant adverse effects after chronic exposure of both ecosystems and humans [1]. Data of PhCs in clams or other bivalves are scarce, as well as a method for their simultaneous quantification. The usual methods of detection of multiresidues in these aquatic products shows, among other disadvantages, complex pretreatment, long time consuming, single detection type and low sensitivity [2]. Therefore, the development and validation of a multiresidue method for overcome these limitations is very important. The QuEChERS (quick, easy, cheap, effective, rugged, and safe) pretreatment method combined with ultra-performance liquid chromatography-tandem mass spectrometry (LC-MS/MS) was proposed for the screening of 24 PhCs belonging to ten pharmaceutical classes.

Due to matrix effects (high ionic suppression/enhancement and low recoveries) standard addition calibration curves were used for quantification. After that, the method showed good results in terms of working range ($r2 \geq 0.995$; $CVm \leq 6.0\%$; $PG \leq F(0.05; 1; N-3)$; RIKILT test, $100 \pm 10\%$) and precision ($RSD < 20\%$). The recovery was in the range of 35 and 119% with RSD lower than 20%. The quantification limits LOQ varied from 0.02 ng/g to 6.3 ng/g, being lower than 1 ng/g for most of the target compounds.

The validated method was applied to the quantification of target compounds in samples of clams (*Ruditapes decussatus*). The most abundant PhC in clams was caffeine with concentrations ranging from 0.10 to 12 ng/g wet weight.

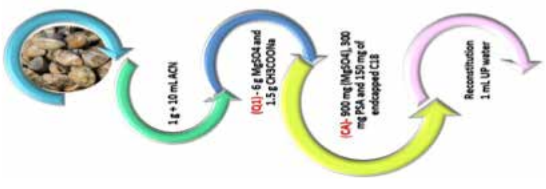

Figure 1: Clams pre-treatment by QuEChERS method.

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Polybrominated diphenyl ethers and their metabolites in European smoked fish products

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Brominated flame retardants are chemicals that are added to many industrial and household products to reduce their flammability. Among them, polybrominated diphenyl ethers (PBDEs) have been increasingly assessed in seafood, the main route of human exposure. In the present study, PBDEs and their biologically active metabolites – the methoxylated PBDEs (MeO-PBDEs) – were determined in several smoked seafood products (N=30) acquired in the European market.

The analyses were performed by an environmental friendly method comprising a "Quick, Easy, Cheap, Effective, Rugged, and Safe" (QuEChERS)-based extraction. Instrumental analyses were performed with gas chromatography coupled to triple quadrupole mass spectrometry using electron impact source (GC-EI-MS/MS) and negative ion chemical ionization (GC-NICI-MS) to assess BDE-209. Statistical validation showed recoveries for all target substances near 100% with average Relative Standard Deviation (RSD) lower than 9% and recovery standards higher than 65% (average RSD below 20%). Average calculated Method Detection Limits (MDLs) were lower than 65 ng·kg^{-1} wet weight (WW). Moreover, the trueness of the developed method was evaluated by the analysis of the SRM 1947 (Lake Michigan Fish Tissue) certified/reference material.

Among all studied products, 80% were contaminated with at least one of these BFRs. As expected, BDE-47 and 6-MeO-BDE-47 showed the highest frequencies of detection and presence in higher amounts, while highly brominated congeners were not detected. All smoked cod liver samples revealed the highest degrees of contamination, i.e. up to 208 **μg**.kg^{-1} WW of total PBDEs and MeO-PBDEs and up to 64 **μg**.kg^{-1} WW of total PBDEs. Following smoked liver samples, smoked European sprat also showed considerable amounts of total PBDEs and MeO-PBDEs (up to 134 μg.kg^{-1} WW).

The outcomes of this survey can be used in future risk assessments of BFRs in seafood in order to improve the quality of fish products and thus consumers' safety.

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Interação de uma mistura de procianidinas com diferentes famílias de proteínas salivares

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Um dos atributos sensoriais organoléticos mais importantes dos produtos alimentares ricos em taninos condensados (procianidinas), uma classe de compostos fenólicos, é a adstringência. Esta sensação está descrita como secura, enrugamento e constrição da cavidade oral [1]. É consensual que um dos principais mecanismos para a sua perceção é desencadeado pela interação das proteínas salivares (PS) com taninos, levando à formação de complexos (in)solúveis, os quais eventualmente precipitam na cavidade oral [2]. O nível de complexidade molecular das procianidinas desempenha um papel importante nestas interações. Quanto maior o grau de polimerização (número de subunidades) e o número de grupos galhoil, maior a capacidade das procianidinas interagirem com as PS e também com as células da cavidade oral [3]. As famílias de PS com maior interação incluem as mucinas e as proteínas ricas em prolina (PRPs), as quais estão subdivididas em três famílias: PRPs acídicas (aPRPs), básicas (bPRPs) e glicosiladas (gPRPs) [4].

A maioria dos estudos de interação proteína-tanino foca-se em compostos puros, incluindo apenas uma proteína e um tanino. Apesar destes estudos permitirem caracterizar estas interações, estão muito longe do que acontece na realidade, em que temos as várias PS e uma mistura de taninos alimentares a interagirem simultaneamente. Deste modo, foi realizado um estudo de interação por HPLC de uma mistura de procianidinas (maioritariamente diméricas) (0.8 e 1.3 gL^{-1}) com saliva de cinco indivíduos com diferente proporção das várias famílias de PS. Observou-se que as procianidinas que mais interagiram na concentração de 1.3 gL^{-1} foram os dimeros B6 e B2-galhato, um trimero e a epigalhocatequina, atingindo uma precipitação máxima de 50 %. Excecionalmente, o dimero B7 apresentou maior interação a 0.8 gL^{-1} atingindo uma precipitação máxima de 31 %. Relativamente às PS, observou-se uma precipitação de várias famílias de PS, diretamente proporcional à concentração de procianidinas. Foi observada uma depleção quase total de estaterina e pPB em todos os indivíduos. Dentro das PRPs, as aPRPs parecem ser as mais afetadas com o aumento gradual da concentração de procianidinas, levando a precipitações até 80 %. As cistatinas, não sofreram qualquer diminuição, exceto no indivíduo com maior teor nesta família de PS, que sofreu uma precipitação até 24%.

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Correlation of aroma characteristics with volatile profile of hops

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Hops (Humulus lupulus L.) are essential beer ingredients not only for bitterness, but also for aroma that are associated with the essential oil fraction that included a large group of volatile compounds. More than 440 compounds have are already been identified, however suggestion is that much more can still be found [1]. The aim of this study was to reach the possible contribution of some compounds to the specific sensorial quality of hops.

A total of 109 different hops from various part of the world were evaluated by sensory analyses and gas chromatography. Hops were grouped by region and partial least squares regression was performed in order to study the correlation of aroma attributes data (Y-variables) with analytical volatile profile data (X-variables). The importance of volatile profile in the projection and their standardized coefficients was also determined, and latent variables were identified.

Methyl geranate and 2-undecanone were highly influential latent variables for all attributes (citrus, fruity/ sweet, and floral). 2-undecanone influenced the panel perception in opposite directions: positive influence for fruity/sweet when the compound was present in higher percentage; and influence for citrus perception with lower percentage. In part, this behavior can be associated to the fruity notes description of pure compound [2, 3], however, 2-undecanone have already been described as citrus and floral in olfactometry of hops [4]. Linalool and 2-decanone had high influence on citrus and floral, and ethyl 4-methylpentanoate had for citrus and fruity. In addition, fruit/sweet aroma was also highly influenced by 3-methylbutyl 2-methylpropanoate, 2-methylbutyl 2-methylpropanoate, and floral by 2-methylpropanoic acid, perillen, 3-methyl butanoic acid, and β-ocimene, these last two showed a negative influence.

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A importância dos polissacáridos do vinho na modulação das interações proteína-tanino

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Dentro dos polifenóis, os taninos estão mais associados ao sabor, nomeadamente à adstringência. A adstringência é um complexo grupo de sensações que envolve secura, aspereza e constrição da cavidade oral. Têm sido descritos diferentes mecanismos para explicar o fenómeno de adstringência, sendo o mais aceite pela comunidade científica a interação das proteínas salivares com os taninos, resultando na formação de complexos e, consequentemente, na sua precipitação [1]. Várias proteínas salivares têm demonstrado grande afinidade para interagir com os taninos, nomeadamente as proteínas acídicas ricas em prolina (aPRPs) e o péptido P-B [2]. Apesar da adstringência apresentar muitas vezes uma conotação negativa, sabe-se que em algumas bebidas como o vinho tinto, um nível equilibrado de adstringência é desejado para a sua qualidade. Desse modo torna-se necessário, muitas vezes, modular a adstringência. Já se encontra descrito na literatura que alguns compostos, como é o caso dos polissacáridos, podem inibir ou reduzir as interações entre os taninos e as proteínas salivares. Os principais polissacáridos do vinho são as arabinogalactanas (AGPs), rhamnogalacturonana tipo II (RGII) e manoproteínas (MPs), podendo estes serem usados para modular estas interações [3].

Assim, o objetivo deste trabalho foi compreender, a nível molecular, como é que as interações entre os taninos e as proteínas salivares podem ser afetadas pela presença de alguns polissacáridos do vinho, como o RGII e as AGPs. A influência destes polissacáridos na interação de saliva humana/proteínas isoladas (aPRPs e péptido P-B) com duas classes de taninos (hidrolisáveis e condensados) foi estudada por diferentes técnicas, tais como cromatografia líquida de alta eficiência (HPLC), extinção da fluorescência, nefelometria, diferença de transferência de saturação (*Saturation Transfer Diference)* STD-RMN e gel de eletroforese (SDS-PAGE).

Os resultados mostraram que, no geral, os polissacáridos estudados foram eficientes na redução/inibição da interação tanino-proteínas salivares. O efeito observado pode ser explicado por dois mecanismos, ternário (formação de um complexo polissacárido-tanino-proteína) ou competição (polissacáridos competem com as proteínas salivares pela ligação aos taninos). Contudo, este efeito é dependente de vários fatores, como estrutura dos polissacáridos, proteínas isoladas vs. proteínas numa mistura (saliva), o par tanino-proteína, entre outros.

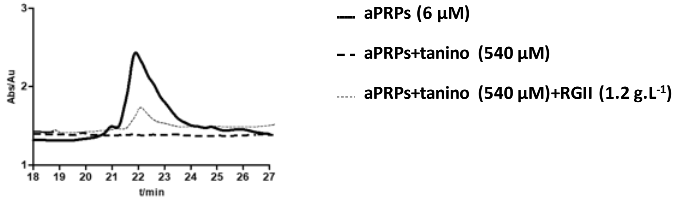

Figura 1 – Cromatograma da família de proteínas aPRPs antes e depois da interação com o tanino, e na presença do polissacárido RGII.

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Influência da acilação enzimática nas propriedades cromáticas de novos derivados de antocianinas monoglucósidas

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O uso de corantes naturais em detrimento dos aditivos sintéticos tem sido impulsionado devido às limitações impostas na utilização de pigmentos sintéticos [1]. As antocianinas são um vasto grupo de flavonóides responsáveis pelas cores atrativas da maior parte das flores, frutos e vegetais, com propriedades biológicas interessantes, como elevado poder antioxidante, atividade antimicrobiana e anti-inflamatória, entre outras [2]. No entanto, a aplicação tecnológica das antocianinas é ainda muito limitada. A estrutura química das antocianinas é facilmente influenciada pelo pH, assim como com a temperatura e a presença de oxigénio e metais [3]. A incorporação das antocianinas em matrizes lipídicas, como produtos alimentares e formulações cosméticas, é ainda dificultada pela baixa lipofilicidade destes metabolitos. No entanto, a acilação com ácidos gordos mediada por catálise enzimática tem vindo a ser descrita recentemente como uma estratégia para aumentar a solubilidade das antocianinas em matrizes lipofílicas assim como um aumento da sua atividade antioxidante em sistemas lipídicos [4] [5; 6].

Este trabalho focou-se na influência da cadeia de ácidos gordos monoinsaturados na estabilidade térmica e química das antocianinas. A degradação térmica da cor das antocianinas aciladas foi estudada em solução aquosa de um tensioativo aniónico (SDS), para diferentes pH's. Estes ensaios demonstraram que todos os derivados lipofílicos são menos suscetíveis à degradação térmica e possuem maior estabilidade cromática para valores de pH entre 3 e 7 comparativamente com o seu precursor [7].

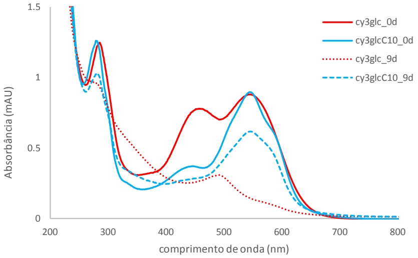

Fig. 1. Espetros UV-Vis de Cy3glc e Cy3glc-C10 em SDS 0.1 M aquoso a pH 7, no início e após 9 dias de equilíbrio.

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Individual phenolic compounds profile from rosé wines aged in contact with different wood chips species (oak and cherry)

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According to OIV, in 2014, global production of rosé wines is estimated at 24.3 million of hectoliters, which is 9.6% of the world still wine production [1]. Thus, the consumption of rosé wines represents a growing trend in the wine market.

Generally the studies using rosé wines focused on the winemaking, in particular on the maceration process [2] and aromatic composition [3] and not in the aging process of this kind of wines, particularly by the use of wood chips. In this context, and in order to deepen the knowledge of the impact of the use of wood chips on chemical composition of rosé wines, the present study aimed to evaluate the individual phenolic compounds evolution of rosé wines during the aging process in contact with different wood chip species (oak and cherry). The individual phenolic compounds analyzed by HPLC-DAD (monomeric anthocyanins, phenolic acids and (+)-catechin) from a *Touriga Nacional* rosé wine aged in contact with wood chips were analyzed during 100 aging days (fig.1).

The results obtained demonstrates that in general, the use of wood chips induces a strong change in the phenolic composition of rosés wines and consequently on the potential characteristics of these wines.

This research is an interesting topic from a practical point of view, especially when the option for aging wines in contact with wood chips is increasingly and widely chosen by the winemakers.

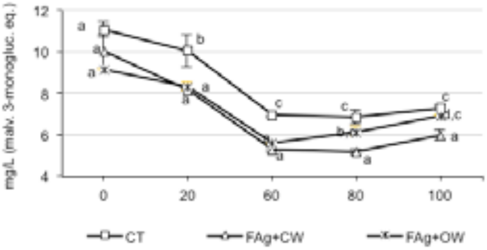

Fig.1. Evolution of total 3-O-monoglucoside anthocyanins in rosé wines aged with wood chips. CT - control wine; Fag+CW - wine with cherry wood chips; Fag+OW - wine with oak wood chips

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Estudo da estabilidade e atividade biológica de bagaço de uva (Merlot) após simulação da digestão gastrointestinal e fermentação colónica

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A produção de vinho representa hoje em dia uma das maiores atividades agroindustriais a nível mundial. Como consequência gera uma enorme quantidade de subprodutos (bagaço e borras) que representam por vezes até 30% das uvas vinificadas, sendo a maioria completamente descartados sem tratamento adequado e/ou outras finalidades [1-4]. O bagaço de uva representa, por isso, um abundante e acessível subproduto industrial que contém uma grande variedade de compostos bioativos, nomeadamente fenólicos, que têm sido relacionados com benefícios para a saúde do consumidor [1].

O objetivo deste estudo foi mimetizar a digestão gastrointestinal e a fermentação colónica de bagaço de uva de Merlot, de forma a avaliar uma possível redução do conteúdo em fitoquímicos, correlacionando o perfil de compostos fenólicos com as suas atividades biológicas. Assim, foram caracterizados três extratos de bagaço (inicial, digerido e fermentado) relativamente ao seu conteúdo em compostos fenólicos antociânicos e não antociânicos por HPLC-DAD-ESI/MS. Além disso, foi também avaliado o seu potencial antioxidante, antibacteriano e citotóxico para células tumorais e não-tumorais.

Os compostos fenólicos mais abundantes identificados nas três amostras estudadas foram um dímero de (epi)catequina tipo B, (+)-catequina e (-)-epicatequina. Foram identificados vinte compostos fenólicos não antociânicos na amostra inicial (66 mg/g de extrato), tendo sido significativamente reduzidos para 11 compostos após digestão *in vitro*. Foram identificadas cinco antocianinas, no entanto, as quantidades diminuíram imenso após digestão e fermentação. Pelos resultados obtidos podemos concluir que o processo de digestão *in vitro* promoveu drásticas reduções qualitativas e quantitativas no perfil de compostos fenólicos no extrato inicial de bagaço de uvas Merlot. Tais alterações podem estar relacionadas com a diminuição de algumas bioatividades do extrato, como é o caso das propriedades antioxidantes e antibacterianas, embora não de forma diretamente proporcional. No entanto, a fermentação colónica teve um efeito positivo sobre o potencial citoóxico do extrato em linhas celulares tumorais humanas.

Há ainda um conhecimento muito escasso sobre a estabilidade dos compostos fenólicos de bagaço de uva e propriedades bioativas durante a digestão gastrointestinal e fermentação colónica, no entanto, os resultados obtidos poderão ser de grande utilidade para o desenvolvimento de novos suplementos nutracêuticos e produtos alimentares funcionalizados.

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Valorization of Portuguese elderberries from Varosa Valley

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Extracts of Sambucus nigra L., European elderberry or black elderberry have a significant amount of bioactive compounds presenting a high commercial value to the food and pharmaceutical industries [1]. Portuguese elderberries are known by their high quality (brix degree and anthocyanins content), indeed almost all the Portuguese production is exported every year to other European countries. In Portugal, the production of elderberries is concentrated in Varosa Valley, being observed a plantation increase in the last two years [2], the major cultivars being the 'Sabugueiro', 'Sabugueira' and 'Bastardeira'.

The goal of this work was the evaluation of some chemical parameters related with the quality of the elderberries, as sugar content, brix degree, phenolic content, anthocyanins content, on mature elderberries fruit from 'Sabugueiro', 'Sabugueira' and 'Bastardeira' cultivars in different years in order to gain insight of which cultivars could be the most attractive for the local economy and for the industries.

The results showed that elderberries presented a brix degree higher than 14 ºBrix, a total sugar content higher than 13 g/100g FW, being glucose the major sugar present in elderberries, a total phenolic content higher than 1400 mg GAE/100 g FW and total anthocyanins content higher than 690 mg/100 g FW, being 'Bastardeira' the cultivar those could provide the best quality of the elderberries. The phenolic profile by HPLC-DAD showed a similar profile between Portuguese elderberries and others European elderberries. However, in many parameters evaluated Portuguese elderberries presented a higher quality than other studies reported.

To conclude, all the cultivars studied in this work could provide elderberries with high quality, however on an industrial point of view, 'Bastardeira' is the most attractive.

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Cytinus hypocistis L. plant as source of phenolic compounds with anti-lipid peroxidation activity

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After a period in which synthetic compounds were preferred, there is an increasing interest in studying the bioactive properties of plants and the active principles behind their therapeutic properties [1]. Polyphenols are the largest and the most widespread group of secondary metabolites in plants. With a great variety of structures, ranging from simple compounds with few aromatic rings, such as phenolic acids, to highly polymeric substances, such as tannins; they are commonly found in both edible and inedible plants, and have been reported to have multiple biological effects, including antioxidant activity [2].

Cytinus hypocistis L. is an endophytic parasitic plant occurring in the Mediterranean region and it was used in a wide variety of traditional healthcare practices, including dysentery, tumour of the throat and eye inflammation treatment [3]. Despite these wealthy traditional uses, its chemical composition is largely unknown. Therefore, the aim of this study was to characterize this plant in terms of polyphenolic composition and capacity to inhibit lipid peroxidation. Plant specimens were collected in June 2018 in Castro Daire, Portugal. After lyophilisation, the phenolic compounds were analysed in four different hydroethanolic extracts of *C. hypocistis* (whole plant, nectar chamber of the flower, petals, and stalks) using an HPLC-DAD/ESI-MS system. Seventeen phenolic compounds were identified, sixteen hydrolyzable tannins (with trigalloyl-diHHDP-glucoside as the major compound) and one flavan-3-ol ((+)-catechin), being the petals the sample that presented the highest concentration of the identified compounds.

TBARS method was used to evaluate the inhibition of lipid peroxidation, a widely recognized primary toxicological event caused by the generation of free radicals [4]. In this study, the hydroethanolic extracts of the four samples were capable of preventing the formation of malondialdehyde (MDA), a secondary product of lipid peroxidation, in a dose dependent manner. The highest anti-lipid peroxidation activity was revealed by the petals extract (342 ng/mL), also exhibiting the highest concentration of phenolic compounds. This activity is much better than the one displayed by the standard Trolox. This study revealed that the extracts might prevent reactive radical species from damaging biomolecules such as lipids in the cells. These features are behind the health benefits for humans and the wide use of tannin-containing plant extracts in herbal medicine [5]. A correlation study will also be performed to understand the influence of phenolic compounds in the bioactive properties of this plant.

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Antioxidant and antimicrobial activities of European hackberry (*Celtis australis* L.) seeds

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The European hackberry (*Celtis australis* L.) is a deciduous tree of the Cannabaceae family frequently found in southern Europe and western Asia. Its fruit is an edible, dark-purple berry-like drupe with a large seed that corresponds to about 38% of the fruit dry weight [1]. Fruit preparations are used in traditional medicine as a remedy for colic, peptic ulcers, dysentery, diarrhea, amenorrhea, and heavy menstrual bleeding [1–3]. However, as far as we know, the antioxidant and antimicrobial properties of *C. australis* seeds have never been explored before, being this the purpose of this study.

The *C. australis* seed extract was obtained by a solid-liquid extraction of the powdered sample with methanol:water (80:20, v/v) [4]. Then, the antioxidant activity was measured *in vitro* via DPPH$^\bullet$ scavenging activity, reducing power, **β**-carotene bleaching inhibition capacity, and thiobarbituric acid reactive substances (TBARS) formation inhibition capacity in brain cell homogenates [4]. The antimicrobial activity was screened against twelve microorganisms, including Gram-positive and Gram-negative bacteria and fungi, by the microdilution method [5].

The seed extract was effective in inhibiting the formation of TBARS as byproducts of lipid peroxidation, which was concluded from the low EC_{50} value. The extract also had an interesting reducing power and capacity to protect **β**-carotene from the free radicals generated from linoleic acid. Regarding its antimicrobial activity, the best results were against *B. cereus*, with MIC and MBC lower than ampicillin, *A. ochraceus*, with MIC and MFC lower than ketoconazole, and *P. funiculosum*, with MIC lower than ketoconazole and bifonazole and MFC lower than ketoconazole.

These results highlighted the potential of *C. australis* seeds as an interesting fruit by-product to be used in the development of bio-based antimicrobials.

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Effect on phenolic composition and biological properties of grape (*Vitis vinifera* L.) stems during long-term storage

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The winery industry is one of the most important industries worldwide, with an economical and social impact in Europe and specially in northern Portugal. This socio-economic activity entail large quantities of by-products generated annually, causing economical and environmental problems. In a close connection with the 40 years history of investigation on agro-food valorization, nowadays, a growing interest has wake up on recycling winery wastes boosted by the more and more reported putative health-promoting effects. Furthermore, the continuous emergence of multidrug resistant bacteria is becoming a huge threat to human, animal and environmental health (One health approach). Therefore, the research for new natural antimicrobial compounds is the most promising alternative to effectively control multidrug bacterial infections. Hence, qualitative and quantitative evaluation of polyphenolic extracts of grape stems as sources of individual phenolic compounds and their biological activity in vitro (radical scavenging power and antimicrobial activity) were assessed during 64 days of storage. Grape stems revealed to be a rich source of phenolic compounds, even after some months of storage. Furthermore, all extracts (with and without storage) were able to inhibit the bacterial growth of the Gram-positive bacteria and Gram-negative bacteria (except E. coli and K. pneumoniae), revealing the potential inclusion of these bioactive compounds in the food, cosmetic, and pharmaceutical industry as functional ingredients.

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In-line phosphate pre-concentration in a flow injection method platform for monitoring fertilizers excess in soil leachates

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Fertilizers have been intensively used in agricultural activities and the inorganic phosphate derived from them is often found in excess in ground waters. Phosphate is a well-known contaminant and its content is an indicator of water quality, so it is important to have an efficient monitoring of the soil leaching process.

The conventional soil testing is based on manual or mechanical soil sampling and extraction processes, which are time consuming. To study the soil leaching process, it is necessary to mimic natural conditions in laboratory models and to develop real-time analytical tools. The aim of this work is the development of an automatic, low cost flow analysis method, capable of real-time monitoring of the soil leaching processes using spectrophotometric detection. The developed system has a pre-concentration step, incorporated in a flow injection (FI) system. Most methods for phosphate determination in water are based on the formation of phosphomolybdate and its reduction to molybdenum blue. The FI system was developed using a commutator to study the use of the anionic resin, AG1-X8, for phosphate pre-concentration. In this FI system, the resin column was loaded with 500 µL of phosphate standard/sample (L1) and then eluted with 75 µL of a sodium chloride solution (L2), before merging with ammonium molybdenum and ascorbic acid solutions.

The developed FI system can be applied to different water samples, namely river water, sea water, estuary water, well water and rain water. In this work, it was used in the monitoring of the soil leaching process by using laboratory scale soil columns (LSSC) to obtain the soil leachates. The LSSC columns were explored to understand the behaviour of ions in soils (mobility, transport and fate).

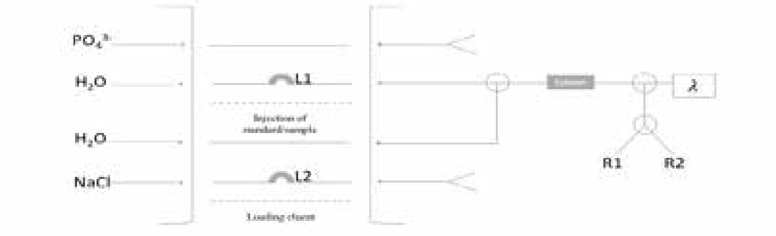

Fig. 1. Flow injection manifold for the determination of phosphate after in-line pre-concentration; L1, sample loop; L2, eluting solution loop, R1, Molybdenum blue reagent; R2, ascorbic acid solution, Column, packed AG1-X8 resin for phosphate pre-concentration.

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Phenolic composition and cell-based antioxidant activity of roots and aerial parts of *Eryngium viviparum* produced *in vitro*

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Eryngium plants have been used for ornamental, agricultural and folk medicinal purposes [1]. Within this genus, *Eryngium viviparum* J. Gay is an endemic plant from the Northwest of Spain and France and Northeast of Portugal that is included in International Union for Conservation of Nature red list for threatened plants [2]. For this reason, it is important to apply *ex situ* biotechnological conservation tools, such as the *in vitro* culture, to preserve this species, but also take advantage of the high growth rates and yields of bioactive secondary metabolites to provide high added-value to this species [3]. Phenolic compounds, among others, have been reported as important compounds in this genus due to their antioxidant properties [1]. However, as far as we know, the phenolic composition and antioxidant activity of *E. viviparum* have never been described, being this the main purpose of this study.

The *in vitro* culture of *E. viviparum* explants was established in solidified MS medium, supplemented with indole-3-butyric acid (0.1 mg L^{-1}), at 24 ± 2 °C under a 16/8 photoperiod in a growth chamber. After five weeks, the aerial parts and roots of the established explants were collected, freeze-dried and reduced to a fine powder. Hydroethanolic extracts were then prepared from both samples by solid-liquid extraction and the phenolic profile was characterized by HPLC-DAD-ESI/MS [4]. The antioxidant activity was evaluated *in vitro* for the lipid peroxidation inhibition capacity by the thiobarbituric acid reactive substances (TBARS) formation inhibition capacity in brain cell homogenates, and for the antihaemolytic capacity by the oxidative haemolysis inhibition assay (OxHLIA) using sheep erythrocytes [4].

Eleven phenolic compounds were identified in both *E. viviparum* hydroethanolic extracts, corresponding to ten phenolic acids and one flavonoid. Rosmarinic acid was the major compound in both samples and the highest concentration was found in roots. Tectorigenin-*O*-glucuronide was the identified flavonoid. The root extract had an interesting antioxidant activity translated by the lowest IC_{50} values. In fact, the root extract was more effective in preventing the formation of malondialdehyde as a secondary product of lipid peroxidation and preventing lysis of erythrocyte membranes. The high levels of rosmarinic acid found in roots may be responsible for the observed bioactivities, since this compound has been reported as a powerful antioxidant [5]. Therefore, this study provided high added-value to *E. viviparum* roots as an interesting source of rosmarinic acid, which could have different industrial applications as natural antioxidants.

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Monitoring the nutritional quality of tomatoes during shelf-life after a post-harvest treatment with Calcium Chloride

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Tomato (*Solanum lycopersicum* L.) is a species with a high economic value and it is one of the most cultivated crops worldwide. The quality and nutritional value of tomato fruits are strongly associated with their bioactive compounds, responsible for antioxidant activity and related with many health benefits for its consumers, particularly the reduced risk of developing chronic diseases [1] [2].

In order to avoid post-harvest damage and decrease of nutritional quality, several treatments may be applied to fresh horticultural crops. This work aimed at the study of the influence of a post-harvest treatment with calcium chloride ($CaCl_2$) in tomatoes quality after 1 and 2 weeks of storage by evaluation and analysis of various parameters. Effects of $CaCl_2$ treatments have already been studied in diverse fruits and vegetables, however the consequences of its application in tomatoes are not fully described [3].

The total phenolic content and DPPH scavenging capacity of methanolic extracts obtained from treated tomato fruits were evaluated during treatment. The main phenolic compounds were also identified by HPLC-MS in order to evaluate the impact of $CaCL_2$ treatment in the phenolic profile of tomato fruits. Glutathione, a molecule with a central role in antioxidant defense system, was also quantified by HPLC-MS. The activity of enzymes involved in synthesis (**γ-glutamyl-cysteinyl synthetase** and Glutamine Synthetase) and recycling of glutathione (Glutathione Reductase) were evaluated in protein extracts of treated tomato fruits.

Post-harvest treatment with $CaCl_2$ did not induced any significative effect in total phenolic content and DPPH scavenging activity of tomato fruits. However, some alterations of the phenolic profile during treatment were observed, regarding the content of dicaffeoylquinic and tricaffeoylquinic acids. It was also observed an increase of the activity of Glutamine Synthetase, associated with a decrease in the activity of Glutathione Reductase, responsible for a decrease of the oxidative state of the tomato fruits after treatment.

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Nutritional and physicochemical characterization of purple and red-fleshed genotypes of potatoes from different geographical regions

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There is a recent increasing interest by food producers and consumers in colored potato varieties, mostly in Europe and the United States [1,2]. This interest is connected not only with the tubers' attractive physical and organoleptic qualities (color and taste), but also with their health beneficial chemical composition [2]. Colored varieties include: red skin/white flesh, red skin/red flesh, purple skin/marble flesh and purple skin/purple flesh [1].

This study reports the characterization of ten potatoes' genotypes with red and purple flesh, in terms of their nutritional and physicochemical composition. Their nutritional value (proteins, fat, ash, carbohydrates, and energetic value) and NaCl content were evaluated according to AOAC methodologies. The chemical composition was evaluated in terms of organic acids, fatty acids, and free sugars content through chromatographic analysis. Moreover, pH and color measurement of skin and flesh were also determined using a calibrated digital pH meter and a colorimeter, respectively. For this purpose, tubers of ten colored potato cultivars were obtained from the Leibniz Institute of Plant Genetics and Crop Plant Research in Germany.

The ten varieties (Salad Blue, Shetland Black, Rosemary, Red Emmalie, Violette, Finish Blue, Red Cardinal, Kefermarkter Blue, Purple and UACH 0917), original from five different countries (Germany, Austria, United Kingdom, Finland and Chile), showed significant differences in their nutritional profiles. Despite of their genetic origin, all tuber samples were grown in the same location in Germany in the year of 2017. The results showed the following nutrient content variation depending on the cultivar: carbohydrates: 174.1±0.1 – 272.2±0.5 g/kg fw; proteins: 18.0±0.3 – 22.4±0.5 g/kg fw; fat: 0.54±0.03 - 4.88±0.04 g/kg fw; and ash: 6.2±0.3 – 14.7±0.2 g/kg fw. The energetic value ranged between 790.7±0.9 and 1203±1 kcal/kg fw. NaCl content and pH measurements showed similar results among all ten studied colored potatoes, whilst color results varied between red and purple-fleshed varieties.

Understanding the nutritional and physicochemical composition of colored potatoes may help the selection of commercially useful genotypes and promote biodiversity [3]. Moreover, the organoleptic and health-promoting properties of purple and red-fleshed potatoes illustrate their potential use in the food and nutraceutical industries.

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Atividade antioxidante de fenolipidos em emulsões alimentares O/A - Correlação entre a atividade antioxidante e propriedades químicas

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A eficiência dos antioxidantes (AO) em emulsões alimentares depende tanto de sua reatividade quanto da sua concentração na região interfacial, onde se acredita que a oxidação tenha início. O hidroxitirosol, o ácido cafeico, o ácido di-hidrocafeico e seus ésteres com cadeias alquilo de 8 e 16 carbonos foram usados neste estudo. Neste trabalho utilizou-se um método cinético[1] que não requer o isolamento das fases para estimar as constantes de partição dos diferentes fenolipidos contendo o mesmo comprimento de cadeia alquílica. Os resultados em emulsões de óleo/água com uma fração de emulsionante de $\Phi = 0{,}005$ mostram que os derivados do hidroxitirosol e ácido cafeico C8, com percentagem semelhante na interface e potencial oxidativo semelhante, apresentaram atividade antioxidante semelhante. O éster do ácido di-hidrocafeico C8 apresentou a melhor atividade antioxidante devido ao seu menor potencial oxidativo. O derivado C16 do hidroxitirosol, no entanto, apresentou menor concentração na interface do que o derivado do ácido cafeico C16 e, portanto, uma menor atividade antioxidante. Estes resultados suportam fortemente a ideia de que a eficiência de um AO se correlaciona com a sua fração na região interfacial e com o seu potencial oxidativo. Um aumento na concentração de emulsionante (Φ_I) promove a incorporação de AOs na região interfacial. No entanto, a adição de mais emulsionante para aumentar a sua percentagem na região interfacial resultou numa diminuição da eficiência de todos os antioxidantes utilizados devido ao efeito de diluição. A analise de regressão linear mostrou uma correlação altamente significativa entre a concentração dos antioxidantes na região interfacial e a sua atividade antioxidante (r= 0,814).

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Efeito da irradiação na estabilidade de vitaminas essenciais em azedas (*Rumex induratus*) armazenadas a 4 °C

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Os vegetais embalados prontos a consumir são cada vez mais populares entre os consumidores devido à sua conveniência e benefícios para a saúde. O crescimento deste setor tem promovido a introdução de novos alimentos e a adoção de tecnologias de processamento pós-colheita mais eficientes e ecológicas, tais como a irradiação. No entanto, uma preocupação comum do consumidor é saber se este tratamento físico afeta negativamente o valor nutricional e a segurança dos alimentos. Este estudo teve assim como objetivo avaliar a adequação do tratamento de irradiação na conservação de vitaminas essenciais em azedas (*Rumex induratus* Boiss. & Reut.) durante o armazenamento refrigerado.

As amostras de azedas, recolhidas na região nordeste de Portugal, foram lavadas em agua corrente, escorridas e uma porção foi imediatamente analisada (controlo não armazenado). O restante material fresco foi embalado em sacos de polietileno, irradiado a 1, 2 e 6 kGy numa câmara experimental de ^{60}Co e armazenado a 4 °C durante 12 dias. Um controle não irradiado (0 kGy) seguiu todo o ensaio. Posteriormente, os teores de ácido ascórbico, tocoferóis e folatos totais foram determinados por diferentes técnicas cromatográficas (HPLC com detetores de fotodíodos ou fluorescência) [1,2].

Relativamente aos tocoferóis, foram identificadas as quatro isoformas; o **α**-tocoferol foi o mais abundante no controlo não armazenado, seguido do **γ**-tocoferol. O tratamento aplicado causou uma diminuição nos teores de **α**-tocoferol, a qual foi mais acentuada com o consequente aumento da dose. Curiosamente, o controle armazenado não irradiado apresentou o maior teor de tocoferóis totais (promovido especialmente pela isoforma **γ**) [1]. Por sua vez, o ácido ascórbico foi mais sensível à irradiação do que ao tempo de armazenamento [1], enquanto os folatos totais foram afetados apenas pela dose de 2 kGy [2]. Portanto, este estudo demonstrou que o embalamento e a refrigeração são suficientes para conservar as vitaminas analisadas em folhas de azedas durante 12 dias a 4 °C.

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Its tea time!
Mycotoxins in teas and herbs destined to prepare infusions

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Consumption of tea (exclusively derived from the plant *Camellia sinensis*) and herbal infusions in general has been increasing, associated with healthier lifestyles and food choices. However, only a few studies evaluated the occurrence of contaminants in these food matrices, namely mycotoxins, secondary metabolites produced by different species of fungi. Zearalenone (ZEA) is a mycotoxin that binds to estrogenic receptors (ER), competing with 17-**β**-estradiol. It is therefore considered an endocrine disruptor and produces haematological, cytotoxic, genotoxic, immunotoxic and hepatotoxic effects. Aflatoxin B1 (AFB1) is the most common aflatoxin (AF) in food and amongst the most potent genotoxic and carcinogenic mycotoxins, classified by IARC as Group 1 [1, 2]. As the human chronic exposure to aflatoxins is considered a serious health risk problem, monitoring programs of this mycotoxin in several commodities, as well as regulatory actions and determination of tolerance limits have been set up globally [1]. Nevertheless, tea and the herbs used in the preparation of infusions are not subject to any regulation concerning mycotoxins. Portugal is the only European country to produce tea at an industrial level. According to FAO [3], Portugal showed a significant increase in both imported (30 ton in 2005 and 134 ton in 2013) and exported (372 ton in 2000 and 1382 tons in 2013) tea. The reports of mycotoxin content of tea and medicinal plants destined to be consumed as infusions, as well as the human exposure resulting from its consumption are scarce. Therefore this study aimed to analyse commercially available teas and medicinal plants destined to be consumed as infusions and assess the resulting exposure to the mycotoxins AFs and ZEA.

With such purpose, 37 (convenience) samples of tea and medicinal plants destined to be consumed as infusions were purchased in Aveiro and Coimbra regions. After extraction with acetonitrile, clean up was completed with an immunoaffinity column (Mycosept® **226** AflaZon+ (Romerlabs, USA) before immunoassay determination though ELISA (LOD 1.75µg/kg; RIDASCREEN® Aflatoxin total and RIDASCREEN® Zearalenone, R-Biopharm AG®, Germany) [4].

Thirty one (83.8%) of the analysed samples were positive for at least one of the mycotoxins and 16 (43.2%) were positive for both AFs and ZEA. None of the samples negative for both AFs and ZEA were tea (i.e. derived from *Camellia sinensis*). Roughly 65% (n=24) of the analysed samples were positive for AF (mean: 14.74±7.18µg/kg; min: 2.78; max: 28.15 µg/kg). Although the two highest maximum determined levels corresponded to medicinal plant destined to preparation of infusion (Chamomile: 28.15 µg/kg and horsetail: 23.56µg/kg), in general, teas featured the highest AFs contamination levels (19.40 **µg/kg)** *versus* medicinal plants (13.51 **µg/kg)** (Figure 1). Is it also noteworthy that all analysed tea samples (n=5) were AF-positive. Twenty four (62.2%) samples were contaminated with a ZEA (mean: 8.87±5.31 **µg**/kg; min: 1.82; max: 19.02 **µg**/kg) Samples of medicinal plants outside the European Union and sold in bulk (i.e. not packed) were those with the highest ZEA levels. The degree of exposure of the Portuguese to these mycotoxins through consumption of tea and medicinal plants destined to prepare infusions, was assessed through the Estimated Daily Intake (EDI). For AFs the EDI (**µg**/kg bw/day) was 0,037 and for ZEA 0.023 (which alone represents 9% of the Tolerable Daily Intake established by EFSA, 0.25 **µg**/kg bw/day). The obtained results proved the need for further studies to evaluate the occurrence of these mycotoxins in these food commodities of increasing consumption, in order to monitor the exposure of the population and, if justified, to serve as the basis for establishing maximum limits for the control of exposure.

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Quantification of biogenic amines in wines using a dispersive solid phase extraction clean-up/concentration method

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Biogenic amines are organic bases compounds found in several foods. Lactic acid bacteria produce them during malolatic fermentation by aminoacid decarboxylation. In low concentration, biogenic amines contribute for physiological functions like regulation of body temperature, stomach pH or brain activity. However, the consumption of foods containing high amounts of biogenic amines, several toxicological effects may occur such as headaches, renal intoxication, nausea, hypotension, hypertension and in severe situations intracerebral haemorrhage or even death [1]. The monitoring of the presence of these compounds in food is very important, not only from the toxicological point of view, but can also be used as an indicator of spoilage. In this work, a simple dispersive solid phase extraction (dSPE) method followed by benzoyl chloride pre-column derivatisation for HPLC-UV determination of twelve biogenic amines (BAs) in wines is proposed for the first time. The dSPE using a strong cation exchange resin increased the selectivity and sensitivity of the analysis by elimination of interfering compounds and a five-fold enrichment of BAs. The method presented an adequate precision and linearity with detection limits ranging from 0.133 to 0.509 mg/L. Recoveries ranging from 72 to 99% prove the accuracy of the method for determining BAs in red, white and Tawny Port wine samples yielding chromatograms clean from interferents [2]. The method was applied successfully to the analysis of 31 young red wines from different Portuguese wine regions. The dSPE method although has a potential of broader application to other food matrixes, other derivatisation procedures than benzoyl chloride and other detectors.

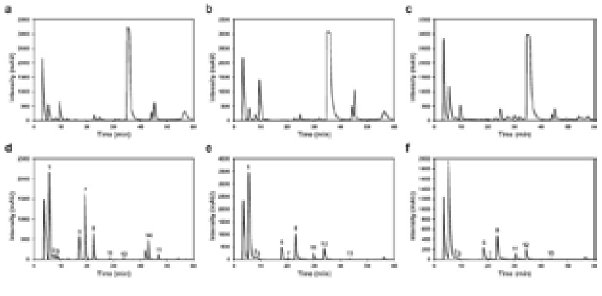

Fig.1. Chromatograms obtained after direct derivatisation of 1 mL of wine using benzoyl chloride by the method of Özdestan and Üren [3] of a red (a) a white (b) and a Tawny Port wine (c) and after application of the dSPE method developed for red (e), white (f) and Tawny Port (g) wines [2].

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Pirano-Estiril-Flavílios – novos pigmentos 'bio-inspirados' e a modelação da sua cor através de sistemas micelares

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Os pirano-flavílios são pigmentos que derivam dos flavílios, apresentam uma ampla gama de cores que vão desde o amarelo ao laranja, vermelho até ao roxo e azul, e podem ser encontrados em alimentos processados como em sumos de fruta e vinhos.[1] Devido à sua estrutura, mais especificamente, à presença de um anel pirânico adicional (anel D), estes pigmentos apresentam uma maior estabilidade das propriedades cromáticas relativamente à variação de pH, em comparação com os seus precursores.[2] Por outro lado, a introdução de uma ligação dupla adicional entre o anel B e C do flavílio leva a uma extensão da conjugação dos eletrões π, podendo provocar profundas alterações na cor e nos seus equilíbrios químicos, exibindo tonalidades mais fortes e mais escuras.[3-4] Neste trabalho, desenvolveram-se novos compostos 'bio-inspirados', nomeadamente, pirano-estiril-flavílios com diferentes grupos substituintes no anel D (figura 1A). As propriedades termodinâmicas destes compostos foram estudadas na ausência e na presença sistemas micelares (SDS, Triton X-100 e CTAB) em solução, determinando-se os pK_{as} para as espécies químicas presentes. De forma geral, verificou-se que os diferentes sistemas micelares estabilizaram diferentes espécies em solução, sendo que o SDS estabilizou as espécies catiónicas AH^+, o triton X-100 estabilizou as espécies neutras (A) e, por sua vez, o CTAB estabilizou as espécies aniónicas (A^-). Esta modelação das propriedades cromáticas, através do ajuste dos valores de pK_a na presença de sistemas micelares poderá ser potencialmente interessante para o desenvolvimento de sensores de pH para a construção de materiais inteligentes, como por exemplo, para embalagens alimentares inteligentes.

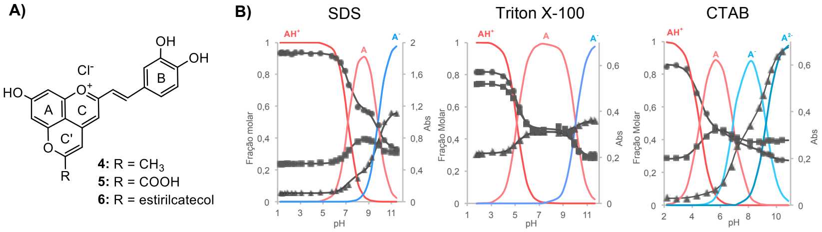

Fig.1. A) Estruturas dos pirano-estiril-flavílios sintetizados (4, 5 e 6). B) Exemplo de modelação dos pKas pelos diferentes sistemas micelares (SDS, Triton X-100 e CTAB) para o composto 4.

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Phlorotannins from *Fucus vesiculosus*: potential for prevention of diabetes and obesity

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According to WHO, worldwide obesity has nearly tripled since 1975 and diabetes almost quadrupled since 1980 [1,2]. Manifestation of these disorders are mainly associated to poor dietary habits and sedentary lifestyles. However, there is currently a growing awareness that, more than the basic nutritional value, food may provide several health benefits and help reducing the risk of developing various illnesses. High consumption of seaweed has been linked to lower diseases incidences, including diabetes and obesity. These are rich and balanced source of nutrients and bioactive phytochemicals, among which phlorotannins, i.e., group of marine exclusive phenolic compounds formed by polymerization of phloroglucinol (1,3,5-trihydroxybenzene) units, have shown to hold promising bioactivities [3].

In this work, the extraction of phlorotannins from *Fucus vesiculosus* was optimized through response surface methodology using three variables (acetone percentage, temperature and solid-liquid ratio). An extract performed under the optimum conditions was then partitioned with hexane and ethyl acetate to obtain a phlorotannin-enriched extract. Both crude extract and ethyl acetate fraction were then analyzed through high performance liquid chromatography equipped with diode array detector coupled to an electrospray ionization mass spectrometer operating in negative mode. Afterwards the extracts were evaluated for their in vitro inhibitory activity against key enzymes from carbohydrate or lipid metabolism, namely α-glucosidase, α-amylase and pancreatic lipase.

Results showed that acetone percentage and solid-liquid ratio were the main factors affecting phlorotannins extraction, which was optimum at 70% acetone, 25 ºC and with a solid-liquid ratio of 1:70 g/mL. The chromatographic analysis confirmed that the ethyl acetate fraction was richer in phlorotannins than the crude extract. Both crude extract and phlorotannin-enriched fraction showed good inhibitory effects towards the target enzymes, particularly against α-glucosidase (IC_{50}=4.5 ± 0.8 and 0.82 ± 0.3 μg/mL, respectively). Notably, in all the enzymes tested, phlorotannin-enriched fraction always presented a much lower IC_{50} values than the crude extract, indicating that phlorotannis might play an important role for the inhibition of these enzymes.

Overall, this study provides evidence that phlorotannins hold potential for weight and glycemia management, suggesting their exploitation as food supplements and/or functional foods ingredients might be a viable approach towards the prevention of these problematics.

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Evaluation of solid-state fermentation with white-rot fungi on the nutritive value of grape stalks as herbivore feed

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This study intended to investigate the effect of white-rot fungi inoculation on the nutritive value of grape stalks (by-products of the wine production industry), namely on *in vitro* organic matter digestibility (IVOMD) and chemical composition. Three strains of fungi were used: *Lentinula edodes* (UF21403), *Pleurotus eryngii* (UF21402) and *Pleurotus citrinopileatus* (UF21401). Substrates were inoculated with fungal spawn and incubated 42 days in controlled conditions of temperature and humidity. Results showed that the treatment with *P. citrinopileatus* promoted the highest increase in crude protein content (94.1%) compared to the control. However, the highest reduction in cell wall contents was obtained by the treatment with *L. edodes*, with a reduction of the neutral detergent fiber (NDF), acid detergent fiber (ADF) and lignin fractions of 14.2%, 20.4% and 51.2%, respectively. The same treatment increased IVOMD in about 90% (261 to 496 g kg-1 OM). Data indicate that *L. edodes* showed the ability to improve the nutritive value of grape stalk for herbivore feeding.

Table 1. Chemical composition (g kg^{-1} DM) and in vitro organic matter digestibility (IVOMD, g kg^{-1} OM) of the grape stalks inoculated with the different fungi for 42 days.

Treatment	**DM**	**OM**	**Ash**	**CP**	**NDF**	**ADF**	**Lignin**	**IVOMD**
Control	342^{a}	946^{a}	54^{d}	51^{d}	684^{b}	617^{ab}	330^{a}	261^{b}
L. edodes	234^{c}	916^{c}	84^{b}	85^{b}	587^{c}	491^{d}	161^{c}	496^{a}
P. citrinopileatus	208^{c}	902^{d}	98^{a}	99^{a}	663^{b}	569^{c}	272^{b}	294^{b}
P. eryngii	280^{b}	935^{b}	65^{c}	63^{c}	722^{a}	655^{a}	319^{a}	293^{b}
SEM	9.9	2.2	2.2	2.0	5.9	5.5	8.5	23.9
Effect	***	***	***	***	***	***	***	***

Values with different superscripts within row are significantly ($P < 0.05$) different. DM, dry matter; OM, organic matter; CP, crude protein; NDF, neutral detergent fiber; ADF, acid detergent fiber; SEM, standard error of mean. * $P < 0.05$; ** $P < 0.01$; *** $P < 0.001$.

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Microencapsulação como estratégia para a compatibilização da microalga *Spirulina platensis* em matrizes hidrofílicas (iogurtes)

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Spirulina platensis (spirulina) é uma microalga azul esverdeada certificada pela FDA (Food and Drug Administration) como segura para ser adicionada em alimentos. É uma matriz rica em nutrientes como proteínas e aminoácidos, vitaminas, minerais, ácidos gordos e pigmentos [1]. No entanto, a sua adição na forma pura apresenta algumas limitações, nomeadamente presença de compostos que conferem sabor e odor indesejáveis [2] e dificuldade de dispersão em matrizes hidrofílicas. A microencapsulação é uma tecnologia que pode solucionar estes problemas sendo capaz de mascarar compostos indesejáveis e melhorar a solubilidade. Assim, o objetivo deste trabalho consistiu na caracterização de uma amostra comercial de spirulina quanto ao valor nutricional e energético, açúcares livres, ácidos gordos, tocoferóis e pigmentos e sua posterior microencapsulação pela técnica de spray-drying. Realizaram-se dois ensaios de encapsulação: i) spirulina/maltodextrina (SM) e ii) spirulina/maltodextrina reticulada com ácido cítrico (SMA), tendo-se feito a caracterização quanto ao rendimento (a eficiência e carga foram estimadas), características de degradação térmica (análise termogravimétrica (TGA/DTG)) e tamanho de partícula. Posteriormente, efetuou-se a incorporação das microesferas em iogurtes naturais, tendo-se comparado com a spirulina livre quanto à sua capacidade de homogeneização no iogurte. A microalga analisada apresentou alto teor em proteínas e cinzas. Foram identificados ácidos gordos essenciais (γ-linolénico) e tocoferóis e ainda pigmentos como: β-caroteno, clorofila e a ficocianina. Esta microalga apresentou temperatura máxima de degradação de 304ºC e resíduo de 27,65% a 600ºC. Para a microencapsulação foi possível obter rendimentos relevantes, sendo 66% para SM e 75% para SMA. Pela análise de TGA/DTG notou-se que as microesferas SM apresentaram duas zonas de degradação mais definidas comparativamente com SMA onde a primeira zona não é tão pronunciada. Esta situação é justificada pela ocorrência da reação de reticulação para a SMA, resultando numa melhor homogeneidade do material e um efeito de proteção superior. Notou-se que a distribuição do tamanho de partícula em volume e em número apresentaram comportamentos semelhantes para SM e SMA. Relativamente aos iogurtes observou-se uma melhor homogeneidade quando a spirulina foi adicionada na forma microencapsulada, tendo os iogurtes adicionados com spirulina livre apresentado heterogeneidade (um aspeto de efeito pontilhado) (Fig.1). Em síntese, conclui-se que a microencapsulação da biomassa de spirulina melhorou a compatibilidade desta microalga em matrizes hidrofílicas, tornando estes produtos de elevado valor nutricional mais atrativos para o consumidor.

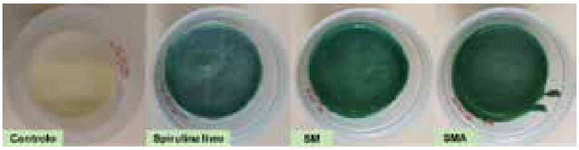

Fig.1. Iogurtes enriquecidos com spirulina livre e microencapsulada.

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Design of a full solar powered food dryer for home excess production

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One of the most serious problems facing small producers of fruits and vegetables is how to prevent these products from spoiling, especially in harvest period peaks, and thereby becoming unfit for consumption [1]. The first solution in most of the times is freezing, but it brings storage difficulties and doesn't prevent the degradation of organoleptic and vitamin properties [2]. To face it, the market started to offer some small electric food driers, however they have high energy consumption. Dehydration is one of the oldest forms of food preservation techniques, but is also used to lower the cost of packaging,

storing and transportation by reducing the weight and volume of the final product. Also, people enjoy dried fruits as a healthy and nutritious snack [3].

The aim of this work was to construct an indirect, environmentally friendly, low-cost solar dryer to dry various whole or sliced agricultural products. The dryer was constructed by using a MDF box with aluminum recycled cans and glass on top, ventilation fans and a styrofoam dryer chamber with four mesh plastic trays (Fig.1). A photovoltaic panel (20 watts) connected to a 12 V battery trough a power

controller, provides energy to the fans. Humidity, light and temperature sensors were placed inside the chamber and data acquisition was made by Arduíno system. The temperature was kept always under 65° to avoid deterioration of properties. Tests were made with sliced golden-smith apple, white mushrooms, zucchinis, quarters of tomato and whole blueberries.

The system proved that sliced samples can be dehydrated from morning to afternoon. However whole samples like blueberries can take as long as seven days to dehydrate under 10% of water content (Fig.2).

Fig.1- Solar food dryer.

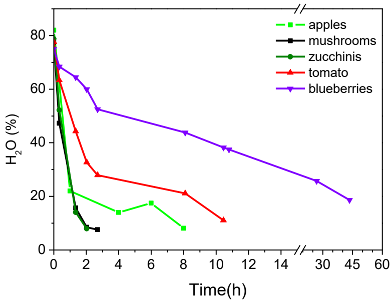

Fig.2- Water content monitorization during tests.

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Improving Gluten Free Bread Quality Using By-Products and Underexploited Resources2

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Nowadays, due to resources scarcity problem in the world, is essential using waste, by-products and underexploited natural raw materials that haven't been valued in the last decades, or never applied in food production. FAO enhance the importance of re-designing food systems production based on circular economy fundamentals, with the objective of reducing food waste, improving resources consume efficiency and recovering value from food chain.

Following market trend of consuming natural products, the attention given to incorporate underexploited raw materials is growing. Most of these ingredients have nutritional and health characteristics/benefits, in particular bioactive compounds and micronutrients. In the other hand, adding value to underexploited products contributes to support local producers.

In the last few years gluten free products have increased its consume not only for celiac disease, but also as new tendency of the market. Gluten free bread presents technology and rheological challenges due to gluten absence, and is nutritionally poorer, what brings many constrains do celiac patients and their health.

The flours that will be studied are: grape stem, olive stone, acorn, apple (cv. Bravo de Esmolfe) and stinging nettle (*Urtica dioica*). For each flour will be performed the following analysis: nutritional profile, bioactive compounds, rheological behaviour of the dough, capacity to bake bread - food technological and sensorial/organoleptic limits, nutritional analysis of bread obtained with different GF flours and assessment about each flour as a potential GF ingredient.

The aim of the present work is to improve both nutritional and sensorial characteristics of gluten free bakery products, especially bread, using by-products and underexploited raw materials as natural gluten free flours.

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CITAB - Centre for the Research and Technology of Agro-Environmental and Biological Sciences.

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Sweeteners in beverages: occurrence and risk evaluation

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Food additives play a vital role in food industry. Some of the most common additives used in food industry include: artificial sweeteners, such as acesulfame-potassium (ACE-K) saccharin (SAC), and aspartame (ASP). Despite the benefits that some sweeteners apparently have, such as the reduction of the calorie intake in soft drinks and sugared fruit juices, several studies reported adverse reactions, such as allergies, behavioural changes and carcinogenicity [1].

The goal of this research was to evaluate ACE-K, SAC and ASP in 56 different beverages (sports drinks, energy drinks, nectars, tea-based soft drinks, traditional soft drinks and soft drinks based on mineral water) purchased in the central zone of Portugal, in order to verify if the levels found comply with the maximum limits set by legislation [2] and evaluate the risk.

The analytical methodology, based on liquid chromatography with ultraviolet detection (LC-UV), using a buffered mobile phase consisting of KH_2PO_4 0.05 M / ACN (85:15), at 254 nm was fully validated. Linearity, accuracy, intra-day and inter-day precision presented adequate results. The limits of detection (LODs) were 9.55, 6.86 and 59.86 mg/L for ACE-K, SAC and ASP, respectively.

ACE-K was present in 49 samples, with mean concentrations ranging between 21.89 and 202.59 mg/L in sports drinks and energy drinks, respectively. The ASP was detected in 62.5% of the matrices, in levels ranging from 69.22 mg/L in soft drinks based on tea extracts and 478.84 mg/L in energetic drinks. SAC was present in 20 samples, with mean levels varying between 44.31 mg/L in soft drinks based on tea extracts and 57.27 mg/L in traditional sport drinks.

The maximum limits set for ACE-K and for ASP were exceeded in a nectar sample and in an energy drink, respectively. SAC exceeded the recommended level in soft drinks based on tea extracts and one nectar sample.

The estimated daily intake (EDI) of ACE-K, SAC and ASP for the Portuguese adult population was found to be well below the acceptable daily intake (ADI). Of the six different categories of analysed samples, traditional soft drinks account for the highest EDI of ACE-K and ASP, with 0.14 and 0.12 mg/kg bw/day, which represents 0.91% and 0.29% of ADI, respectively. Soft drinks based on tea extracts showed an EDI of 0.24 mg/kg bw/day for SAC corresponding to 9.76% of ADI.

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Comparison of ion exchange resins at industrial scale and enological stabilizers treatments for tartaric stabilization of white Port wine: Impact on wine physicochemical and sensory profile

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A frequent cause of stability loss in a wine is the formation of crystalline salts of potassium bitartrate (KHT) that appears mainly at low temperatures, as a consequence of a large decrease in its solubility [1, 2]. Although important for consumer's acceptance, there are only few studies regarding white Port wine tartaric stabilization. Therefore, tartaric stabilization has been carried out in a white Port wine by ion exchange resins, at an industrial scale, and by the addition of enological stabilizers, with the main objective of comparing the impact of these treatments on wine physicochemical and sensory profile. Port wine is a Portuguese fortified wine produced exclusively in the Douro Valley demarcated region. In this study, a white Port wine from the 2015 vintage from Gran Cruz winery, Portugal was used and almost 20% from the total wine volume was treated by ion exchange resins (pH-Stab®). The stabilizers used were metatartaric acid and carboxymethylcellulose (CMC1 5%, CMC2 20%; CMC3 solid) with different structural characteristics. Wine tartaric stability was measured by the mini contact test. Wines phenolic composition - total phenols, flavonoid and non-flavonoid compounds, as well as the chromatic characteristics by the CIELab method, were also evaluated. Sensory analysis was performed by a panel of eight trained tasters. Twenty-one attributes were selected and were quantified using a five-point intensity scale.

As expected, all treatments assayed stabilized the white Port wine. All the samples presented a slight decrease in total phenolic compounds and non-flavonoid phenolic compounds. Concerning sensory analysis, wine treatment with ion exchange resins was more scored for the visual limpidity attribute and for the aroma attributes citrus and tea.

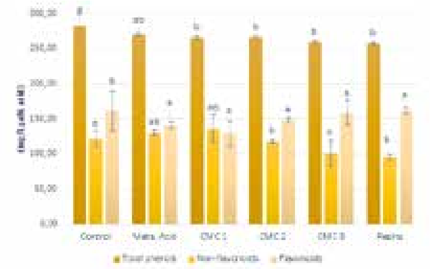

Fig.1. Total phenols, non-flavonoid and flavonoid phenolic compounds of treated and untreated wine.

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Rheology of chestnut starch gels with the addition of common biopolymers

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The rheology of the interplay between biopolymers in gelled matrices can give critically relevant information to select the most suitable conditions for industrial processing. The potential use of alternative starchy sources as chesnut fruit must be studied [1]. Its starch content ranges from 38 to 80%, being a good alternative to conventional sources from cereals and tubers. This work deals with the effect of usually used biopolymers on the mechanical properties of chestnut starch gels.

Aqueous chestnut starch dispersions were prepared at fixed starch content (40% w/w) following the optimised protocol to form gels previously reported [2]. k-Carrageenan, guar or locust bean gums were added (1% w/w) to the starch dispersions. For rheological tests, the dispersions were directly placed on the Couette measuring system of the rheometer to monitor the gelatinisation in situ. Dispersions were heated to 90°C (1°C/min). Then, time sweep tests were carried out at 90°C for 60 min. After this, samples were cooled down to 25°C (1°C/min). Temperature sweep tests were made at 0.1 Hz and shear stress of 5 Pa. After cooling, time sweep tests were made at 25°C for 60 min (1 Hz, 30 Pa). Afterwards, mechanical spectra of the gels (from 0.01 to 10 Hz, 30 Pa) were conducted at 25°C.

Results indicated that the mechanical spectra of chestnut starch gels (Figure, left) were notably modified by the k-carrageenan, guar or locust bean gum addition (see Figures). The magnitude of both elastic (G') and viscous (G") moduli dramatically drop (about one decade) when biopolymers were added, achieving the highest decrease in the presence of k-carrageenan. The elastic and viscous dependency of both moduli with frequency was also promoted. It should be highlighted that the presence of tested biopolymers involved a strong softening of the chestnut starch gels, which is critically relevant from the industrial point of view.

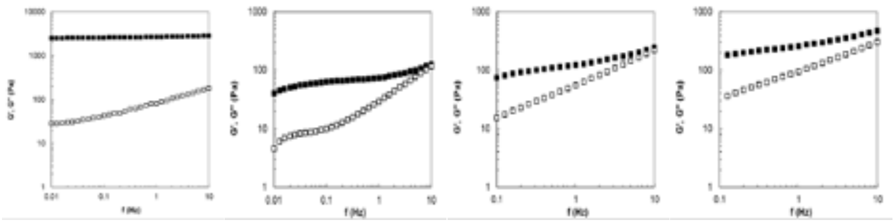

Fig. Mechanical spectra of chestnut starch gels (40% w/w) (first) with k-carrageenan (second), guar (third) or locust bean (fourth) gums (1% w/w) at 25°C. G' – closed, G" – open.

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Ice cream enriched with aqueous extract of *thymus citriodorus* by-product: phenolic compounds and antioxidant activity evalutation

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Annually, 1.3 billion edible food produced worldwide are wasted, discarded or lost throughout the food chain [1]. This creates two major problems: the negative economic impact in the value chain and the environmental impact of discarded by-products. As a way of responding to these problems food by-products have been used to prepare fertilizers, to produce animal feed, to generate biofuel or to recover bioactive compounds that have shown to possess antioxidant, antimicrobial and anti-inflammatory properties, following strategies of circular economy [1-4].

The present work was developed within the framework of Waste2Value project and aims, among other aspects, to develop forms of valorization of agricultural and agro-industrial by-products. Lemon thyme (*Thymus citriodorus*) stems are some of the by-products originated by our consortium company that commercialize teas and infusions. Studies in the scientific literature have demonstrated that *Thymus citriodorus* has antimicrobial and antioxidant properties and a high level of phenolic compounds in its composition [3]. In this work, we had explored the extraction of phenolics from lemon thyme by-product using ecologically viable solvent and its impact on incorporation into a dairy based red berries ice-cream. The extract was obtained by adding water at 50 °C to dried thyme by-products and stirred for 1 hour at a concentration of 75 mg/mL. Before using the extract was filtered and stored at -4°C until use. The results showed an increase to almost the double of the total phenolic compounds content measure by Folin-Ciocalteu with the incorporation of 10 mL of aqueous thyme extract to 150 g of ice cream (101,2 ± 19,3 mg GAE / 100 g of ice cream) when compared to the ice cream without extract (58,2 ± 6,7 mg GAE / 100 g of ice cream). The ice cream with the addition of extract has also shown a higher antioxidant activity, approximately to the double, using the inhibition of the 2,2-diphenyl-1-picrylhydrazyl (DPPH•) radical method. In the continuity of this work the antioxidant capacity of aqueous extracts from this and other plant by-products and its applications in the food formulation will be explored.

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Produção e deteção de γ-glutamil-S-etenil-cisteína (GEC) em 24 acessos de Vicia narbonensis L.

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Enquadramento

Espera-se que em 2050, a população mundial atinja os 10 biliões de habitantes, aumentando em 50% as exigências agrícolas comparativamente com 2013 [1]. É possível que ocorra uma escassez de recursos naturais como água e solo, devido ao aumento da produção e às alterações climáticas [2]. Pelo referido, práticas agrícolas sustentáveis serão imprescindíveis no futuro.

A família das leguminosas está associada a sistemas de agricultura sustentável assim como à disponibilidade alimentar [3].

A Faveta-de-Beja (Vicia narbonensis L.) é uma espécie leguminosa do género Vicia que se adapta bem a solos marginais, é tolerante à seca, assim como a temperaturas baixas e pouco exigente em fertilizantes e pesticidas. É considerada uma cultura de interesse para sistemas agrícolas sustentáveis, como rotação de culturas com cereais. Constitui um bom suplemento na dieta animal devido ao seu alto teor de proteína que pode atingir os 300g/kg no grão [4]. Contudo, o grão produzido por esta espécie é de baixa palatabilidade devido à presença do composto -glutamil-S-etenil-cisteína (GEC). Este é também responsável pela sua toxicidade e pode levar a danos nos rins, em monogástricos, quando ingerido em grandes quantidades [5].

Este trabalho teve como objetivo avaliar a produção de 24 acessos da espécie Vicia narbonensis e detetar a presença de GEC por HPLC de fase reversa, não só nos diferentes acessos, mas também em diferentes partes da planta (folha, vagem e grão) para, por fim, identificar o acesso com maior rendimento e menor percentagem relativa de GEC.

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Histamine detection by electrochemical sensors employing commercial and non-commercial instrumentation

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The concentration of histamine is a widely recognized indicator of fish safety and quality. Due to its toxicity, histamine is the only biogenic amine of which the maximum concentration is legally established (according to European Regulation, fish samples cannot exceed 200 $mg \cdot kg^{-1}$) [1]. Conventional methods for histamine analysis, that mainly involve chromatographic techniques, are time consuming and require expensive and complex instrumentation [2]. Electrochemical sensors are an interesting alternative since they offer a simple, low cost and user-friendly solution. Therefore, in this work, an enzymatic sensor coupled with a small-size potentiostat was developed with the aim of creating a portable device that allows the monitorization of histamine in fish along the whole food chain, from fishing to costumer. The electrochemical sensor was based on miniaturized electrodes (screen-printed carbon electrodes) and diamine oxidase. For signal transduction a platform capable of performing amperometric and voltammetric measurements was developed. This platform was designed and assembled as a compact-size prototype with a complete software package for data acquisition. The results obtained with the developed platform were compared with those obtained by a commercial potentiostat/galvanostat.

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Identificação em vinhos de uma nova família de compostos derivados da cortiça - Corklinas

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As rolhas de cortiça são tradicionalmente utilizadas em garrafas de vinho e estão associadas ao bom envelhecimento do vinho. Diferentes polifenóis foram encontrados, resultado da migração da rolha de cortiça, em vários tipos de soluções de vinho engarrafado [3], sendo os Elagitaninos os mais relevantes. O objetivo deste estudo é identificar e caracterizar novos compostos derivados de elagitaninos que resultam da interação destes compostos com um importante componente de vinho, (+) - catequina. Esta reatividade resulta na formação e identificação de vários compostos derivados de elagitaninos-catequina com uma estrutura mais complexa. Estes compostos formados podem ter um impacto nas propriedades sensoriais do vinho. Uma dessas novas classes de compostos derivados de elagitaninos-catequina são as corklinas.

Além disso, o trabalho tem evoluído no sentido da deteção das corklinas em vinhos comerciais e pode que pode eventualmente ser usado como marcadores de vinho de engarrafados com cortiça.

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Vicinal diketones and nitrogenous compounds monitoring during lager beer fermentation: effects of yeast re-pitching

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The availability and quality of nitrogenous compounds found in beer wort is intimately related with fermentation rates and volatile organic compounds formation by the brewing yeast, including beer off-flavours [1]. Vicinal diketones (VDKs), diacetyl and 2,3-pentanedione, are spontaneously produced as intermediates of amino acids synthesis by yeast during beer fermentation. These compounds impart an unpleasant buttery aroma to beer even if present in low concentrations, due to their low odour threshold limit. Therefore, VDKs affect beer organoleptic characteristics and their formation must be controlled during fermentation in order to guarantee final beer quality [2]. The influence of valine and other amino acids like leucine and isoleucine in VDKs levels was demonstrated before [3]. It is also known that repitching can affect yeast vitality and, consequently, its ability to reduce beer off-flavours [4].

Three wort batches produced from the same raw materials were inoculated with a 2nd generation yeast and other three with a 4th generation yeast. The samples were obtained in a local brewery company from Madeira island, Portugal, *Empresa de Cervejas da Madeira* (ECM) and the batches were monitored during primary fermentation. Ten samples were collected during this period, which lasted for 12 days and a sample was also collected at the end of maturation. VDKs were determined by GC-MS, following a 20-minute extraction at 40°C, by exposing a Car-PDMS fibre in a 20 mL vial containing 10 mL of sample and 3.3 g of NaCl. Valine, leucine and isoleucine were determined by HPLC-fluorescence, including an on-line derivatization step with OPA (*ortho*-phthalaldehyde) and mercaptoethanol. Additionally, FAN (free amino nitrogen), fermentation temperature and extract were also monitored during fermentation.

Major changes in diacetyl and 2,3-pentanedione concentrations were observed in the first 200 hours of fermentation. Low free amino nitrogen content may explain low fermentation rates and can be related with delayed vicinal diketones formation/reduction [5]. Almost complete exhaustion of valine and leucine seems to lead to the occurrence of two diacetyl peaks, resulting in an increased fermentation time [6]. Also, results show similar fermentation performances when using re-pitched yeast until day 10 of primary fermentation.

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Evaluation of the phenolic composition and antioxidant and antimicrobial activities of grape (*Vitis vinifera* L.) stems extracts from the Moscatel variety of different geographic regions

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Nowadays, the antimicrobial resistance is one of the greatest threats of public health. This problem has been growing all over the world, and according to the WHO (World Health Organization), it can be in the next decades one of the three major threats. It is therefore necessary for the world to change the way it prescribes and use antibiotics, because even if new antibiotics are developed without changing behavior, resistance to antibiotics will continue to be a major threat. Therefore, it is fundamental to discover new ways to minimize antimicrobial resistance, being one of the forms found the use of extracts of grape stems, since these present great biological activities due to their antioxidant and antimicrobial properties. In this way, we will also combat the excess of these kind of residues produced by the wine industry, once they are essentially directed to composting or discarded in open areas, in the case of grape stems, causing potential environmental problems and compromising the economic sustainability of this industry.

The main goal of this work was to very the possibility of grape stems to be an alternative for the use of antibiotics, by the quantification of the phenolic compounds present in Moscatel variety from different geographic regions - Penajóia, Medrões and Sanfins do Douro, as well as by the determination of the antiradicalar activity through two methods (ABTS and DPPH), and the verification of the potential antimicrobial activity by the disc diffusion method.

With this work, it was verified that Moscatel samples from Penajóia presented the highest content of total phenols (95.87 mg AG g^{-1}), *ortho*-diphenols (94.22 mg AG g^{-1}), and flavonoids (49.98 mg CAT g^{-1}), as well as the highest antiradicalar activity (ABTS: 0.044 mmol Trolox g^{-1}; DPPH: 0.032 mmol Trolox g^{-1}) and antimicrobial activity. I this sense, we can infer from this study that the grape stems phenolic composition is extremely dependent on the soil and climatic conditions and present a marked antimicrobial activity which may indicate the possibility of becoming an alternative to antibiotics.

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Comparative analysis of sensory properties of French fries made by vacuum and deep fat frying

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Deep-fat frying is one of the oldest and most popular food preparation processes and consists basically in the immersion of food pieces in hot oil. The results are products with unique and distinctive qualities of flavor, color, appearance, taste, aroma and texture however, with a high fat content. Diet with this type of food has been linked to many diseases common in developed countries, such as obesity and coronary heart disease [1]. Consequently, there has been a growing movement to reduce the fat content of deep fried products. Vacuum frying could be a feasible alternative since the food preparation is done by convention, requiring less oil quantity than in the conventional process therefore, producing low-fat foods [2].

The aim of this work was to evaluate and to compare the sensory profile of raw potato and pre-frying frozen chips (French fries) fried in vegetable and sunflower oil using traditional electric fryer and a vacuum fryer (Actifry, Tefal). In the deep fat frying process the oil was used in three batches of frying potatoes however, when the Actifry fryer was used only one frying was made.

All fried potatoes samples were evaluated by eleven judges with experience in sensory evaluation. The sensory attributes used were: appearance (*color, stick shape, oil content*); odor (*characteristic odor, rancid*); taste and mouth-fell (*astringency, bitterness, salty*); flavor (*French fries characteristic flavor, oiliness, rancid*), texture (*firmness, crunchiness*) and *global appreciation*. Each sensory attribute was evaluated using an increasing 5-points scale (from 1 to 5). Sensory attributes data were statistically tested by analysis of variance (ANOVA). Duncan test ($p<0.05$) was applied to the data to determine significant differences between samples. In addition, Principal Component Analysis (PCA) and a Cluster Analysis (CA) were used to analyze the data and study the relations between oil type and French fries sensory characteristics using different fryers, by the use of STATISTICA 2010.

In general, the results showed significant differences in several sensory attributes (*color, oiliness* and *French fries characteristic flavor*) either when were used the raw potato or pre-frying frozen chips into the frying process, in both fryers processes; also when the two oils were compared (vegetable and sunflower oil). However, higher values for the attributes *color*, *oiliness* and *global appreciation* were observed in the 1st frying process by the traditional electric fryer and lower in Actifry.

A hierarchical grouping was performed to test the sample relationship. When the raw potato was used in the frying process, the hierarchical grouping was carried out by the type of oil (vegetable and sunflower) in conventional frying. Although, when the pre-frying frozen chips were used the hierarchical grouping was arranged by the number of frying and not the type of the oil. Still, whether the potatoes before frying are raw or frozen, in the Actifry process a single group was formed, independently of the type of oil. Despite the healthy aspects of using Actifry in the frying process, in terms of sensory attributes, the process needs to be improved for major consumer acceptability.

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Nutritional and physicochemical characterization of purple and red-fleshed genotypes of potatoes from different geographical regions

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There is a recent increasing interest by food producers and consumers in colored potato varieties, mostly in Europe and the United States [1,2]. This interest is connected not only with the tubers' attractive physical and organoleptic qualities (color and taste), but also with their health beneficial chemical composition [2]. Colored varieties include: red skin/white flesh, red skin/red flesh, purple skin/marble flesh and purple skin/purple flesh [1].

This study reports the characterization of ten potatoes' genotypes with red and purple flesh, in terms of their nutritional and physicochemical composition. Their nutritional value (proteins, fat, ash, carbohydrates, and energetic value) and NaCl content were evaluated according to AOAC methodologies. The chemical composition was evaluated in terms of organic acids, fatty acids, and free sugars content through chromatographic analysis. Moreover, pH and color measurement of skin and flesh were also determined using a calibrated digital pH meter and a colorimeter, respectively. For this purpose, tubers of ten colored potato cultivars were obtained from the Leibniz Institute of Plant Genetics and Crop Plant Research in Germany.

The ten varieties (Salad Blue, Shetland Black, Rosemary, Red Emmalie, Violette, Finish Blue, Red Cardinal, Kefermarkter Blue, Purple and UACH 0917), original from five different countries (Germany, Austria, United Kingdom, Finland and Chile), showed significant differences in their nutritional profiles. Despite of their genetic origin, all tuber samples were grown in the same location in Germany in the year of 2017. The results showed the following nutrient content variation depending on the cultivar: carbohydrates: 174.1±0.1 – 272.2±0.5 g/kg fw; proteins: 18.0±0.3 – 22.4±0.5 g/kg fw; fat: 0.54±0.03 - 4.88±0.04 g/kg fw; and ash: 6.2±0.3 – 14.7±0.2 g/kg fw. The energetic value ranged between 790.7±0.9 and 1203±1 kcal/kg fw. NaCl content and pH measurements showed similar results among all ten studied colored potatoes, whilst color results varied between red and purple-fleshed varieties.

Understanding the nutritional and physicochemical composition of colored potatoes may help the selection of commercially useful genotypes and promote biodiversity [3]. Moreover, the organoleptic and health-promoting properties of purple and red-fleshed potatoes illustrate their potential use in the food and nutraceutical industries.

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Optimisation of a method to predict red wine colouring matter instability

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Wine colour stability is of great importance for the wine sector, since colour is generally the first sensory property of a wine that is perceived by consumers and it is, therefore, responsible for the consumers' first opinion of a given wine. Wine colour instability is normally evaluated trough methods that are mainly based on the measurement of the wine turbidity and visual analysis of the colouring matter that precipitate in the bottom of the bottle after 48 h at 4ºC [1]. Given the importance of this instability to the wine industry and its impact to the economy, the development of reliable methods to predict colouring matter instability, applicable to all types of red wines, is imperative, to help wineries implement adequate actions when necessary during the winemaking processes. No experimentally tested test allowed an anticipation of the overall colour loss. A quick analysis revealed that the standard procedure (4 days, at 0 to 4ºC) does not guarantee the precipitation of all the unstable colouring matter, since it may depend on the degree of the wine colour instability. When increased the exposure to low temperatures to seven days, the pellets increased and stabilised. Analysis trough colorimetric methods (anthocyanin's and co-pigments) and HPLC-DAD of all wines after filtration and centrifugation as well as of the pellets residues from both methods allowed a qualitative and quantitative quantification of the unstable matter in five wines. Additionally, the optimisation to a smaller scale was performed to allow to reduce the volume of samples and reagents required, meaning that a smaller quantity of sample is required. In order to better apply to the wine industry, in this work a method for predict wine colour stability was optimised. These methodologies allow a study over time, saving samples and reagents, and more important, a method that can be applied to all type and age of wines for anticipation of the overall colour loss.

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Variação anual das famílias de proteínas salivares de diferentes indivíduos

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Um dos atributos sensoriais organoléticos mais importantes dos produtos alimentares ricos em taninos condensados (procianidinas), uma classe de compostos fenólicos, é a adstringência. Esta sensação está descrita como secura, enrugamento e constrição da cavidade oral [1]. É consensual que um dos principais mecanismos para a sua perceção é desencadeado pela interação das proteínas salivares (PS) com taninos, levando à formação de complexos (in)solúveis, os quais eventualmente precipitam na cavidade oral [2]. As famílias de PS com maior interação incluem as mucinas e as proteínas ricas em prolina (PRPs), as quais estão subdivididas em três famílias: PRPs acídicas (aPRPs), básicas (bPRPs) e glicosiladas (gPRPs) [3].

Neste estudo foram analisadas por HPLC as variações dos perfis das PS mais relevantes para a perceção da adstringência de dezassete indivíduos ao longo de um ano. Foi observado um aumento no conteúdo total de proteínas entre os meses de março e maio (Primavera). Por oposição, é observada uma diminuição deste conteúdo entre os meses de junho e agosto (Verão). Neste último foram obtidos os valores mais baixos para o conteúdo total de PS, sendo estes bastantes semelhantes aos de fevereiro. Esta tendência foi acompanhada pelos perfis de bPRPs e gPRPs de todos os indivíduos que, juntamente com a aPRPs, constituíram aproximadamente entre 66 a 80 % do conteúdo total de PS. Relativamente a estas três classes, as aPRPs são as que apresentam menor variabilidade anual comparativamente ao conteúdo total de PS. Também se observou ao longo do ano que os níveis individuais de estaterina, pPB e cistatina se mantêm constantes.

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Transferencia de metales pesados a *Lolium perenne* en suelos tratados con purín de vacuno

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La aplicación a suelos agrícolas de purín de vacuno, fuente de nutrientes y materia orgánica, presenta riesgos ambientales, particularmente cuando el manejo no es adecuado. Entre estos riesgos cabe destacar la transferencia de metales pesados al suelo, desde el cual pueden pasar a aguas superficiales y subterráneas así como a la cadena trófica a través de la vegetación. Por otra parte, algunos de estos metales pesados tienen el carácter de micronutrientes, siendo imprescindibles para el crecimiento vegetal a concentraciones bajas y tóxicos a concentraciones elevadas.

En este trabajo se estudia la transferencia de metales pesados a la vegetación mediante ensayos en macetas, a las que se aporta purín de vacuno para la producción de *Lolium perenne* L. Se aplicó una dosis conocida del mismo purín a muestras de horizontes superficiales de suelos de tres zonas ganaderas de Galicia en los que se sembró *Lolium perenne*. Se utilizaron como controles macetas a las que se aplicó, en lugar de purín, el mismo volumen de agua destilada. La cantidad de purín aplicada equivale a 166 m^3/ha, dosis que puede considerarse elevada en relación con la aplicada habitualmente en el campo. Durante 10 semanas se aplicó agua (equivalente a un total de 246 mm) a las macetas y se recogieron y analizaron los lixiviados. Transcurridas 10 semanas desde la aplicación del purín, se cortó, pesó y analizó la vegetación. El suelo se analizó al principio y al final del ensayo.

Las concentraciones de metales pesados totales y asimilables en suelos al final del ensayo se encontraron dentro de los rangos normales citados en la bibliografía y por debajo de los límites de fitotoxicidad [1].

La aplicación de purín dio lugar a un incremento de la producción vegetal y disminución del porcentaje de materia seca. Las concentraciones de metales pesados en la vegetación (*Lolium perenne* L.) estuvieron en todos los casos por debajo de los límites de toxicidad citados en la bibliografía [1]. En el caso de los micronutrientes Zn, Mn y Cu, las muestras de las macetas tratadas con purín se encontraron dentro de los rangos normales y las muestras control estuvieron con frecuencia por debajo del umbral de deficiencia. Raramente se encontraron correlaciones significativas entre las concentraciones en la vegetación y las concentraciones en el suelo en forma asimilable, lo que parece indicar que el mecanismo de absorción de estos elementos por las plantas es complejo y sugiere que los métodos habituales de determinación de metales asimilables no son plenamente satisfactorios.

La vegetación de las macetas que recibieron purín presenta contenidos de diversos metales pesados (Fe, Zn, Mn, Cu, Co y Ni) superiores a los de la vegetación de las macetas control. Este hecho indica la transferencia de estos metales aportados por el purín a la vegetación. Fe, Zn, Mn, Cu y Ni son elementos esenciales, mientras el Co se considera un elemento beneficioso. Se pone de manifiesto, por tanto, que el valor fertilizante del purín radica no sólo en el aporte de macronutrientes, sino también de micronutrientes. De hecho, se encuentran correlaciones positivas significativas ($p<0,01$) entre la producción de materia seca y las concentraciones en planta de hierro, zinc, cobre y cobalto. Por el contrario, los contenidos de los metales pesados más tóxicos (Cr, Cd, Pb) no difieren significativamente entre suelos tratados y no tratados con purín.

Las concentraciones de metales pesados en los lixiviados de los suelos tratados son altas en las primeras semanas del ensayo y disminuyen progresivamente hasta aproximarse a los lixiviados de las macetas control. En cualquier caso, no son preocupantes desde un punto de vista ambiental.

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COMPARISON BETWEEN EXTRACTS FROM *ACACIA DEALBATA* LINK FLOWERS OBTAINED BY MICROWAVE HYDRODIFFUSION AND GRAVITY (MHG) AND DISTILLATION TECHNIQUES

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The innovative microwave assisted hydrodiffusion combined with gravity (MHG) is a green technology with limited environmental impact and energy, time and resource costs and high industrial potential [1]. This extraction method protects thermolabile bioactive compounds in an efficient way at atmospheric pressure without solvent [2]. In this study MHG was compared with the traditional steam distillation without cohobation, using *A. dealbata* flowers as raw material. The antioxidant properties and the colour features of aqueous extracts obtained were provided.

Different irradiation powers (50, 75, 100 and 125 W) were employed with the MHG technique. Frozen flowers (100 g) were placed in the Milestone NEOS-GR MA126 equipment and fractions of 5 mL were drained and collected. Deionized water (250 mL) was put in contact with flowers (50 g) in the distillation system; fractions of 30 mL were collected. The last fraction, which presented a negative odour profiling, was discarded. The suitable aqueous extracts were mixed and stored at 4 °C in the light absence until use. All extraction experiments were carried out in duplicate.

The total phenolic content (determined by the Folin-Ciocalteu procedure), antioxidant properties (determined by Trolox equivalent antioxidant capacity (TEAC) method, Ferric Reducing Antioxidant Power (FRAP) assay and DPPH free radical trial) and colour features (by CIEL*a*b* system) of the set of fractions obtained were compared. All determinations were carried out in triplicate.

The distillation extract presented higher total phenol content and antioxidant capacity (TEAC and FRAP assays). The optimum irradiation power by MHG extraction was 75 W. This operational condition was selected because the energy consumption estimated for distillation method was significantly higher than for this MHG process (over 2 times). Coordinates and magnitude values of colour did not show noticeable differences among different samples.

In conclusion, microwave hydrogravity is an alternative and sustainable environmentally friendly technique for providing aqueous extracts from renewable sources such as *A. dealbata* flowers. Further studies are required to better assess the chemical characterization of the antioxidant compounds present in these extracts as well as their use in different food, pharmaceutical and cosmetic industries.

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QUÍMICA AGRO-MAR-ALIMENTAR

Water adsorption isotherms of dextrinized potato starches

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Roasted starchy materials have recently gained attention as matrix not only for energy foods, but also for multiple non-food industrial applications as adhesives, inks, textiles, insecticides or leather [1]. Their hygroscopic nature is a relevant aspect on quality and stability of the final bioproducts since tend to develop physical and chemical changes strongly dependent on their temperature/moisture. The aim of this work is to study the effect of roasting conditions on the water adsorption isotherms of potato starches. Commercial potato starch (moisture content, 20.9 ± 0.5 %, dry basis, d.b.) was dried at 40ºC in a vacuum oven before roasting to reduce the moisture content (around 5.9 ± 0.6%, d.b) to values usually used in roasting starch processes [1]. Then, starch samples (25 g) placed on a Petri dish in thin layer were roasted in an air convective oven at 170 and 230 ºC for 8 h, labelled as DPS170:8 and DPS230:8, respectively. The effect of roasting time at 24 h was also studied (DPS170:24). Experimental equilibrium moisture content of DPS over a wide range of water activities (from 0.09 to 0.91) and temperatures (5, 25, 45, and 65ºC) were determined, using a static gravimetric method reported elsewhere [2].

Water adsorption isotherms of dextrinized potato starches were clearly influenced by the roasting temperature (Fig. 1). In all cases, the largest hygroscopic properties were identified for starches roasted at the highest temperatures (DPS:230), corresponding with the lowest crystallinity values. No significant differences were observed in the equilibrium moisture content of samples roasted during different times at 170ºC. The equilibrium moisture content at fixed water activities are larger (about double) than those reported for un-treated potato starches [2].

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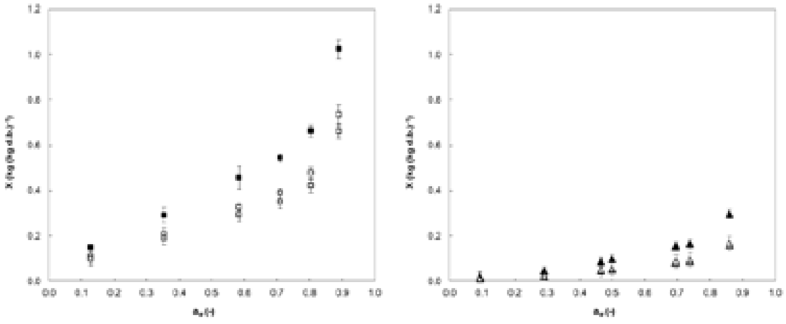

Fig. 1. Water adsorption isotherms of dextrinized potato starches (DPS) at 25 ºC (squares) and 65 ºC (triangles). Crystallinity values are presented in the last plot. Symbols: white - DPS170:8, grey - DPS170:24, black - DPS230:8.

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Structure characterization of water soluble polysaccharides from two species of *Cinnamomum*

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Cinnamon is a very well-known spice whose applications go from the use as a flavouring agent to the cosmetics and pharmaceuticals [1]. In addition, its biological properties are mainly attributed to the essential oil and phenolic compounds [2,3]. There are several species of *Cinnamomum* but two species, *Cinnamomum burmanii*, known as cassia, and *C. zeylanicum,* known as verum, are the most popular ones. They are quite different regarding their organoleptic and visual characteristics, cassia presents gel-like characteristics in aqueous solution whereas verum does not show such characteristics. Additionally, sticks of verum are leafy and thinner than the ones from cassia and the powder of this last variety is darker and has a more pungent aroma.

As the polysaccharides are the gelling agents of *Cinnamomum*, in this work the water soluble polysaccharides of both species were extracted from the powder with hot water and fractionated by sequential ethanol precipitation. The fractions were analysed for their monosaccharides and glycosidic-linkage composition [4].

The water extract from cassia presented a sugar content (66%, w/w) higher than verum (24%, w/w), and the monosaccharides profile also showed to be different, cassia was richer in Ara (51 mol%) and Xyl (34 mol%), and verum had a higher content of Glc (28 mol%) and uronic acids (27 mol%) and lower contents of Ara (24 mol%) and Xyl (14 mol%). Additionally, most of the soluble polysaccharides of cassia precipitated in 50% ethanol while those from verum remained soluble in 75% ethanol. Linkage analysis suggested the presence of highly branched arabinoxylans composed by a 1,4-linked Xyl backbone substituted at *O*-2 and/or *O*-3 by 1,3-linked Ara. Similar arabinoxylans were observed in verum, along with high amounts of 1,4-linked Glc, suggesting the presence of a glucan.

The higher viscosity of cassia extracts seems to be related with the presence of higher amount of highly branched arabinoxylans. Considering the characteristics observed in this study for the two species of Cinnamomum, cassia could be the choice to increase thickness in the product, while verum extracts could be used in foods with low viscosity.

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Effect of different conservation treatments for unfiltered wort and beer samples during storage

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The presence of suspended yeast cells in packed beer greatly affects its quality during storage [1]. Studies show that temperature [2] and oxygen [2,3] are critical parameters that affect yeast metabolic activity, causing substantial changes in beer composition in this period [1]. Specifically, volatile organic compounds are affected if yeast cells are not fully removed before bottling [3]. Besides the application of physical treatments such as filtration and centrifugation [1], previous publications show that chloride salts addition [4], low temperatures [2] and pasteurization [5] can be effective measures in yeast immobilization in beer. In the brewing industry, it is crucial to study beer during the alcoholic fermentation process [1] and the conservation of unfiltered samples with higher amounts of yeast is critical. Therefore, it is important to study which conservation treatments allow to achieve proper yeast immobilization in beer fermentation samples in order to minimize major changes in their composition during storage.

Three different sample preservation strategies were evaluated to ensure yeast immobilization, by testing lager beer fermentation samples obtained from a local brewery: i) storage temperatures ii) calcium chloride addition and iii) sample pasteurization. The temperature treatment was also evaluated when combined with pasteurization and addition of calcium chloride. A set of samples without any treatment was also analysed. The analysis of the samples under study in terms of amino acids, sugars, volatile organic compounds and free amino nitrogen were carried out in HPLC-fluorescence/diode array, GC-MS and by UV-spectrometry, respectively. A Tukey statistical test with a significance level of 0.05 was used to compare the data from the different conservation treatments that were studied.

Vicinal diketones concentration is greatly affected when beer fermentation samples are pasteurized and when controlled storage temperature is the only treatment. Results show that the implementation of chloride salts addition and storage at -26°C are important steps for avoiding beer fermentation samples evolution during storage. When no storage treatment was applied to samples, vicinal diketones were the most affected compounds, when compared to nitrogenous compounds and sugars.

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Macronutrients and secondary metabolites from seeds of *coix lachryma-jobi* l.: potential prebiotics for ibd complementary treatment

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Recently the gut microbiome has been shown to play important roles in a number of innate physiological functions, including bioconversion of plant polyphenolic secondary metabolites and fermentation of non-digestible food components [1]. Carbohydrates are the main substrate for the microflora and imbalances may be prevented by a sufficient dietary supply of nondigestible saccharides such as resistant starch (RS) [2]. These prebiotics are microbially well-fermented forming short-chain fatty acids which are important anti-inflammatory agents. Adlay (*Coix lachryma-jobi* L.) has gathered a great attention in recent years due to many health-beneficial components, including proteins, polysaccharides, coixol, and lipids [3]. The claimed health benefits include several biological activities like antioxidant, anti-inflammatory and modulating gut microbiota. In the present work we have evaluated the effects of a diet enriched with whole-fruit flour of adlay (WFFA; proportions of 5,10 and 20%) in TNBS intestinal inflammation model in rats. Macroscopic parameters, myeloperoxidase and alkaline phosphatase activity, and total content of glutathione were evaluated. Macronutrients analysis of Adlay showed that WFFA contains high amounts of dietary fiber (55.3% insoluble and 1.1% soluble), total proteins (7.8%), carbohydrates (20.3%), ash (9.4%), and low amounts of fatty acids (2.2%). Seeds presented 0.58% insoluble and 0.02% soluble dietary fiber, total proteins (21%), carbohydrates (57.8%), ash (2.4%), and fatty acids (6.7%). None of the analyzed proportions of WFFA was able to change the macroscopic parameters or decrease myeloperoxidase or alkaline phosphatase activity, or even prevent depletion of total glutathione content. The proportion of 10% was able to significantly decrease the incidence of intestinal adherence with other organs. Based on those results the proportions of WFFA evaluated were not able to decrease intestinal inflammation induced by TNBS in rats. On the other hand, further assays should be undertaken to better understand the potential biological activities of Adlay seeds, since they show high amounts of total carbohydrates (57.8%), where RS is included, showing an important potential for the complementary treatment of IBD.

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Comparative analysis of phenolic composition from two different oak wood species used for wine aging: (*Q. petraea* L. and *Q. pubescens* Willd)

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The use of oak wood has been recognized as an integral part of winemaking for over 200 years. The concentration of potential extractable compounds (in particular phenolic compounds) found in oak wood is influenced by several factors, namely by, oak species and geographic origin, and also the processing of the wood in cooperage [1]. In Europe, wines are traditionally aged in barrels made mainly from the 3 oak species, *Q. alba* (American oak), *Q. robur* and *Q. petraea* (both from French forests). However, in last years, other oak wood species and geographical origins have been exploited for the use in wine aging, such as, *Q. pyrenaica* from Iberia Peninsula, and *Q. humboldtii* from Colombia [1, 2].

Thus, in order to deepen the knowledge of other oak wood species composition and evaluate the potential use for wine aging, this study is aimed to evaluate the phenolic composition of 2 oak wood species, one from France (*Q. petraea* L., one of the most used oak species), and other from Serbia (*Q. pubescens* Willd, where there is scarce knowledge about its composition).

Several individual phenolic compounds were analyzed by HPLC-DAD, such as, *p*-coumaric acid, gallic acid, vanillic acid, rutin, (+)-catechin, vescalagin and castalagin. The results obtained demonstrate similar phenolic profile between the 2 oak wood species studied (Figure 1). However, for a quantitative point of view the 2 oak wood species showed several differences for some individual phenolic compounds.

This research is an interesting topic from a practical point of view, especially when the option for aging wines in contact with other non "traditional" oak wood species can contribute to the production of wines with different sensory profiles.

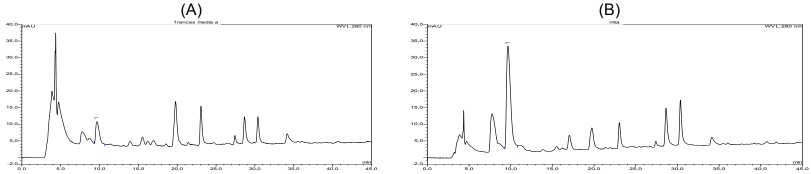

Fig.1. HPLC chromatographic profiles found in oak wood extracts from Q. petraea L. (A) and Q. pubescens Willd (B) species at 280 nm.

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Edible macro and microalgae: assessment of chlorophylls and carotenoids

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Marine algae are traditionally classified as brown, red or green according to the presence of specific pigments as chlorophylls, carotenoids and phycobiliproteins. Brown algae have brown or yellow-brown color mainly conferred by fucoxanthin, their major carotenoid. Red algae, in turn, have dominant proteinaceous pigments (phycoerytrin and phycocyanin), while green algae contain mainly chlorophyll *a* and *b*, the primary photosynthetic pigments. Chlorohylls and carotenoids are algae non-polar pigments and their absorbance properties allows their qualitative and quantitative analysis by spectrophotometric assays. Easly degraded upon heat and light exposure, many solvents (*N,N*-dimethylformamide, acetone, methanol and ethanol) have been used for pigments extraction. The choice of solvent and its percentage depends on the algal species as well as ecological factors, moreover short and rapid extraction steps are required due to their instability [1,2]. Pigments from some algae species have been mainly used by food, textile and cosmetic industries as natural colorants. Recently, important bioactivities and health benefits as antioxidant, neuroprotective, anti-diabetic, antimutagenic and anti-inflammatory activities have been described for algae pigments [3]. Their concentration and composition can vary as response to the environmental conditions. For instance, lower solar radiation and temperatures during autumn and winter lead to an increase in chlorophyll and phycobiliprotein levels. Nowadays, due to the high increase in algae production and their consumption as food, the knowledge of major pigments with potential bioactive properties on human health represents a mandatory research field, particularly for the most popular edible algae [4].

The aim of this study was to evaluate the content of non-polar pigments (total chlorophylls and carotenoids) of: three brown edible algae, *Himanthalia elongata, Laminaria ochroleuca* (Kombu), *Undaria pinnatida* (Wakame); a red one, *Porphyra spp* (Nori); and a microalgae (*Spirulina*). Different solvents (*N,N*-dimethylformamide, acetone, methanol and ethanol) and extration times were employed. The pigment amounts were determined using a spectrophotometric technique based on measuring the absorbance of each extract at the wavelengths corresponding to their maximum absorption. All experiments were performed in triplicate. Accurate equations take into account the extracting solvent and the molar extinction coefficient of chlorophylls (*a, b, c, d*) and carotenoids were used according to S. Connan (2015) [5].

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Tartrazine determination and quantification in foodstuffs and beverages

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Synthetic colorants are used worldwide in food, medicine, textiles, etc. Although the amount of synthetic colorants permitted has been reduced in recent years, many of their kind are widely used because of their low price, high effectivity, and good stability [1]. Tartrazine (E 102) is an azo colorant, with proved effects on children's behavior [2], authorized as a food additive in the EU [3].

The present work deals with the optimization and application of a rapid and simple methodology for the determination and quantification of tartrazine in foodstuffs and beverages. The validated analytical methodology was based on centrifugation, filtration and sonication of the samples following liquid chromatography with UV detection (LC/UV) analysis at 429 nm.

Tartrazine linearity, evaluated between 2.5 and 25 mg/L, both in mobile phase and matrix-matched calibrations was adequate as shown by the obtained R2 values of 0.999 and 0.994, respectively. The matrix effect obtained was of 104.99% that can be considered negligible. The limit of detection (LOD) and quantification (LOQ) were of 0.84 mg/L and 2.54 mg/L, respectively. The accuracy of the method was assessed at three different levels, 5, 10 and 25 mg/L, and mean recoveries of 73.53%, 89.86% and 97.35%, respectively were obtained. Inter-day and inter-day repeatability ranged from 1.00 to 9.09% and from 3.12% to 7.36%, respectively.

A total of 30 samples were commercially acquired, comprising syrups, gelatin preparations, ready-to-eat gelatins, puddings preparations, solid-based beverages (2) and a food coloring sample. The results showed that tartrazine was present in 8 samples at concentrations that varied between 1.36 and 12.65 mg/L, levels lower than the maximum values set by European legislation [4]. Nonetheless, 2 out these 8 positive samples presented concentration levels above those reported in the product labels.

In conclusion, a simple, selective and rather fast LC-UV method for the determination and quantification of tartrazine in commercial foodstuffs is proposed and proved to be adequate with good analytical performance. Monitoring studies are necessary to assure the information presented in the labels.

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Hibiscus sabdariffa L. calyces as a source of anthocyanins rich extracts to be used as a natural food colouring agent

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Colour is the most important sensory perception when it comes to setting people's expectations regarding the likely taste and flavour of food [1]. Since the consumers are more aware regarding the additives that are incorporated into food products, they have shown a preference for the consumption of natural additives over the artificial ones. This has been one of the research lines of the scientific community, searching for natural additives to replace the artificial counterparts [2].

The present work studies the stability of an extract obtained from hibiscus calyces (*Hibiscus sabdariffa* L.), to test its possible use as a natural colourant in foods. The aqueous stability of the extract was monitored using the total anthocyanins' content (TAC) as response (determined by HPLC-DAD) in function of time (t, 14 days), temperature (T, 4 to 70 °C), and pH (2 to 6). Aided by mechanistic/phenomenological models, the conditions favouring the stabilization of the extract were provided.

The results obtained showed that the aqueous stability of the *H. sabdariffa* extracts was higher at lower pH values, shorter t values and T between 4 to 35 °C. However, certain new stable combinations of conditions were found, providing a wide range of conditions, in which the TAC of *H. sabdariffa* extracts will remain stable at values of T within the range of 50 to 70°C. Such facts, will help to understand how to incorporate stable natural extracts, rich in TAC, as natural colorant additives in food products, that may require strong processing conditions, such as bakery and dairy products.

These results provide useful information for: i) potential industrial use of *H. sabdariffa* extract as alternative sources of natural additives rich in TAC; and ii) shelf-life calculations and TAC loss predictions at specific conditions of T and pH. Finally, the results obtained showed a certain agreement with previous reports regarding the stability of anthocyanin compounds, but providing a new alternative source.

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Polycyclic aromatic hydrocarbons levels in commercial meagre fishes

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Fish regular consumption has been strongly advised by health organizations because of its healthy-relevant nutrients and potential health benefits [1-2]. According to Food and Agriculture Organization, Europe presents the third highest fish per capita consumption comparatively with the other continents, being demersal and pelagic fishes the most consumed group of fishes in some of the European top fish consumers, including Portugal, Spain, France, Italy, and United Kingdom [3-4]. Polycyclic aromatic hydrocarbons (PAHs), an ubiquitous group of organic compounds, are classified as endocrine disrupting chemicals and present toxic, mutagenic, and carcinogenic properties [5-7].

This work characterizes the levels of 18 PAHs in the edible tissues of wild and aquacultured meagre fishes (*Argyrosomus regius*) captured in FAO 34 (Eastern Central Atlantic Ocean) and FAO 27 (Northeast Atlantic Ocean) fishing areas, respectively. Samples were biometrically characterized according to the EPA Guide No. 823-B-00-07 and EC Regulation No. 333/2007 and manually eviscerated. Fish edible tissues were extracted by microwave-assisted extraction and analyzed by liquid chromatography with fluorescence and UV-Vis detection [8].

Overall, the total PAHs determined in farmed fishes (18.0 μg/kg ww) were 7 times higher than in wild-caught meagre samples (median: 2.66 μg/kg ww). Naphthalene, fluorene, and phenanthrene were detected in 25-100% of wild meagre samples, while the remaining PAHs (except dibenz(ah)anthracene, benzo(ghi)perylene, and indeno(1,2,3-cd)pyrene) were exclusively detected in 8-100% of farmed fishes. Benzo(a)pyrene, known carcinogenic PAH, was detected in 17% of the aquacultured meagre fishes (0.06 to 0.34 μg/kg ww). Crude oil refining and combustion sources were identified as the major sources of PAHs. Assessment of carcinogenic risks suggested that a diet exclusive on wild-caught, and principally farmed meagre fishes may pose additional risks for the health of European top consumers of fish.

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Low pressure assisted volatile compounds extraction for carbonyl compounds study in green coffee beans

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The volatile fraction of green coffee beans is a field of research still scarcely exploited. The majority of the published works upon coffee volatile compounds focuses roasted coffee samples. Nevertheless, volatile fraction characterization of green coffee may provide important information, namely chemical markers that may correlate with distinct coffee quality parameters, such as, coffee origin, storing conditions or post-harvest processing [1].

In this work, an analytical strategy based on low pressure assisted volatile compounds extraction, focusing the analysis of carbonyl compounds in green coffee beans will be presented. Low pressure systems have been described [2] to enhance the analytical signal of volatile compounds using SPME. Briefly, the experimental procedure under evaluation can be described as follows: the coffee sample and a small volume of an acceptor solution are poured inside a vessel, thereafter closed and connected to a vacuum pump. After a fixed period under low pressure conditions, the vessel is opened and the acceptor solution analysed through HPLC-DAD-MS/MS. The main idea underlying this approach is to attain higher sensitivity at room temperature conditions without heating the sample. This strategy is therefore particularly attractive for samples that may be easily adulterated if heated as green coffee.

The on-going low-pressure system in use together with some preliminary results are presented, exhibiting the impact of this strategy upon sensitivity. Green coffee beans of different provenances are evaluated. A tentative correlation of the identified carbonyl compounds with certain quality parameters is discussed.

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Análise proximal e perfil lipídico de diferentes bagaços de azeitona

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A azeitona, fruto da *Olea europaea* L., possui um elevado teor de nutrientes e compostos bioativos com interesse para a saúde humana. Após o processamento do azeite, grande parte dos componentes da azeitona fica retida no bagaço de azeitona (BA), incluindo alguma gordura. Considerando o crescente aumento da produção de azeite e consequente aumento de BA gerado, torna-se cada vez mais imprescindível valorizar este subproduto. Adicionalmente, há uma procura crescente, por parte do consumidor, por produtos com ingredientes de origem natural [1].

O objetivo deste estudo foi determinar a composição proximal de diferentes BA bem como os perfis em ácidos gordos e vitamina E. As amostras eram BA obtidos das variedades Arbosana, Arbequina, Oliana e Koroneiki (Alentejo, Portugal), após o processamento do azeite. Determinaram-se humidade (balança infravermelho), proteína total (método Kjeldahl; fator de conversão=6,25), cinzas (incineração direta), gordura total (Soxhlet, 8h) e hidratos de carbono (por diferença) [2], sendo os resultados apresentados em peso seco. Para a análise do perfil lipídico, foi extraída a gordura (Soxhlet, 4h) e os ácidos gordos analisados por GC-FID após transmetilação básica. O perfil de vitamina E foi analisado por HPLC-DAD-FLD [3].

No presente estudo, o BA Arbosana apresentou o maior teor de humidade (70%), seguido do Arbequina (68%), Oliana (67%) e Koroneiki (66%). Relativamente ao teor de proteína, os BA Arbequina e Oliana apresentaram um teor de ≈8% enquanto as outras duas variedades apresentaram ≈7%. O teor de cinzas nos BA Arbosana e Koroneiki foi de ≈5% e nos Oliana e Arbequina, de 4%. O BA Arbequina apresentou a maior percentagem em hidratos de carbono (≈80%). Relativamente à gordura total, o BA Arbosana apresentou um teor superior (≈15%), comparativamente a Oliana=13% > Koroneiki=10% > Arbequina > 8%.

A fração lipídica é, particularmente, rica em ácido oleico em todas as variedades. A variedade Koroneiki apresentou o maior teor de ácido oleico (75,2%) seguida das variedades Oliana (72,8%), Arbosana (71,5%) e Arbequina (70,4%). Esta, apresentou ainda o maior teor em ácido linoleico (10,7%). Na análise do perfil de vitamina E foram identificados α-tocoferol, β-tocoferol, α-tocotrienol e γ-tocoferol, sendo o α-tocoferol o vitâmero maioritário. O teor de vitamina E total da fração lipídica do BA Arbosana é superior ao das outras variedades (1,4 mg/g de óleo), sendo o BA Koroneiki a amostra com o teor inferior (0,52 mg/g de óleo).

O BA pode constituir uma fonte importante de ingredientes naturais. O BA Arbosana apresenta particular interesse, não só devido ao teor de gordura total, mas também devido ao teor de vitamina E e perfil de ácidos gordos.

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Influencia de las condiciones de secado en la actividad antioxidante de fracciones de florotaninos obtenidas a partir de *Fucus vesiculosus*

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Se estudió la actividad antioxidante de extractos del alga parda *Fucus vesiculosus* secada en condiciones suaves a 35°C durante 24 h y en condiciones de alta temperatura a 75°C durante 2 h, en un secador convectivo. El material seco y triturado se empleó para la obtención de extractos empleando acetona-agua 70/30 p/p. Posterioremente, se evaporó el disolvente y el extracto se liofilizó. El material liofilizado fue caracterizado en cuanto a contenido en polifenoles totales por un método [1], expresándolos como (mg equivalentes de floroglucinol)/(mg de liofilizado) con el fin de obtener valores de EC_{50} (concentración equivalente al 50% de inhibición) en el ensayo de inhibición de DPPH [2].
Los extractos *de Fucus vesiculosus* muestran una cinética mucho más lenta, Fig. 1, en el ensayo DPPH comparado con trabajos previos con extractos vegetales conteniendo flavonoides, ácido cinámicos y derivados de ácido gálico [3]. Este comportamiento cinético se explica por la naturaleza oligomérica de los florotaninos y por la posibilidad de que según la reacción avanza, cambios en la estructura permiten el acceso de más grupos hidroxilo al radical DPPH. La actividad donante de protones se ve drásticamente reducida por el tratamiento térmico, como se aprecia en los valores de la Tabla 1.

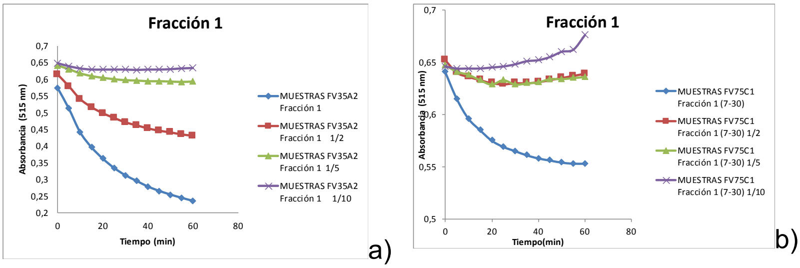

Fig. 1. Inhibición de DPPH de extractos de Fucus vesiculosus secado a 35°C (a) y 75°C (b), a partir de 500 mg de liofilizado/L y diversas diluciones (de 0 a 1/10).

Tabla 1. Contenido en polifenoles de extractos acuosos de Fucus vesiculosus

166 ± 21		Polifenoles totales (mg eq. floroglucinol/L)
19,76 ± 4,47	Secado a 35 °C	EC50 (mg eq. floroglucinol/mmol DPPH)
48.75 ± 8.84		EC50 (mg eq. liofilizado/mmol DPPH)
n.d. (36,9 ± 0,28% Inhibicion)	Secado a 75 °C	EC50 (mg eq. liofilizado/mmol DPPH)*

*: a 500 mg eq. de floroglucinol/L, no se llegó al 50% de inhibición de DPPH

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Electron beam irradiation preserves organic acids in *Agaricus bisporus* Portobello

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The analysis of organic acids has become increasingly important due to the role of these compounds in the physiological activity of plants and mushrooms, exerting a determinant activity in maintaining their quality and organoleptic characteristics. Furthermore, organic acids profile has been continuously used as a quality control indicator [1]. The short shelf life of mushrooms is a barrier to their distribution and, therefore, there has been extensive research to find technologies that ensure the preservation of mushrooms, maintaining their organoleptic properties. Irradiation is an alternative that has already been successfully applied in various food products [2].

In the present study, the effects of electron beam irradiation and storage period (0, 4 and 8 days) over the organic acids profile of the widely cultivated mushroom *Agaricus bisporus* Portobello, were evaluated. The irradiation was performed with a 10 MeV energy irradiator at the doses of 1, 2 and 5 kGy and organic acids were determined using ultrafast liquid chromatograph (UFLC) coupled to photodiode array detector (PDA) and 215 nm as preferred wavelengths, using a Shimadzu 20A series UFLC (Shimadzu Cooperation).

In general, irradiated samples conducted to higher concentrations of all the quantified organic acids (oxalic, quinic and malic acids), particularly when using 2 and 5 kGy doses (ranging between 0.6 - 1.8 g/100g and 0.6 - 1.9 g/100g respectively).

Overall, irradiation might be an alternative process to extend the shelf-life of mushrooms, while preserving the composition in organic acids.

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Chemical composition of Vegetable oils for food and cosmetic purposes

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The worldwide supply of vegetal oils is a great issue due to the demand trends of edible virgin oils for food and cosmetic industries. Their incorporation as natural ingredients of cosmetics or foodstuffs is required by an increasing number of consumers, avoiding refined and animal or petroleum-based oils. For instance, olive oil industry is one of the larger agro-food business sector, being this oil one of the most important for food purposes and human nutrition, particularly in Mediterranean diet [1]. Furthermore, many olive oil based cosmetics have been developed by industry. Also, dietary supplementation and/ or cosmetics application of argan oil or hemp oil have been related with skin elasticity and skin hydratation improvement and anti-aging effect [2, 3]. Chia seed oil is considered as unique among all natural sources due to its high content of omega-3 linolenic acid [4]. Coconut oil, rich in medium-chain fatty acids, has an high stability to oxidation even in long heating periods such as food frying [5] is also related to health promoting effects.

Lipids are essential nutrients for human health once through their metabolism are generated fundamental bioactive molecules. In addition, they are also indispensable compounds of cell membranes. Also Vitamin E is known as the most effective natural dietary lipid-soluble antioxidant, protecting cell membranes from peroxyl radicals and mutagenic nitrogen oxide species. Tocopherols (α, β, γ and δ) and the respective tocotrienols are known as vitamin E, being exclusively synthesized by photosynthetic organisms, varying the vitamers profile according to the plant species. Oxidation is the major cause of oils deterioration, and due to this, the oxidative stability is an important parameter to determine their shelf life as well as oil oxidation resistance when subjected to high temperatures/frying process. The fatty acids and vitamin E profiles as well as the oxidative stability are fundamental parameters of oil quality and nutritional potential. Nevertheless, in what concerns to the use of oils in cosmetics and skin care products, the above-mentioned parameters are also of relevant importance in the formulation and bioactivity characteristics of such products. This is the case of skin nourishing contribution of fatty acids and vitamin E as well as the emollient and moisturizing properties and its stability over time.

The aim of this work was to compare the composition of eight vegetable oils attending to their fatty acids (GC-FID) composition, tocopherols and tocotrienols (HPLC-FL-DAD) profile, and oxidative stability by Rancimat method. Samples were virgin oils from first cold pressing and from organic farming, purchased at a local market. Four samples were edible vegetable oils (chia, coconut, olive and tiger nut), and the others (argan, castor, hemp and jojoba) were used in cosmetic industry. All experiments were performed in triplicate. Considering the recent market placement of "new" vegetable oils (*e.g.* hemp and chia oils) as ingredients and/or whole food, oils chemical characterization is of utmost importance to know the consumption cost-benefit.

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Chia seed oil: a n-3 fatty acid source

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Nowadays, ensuring an adequate intake of nutrients is fundamental and consumers look for new food sources. The consumption of seeds, such as *Salvia hispanica* L., commonly known as chia, is increasing, not only the whole seed, but also chia-derived products, particularly its oil. The recent inclusion (December 2017) of chia seed oil in a monography in the United States Pharmacopeia regards this oil as safe [1]. Therefore, the aim of this work is to perform a review on its particularities, in what concerns to composition and nutritional properties, and possible human health benefits, highlighting its diverse applications.

Chia seed oil can be obtained by different techniques, namely by chia seed compression: cold pressing or komet screw press; with solvents (Soxhlet method with hexane) or with supercritical fluids, such as, carbon dioxide. Each method favours a different enrichment either in higher contents of lipids or bioactive compounds [2]. Regarding its fatty acids composition, it has more than 60% of α-linolenic acid (ALA, n-3) and almost 20% of linoleic acid (LA, n-6). Consequently, it has a very low n-6/n-3 ratio, around 0.30. It also presents phytochemicals with antioxidant activity, such as phytosterols, carotenoids, tocopherols and phenolic compounds [3].

Since ALA is an essential polyunsaturated fatty acid, this oil is already being used in omega-3 diet supplementation. Due to its oxidative instability, tocopherols are added to those health supplements to avoid oxidation. ALA is able to compete with arachidonic acid in membrane incorporation, inducing an anti-inflammatory response [4]. Moreover, it is slowly converted into EPA and DHA, both essential fatty acids also correlated with numerous benefits for the organism: triglyceride and cholesterol decrease, resulting in lower blood pressure and lower risk of heart-related diseases; anti-inflammatory, antidiabetic, cardio and hepatic protective activities (redistributing lipids in the organism, specially away from visceral fat and liver); protection against arthritis, autoimmune diseases and cancer [2].

Additionally, chia seed oil has several applications: health supplementation, topical application (skin treatment and body emollient), in artistic purposes (painting and as a pottery lacquer), also in obstetrics, ophthalmologic and respiratory infections treatment, gastrointestinal uses and, in the past, as an antipyretic [5].

Nevertheless, another interesting approach could be reusing the by-products obtained after the oil extraction process. This is the case of dietary fibre and protein, rich in high biological value compounds, as well as, the natural phenolic compounds with antioxidant activity which remain enriching those by-products.

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Cooked integral pasta with and without algae (*Spirulina* and *Himanthalia elongata*): Effect on antioxidant properties

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In general, cereal grains require processing to be transformed into edible foodstuffs. Usually, pasta is obtained from wheat flour, being integral when manufactured from whole durum wheat. Besides its nutritional value, due to carbohydrates content, integral pasta is also a good source of dietary fibre. In recent years, pasta manufacturers have been innovating by using healthy ingredients as macro and microalgae to offer functional foods [1].

Several studies report the brown seaweed *Himanthalia elongata* as a good source of biological compounds, particularly polyphenols [2]. The microalga *Spirulina* has also attracted attention due to its high protein content (60-70 g/100 g) and bioactive compounds with antioxidant activity [3].

The objective of this study was to evaluate the antioxidant properties of an integral wheat pasta enriched with 2% of *Himanthalia elongata* and 1.5% of *Spirulina* and compare with a sample without enrichment. Pasta (250 g) was cooked 15 minutes in 700 ml of water and 5 g of salt. After cooling, it was freeze-dried. The remaining water was collected and used to determine the same parameters. Afterwards a similar procedure was carried out for dry *Himanthalia elongata* and *Spirulina*. Total phenolic and total flavonoids content were assessed in all six samples, in triplicate. The results show the polyphenolic behavior between the pasta and the cooking water.

Fig.1. Cooking water and baked enriched pasta

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Estudo da interação proteína-polifenol de um extrato proteico de leveduras nas colagens de vinhos

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Um dos objetivos principais do setor vitícola é melhorar a qualidade dos vinhos, atendendo sempre ao consumidor final e às suas exigências [1]. Os polifenóis têm um papel fundamental na indústria do vinho, sobretudo no caso dos vinhos tintos desempenhando um papel crucial nas caraterísticas organoléticas, cor, aroma e sabor. As classes de polifenóis mais importantes na química dos vinhos são as antocianinas (pigmentos vermelhos) e os 3-flavanóis (taninos) [2]. É fundamental que durante o período de armazenamento de um vinho até ao seu consumo, a cor e a limpidez do mesmo permaneçam inalterados [3]. O vinho possui partículas em suspensão capazes de formar uma turvação que afeta a aparência e até mesmo o sabor do vinho. Esta turvação pode ser removida recorrendo a uma clarificação, um processo que ocorre por vários fenómenos físicos e químicos e que leva à precipitação de alguns polifenóis do vinho mais reativos ou instáveis [4]. Este fenómeno ocorre devido à capacidade de interação polifenol-proteína que leva à formação de agregados (in)solúveis, sendo acelerado pela utilização de agentes de colagem (e.g. proteínas de origem animal, como a gelatina e a caseína) de modo a obter vinhos mais límpidos e estáveis num curto período de tempo [1, 5]. Atualmente surgiu a necessidade de desenvolver novos agentes de colagem dado que a incidência de alergias alimentares tem sido relacionada com algumas proteínas de origem animal. Assim, tem sido estudada a possibilidade em utilizar agentes de colagem feitos à base de extratos proteicos de levedura (EPL). Sob o ponto de vista enológico pretende-se que novos agentes de colagem promovam não só a limpidez e a estabilização do vinho, mas também potenciem algumas propriedades organoléticas do mesmo, eliminando polifenóis relacionados com fenómenos de oxidação ou adstringência [6].
Este trabalho tem como objetivo avaliar a interação de um extrato proteico de leveduras (EPL) (desenvolvido pela Proenol, indústria biotecnológica) com alguns compostos fenólicos presentes no vinho tinto, nomeadamente a malvidina-3-glucósido (mvc-3-glu) e 1,2,3,4,6-pentagalhoil-glucose (PGG), por extinção de fluorescência, *SDS-PAGE* e difusão dinâmica de luz. Por fluorescência foi possível obter as constantes de afinidade (K_a) para os dois compostos em estudo, sendo a constante da PGG significativamente superior à da mvc-3-glu. Através dos resultados de *SDS-PAGE*, verificou-se que não existia seletividade nas proteínas do EPL que interagiam com estes compostos fenólicos, não sendo visíveis diferenças nos perfis eletroforéticos do EPL. Por difusão dinâmica de luz foi possível avaliar a diferença do tamanho dos agregados formados resultantes da interação, observando-se que os agregados resultantes da interação entre o EPL e a PGG são menores que os agregados formados entre o EPL e a mvc-3-glu. O estudo destas interações proteína do EPL-composto fenólico pretende mimetizar e compreender o que acontece na clarificação dos vinhos ao utilizar este EPL como alternativa às colas comerciais tradicionalmente utilizadas no sector vinícola.

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Apple pomace as a source of phenolic compounds with potential application in cosmetic products

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Apple pomace is a by-product that might be considered as a competitive source of a large number of bioactive compounds (particularly phenolic compounds) with potentially valuable applications. Interestingly, the major part of these bioactive compounds is found in apple peel, thereby becoming more concentrated in apple pomace when compared to the fresh fruit [1]. Phenolic compounds in apple pomace (*e.g.*, hydroxycinnamic acids, flavonoids and dihydrochalcones) display health promoting activities, mainly based on their antioxidant, anti-inflammatory and antimicrobial properties [2]. Therefore, these compounds represent a promising cosmeceutical potential. In fact, apple polyphenols already showed to inhibit the fat production of sebaceous cells, making them appropriate to be used in anti-acne cosmetic formulations [3]. In the work described herein, apple pomace was dehydrated using two different processes: oven drying (60 °C) and lyophilisation. Phenolic compounds were extracted from apple pomace using food grade solvents (water and ethanol) in different proportions. Phenolic compounds' profiles were further characterized by high performance liquid chromatography using a diode array detector coupled to a mass spectrometer. In what regards dehydration process, lyophilized samples showed a higher number of phenolic compounds, as also higher quantities of those detected in all prepared extracts. The major phenolic compound was 5-*O*-caffeoylquinic acid (»108 mg/100 g dw), but flavonoids, specifically flavan-3-ols, were also detected in significant levels. Among these, four quercetin derivatives (differing in the sugar unit) and isorhamnetin-3-*O*-rutinoside were quantified in similar concentrations (»20 mg/100 g dw). The remaining compounds were 4-*O*-caffeoylquinic acid (»16 mg/100 g dw), B-type (epi)-catechin dimer, trimer and tetramer (»16 mg/100 g dw, »5 mg/100 g dw and »3 mg/100 g dw, respectively), and phloretin-2-*O*-xyloglucoside (»5 mg/100 g dw). Overall, the detected profiles raise the possibility of using apple pomace, which is a competitive starting material when compared to other natural matrices, as an alternative source of this type of phenolic compounds. Owing to their reported bioactivity, these compounds may further be included in different applications as exemplified by cosmetic formulations, considering their ability to inhibit fat production in sebaceous cells.

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Evaluation of the thermal processing and food matrix on the soybean allergenic proteins

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Owing to several technological and functional characteristics, soybean is a food ingredient with numerous applications in processed foods, whose use has been greatly increasing in the past decades [1]. Among its different uses, soybean is widely applied by the food industry in processed meat products, such as sausages, hamburgers or cooked hams due to its emulsifier properties, gelling capability, texture improving and water-binding capacity. Accordingly, soybean may be incorporated as a declared ingredient in a wide range of highly processed foods, but it can also be present as a hidden allergen. Therefore, it is important to assess the impact of different food processing, as well as, the effect of the matrix (presence of lipids, carbohydrates, protein aggregates) on the immunoreactivity of soybean allergenic proteins.
With this work, it is intended to evaluate the effect of two different types of food processing, namely autoclave and cooking, and two distinct food matrices (cooked hams and sausages) on the immunoreactivity of soybean allergens. For these purpose, model mixtures of pork meat containing known amounts of soybean technological aids (soybean protein isolate and soybean protein concentrate) were prepared in a concentration range of 10-0.001% (*n*=5). The model mixtures of pork meat containing soybean protein concentrate (~65% of total protein content) were submitted to cooking process (5 h, 68ºC) to simulate the preparation of hams, while the binary mixtures of pork with soybean protein isolate (~85% of total protein content) were autoclaved (15 min, 121ºC) to mimic the production of sausages. Protein extraction was performed with Tris-HCl 100 mM buffer and protein concentration was determined by UV spectrophotometry using a micro-volume plate. Samples were run, both in denaturing and native conditions, in SDS-PAGE or native gel electrophoresis, respectively. In denaturing conditions, the preliminary results evidenced a distinct protein profile between soybean and pork meat. The model mixtures simulating cooked ham production were clearly affected by the thermal process, leading to the elimination of most bands, from pork and soybean sources. Model mixture containing 10% of soybean protein presents clear bands with molecular weights of 37, 17-18 and 15 kDa corresponding to soybean proteins, which are most likely resistant to heat. Soybean protein at 17-18 kDa might correspond to a 2S albumin since it is a highly thermostable allergen. In the case of model mixtures mimicking sausages, the effect of thermal processing was also very drastic in terms of protein profiles.
Currently, native conditions are being tested to both sets of model mixtures, in order to understand the effect of processing on the conformational pattern of soybean proteins. Immunoreactivity assays using specific antibodies against soybean proteins (e.g. trypsin inhibitors) will also be performed to identify soybean allergens.

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Optimization and stabilization of a cyanidin-3-*O*-glucoside rich extract obtained from fruits of *Arbutus unedo* L.

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Currently, there is a tendency for consumers to choose more natural foods [1]. Anthocyanins are secondary metabolites of plants that have aroused industry attention for its coloring potential combined with confirmation of various beneficial effects to human health [2]. However, due to their very sensitive chemical structure to several factors such as temperature, pH, oxygen and light, studies that allow its stabilization are indispensable [3].

This work aimed to study the stability of an extract obtained from *Arbutus unedo* L. fruits, considering 3 variables (time, temperature and pH) in aqueous solution by analyzing the content of anthocyanins. The extract was obtained by a heat-assisted extraction technique, with the optimal conditions of 5 minutes, 90ºC, 80% ethanol and 15 g/L solid/liquid ratio, obtained after an optimization process by applying a response surface methodology. The identification of three anthocyanin compounds (cyanidin-3-*O*-glucoside as the major molecule) was performed by HPLC-DAD-ESI/MS, and revealed the following responses, 60.9 %, with a total anthocyanin content of 500.9 **µg**/g of dry fruit and 800.9 **µg**/g of extract. Moreover, the extract was analyzed in terms of its antioxidant, antimicrobial and cytotoxic activity revealing a high bioactive potential.

Finally, the anthocyanin-rich extract was stabilized by subjecting it to adverse storage conditions. Time, temperature and pH were the variables considered to evaluate the behavior of the extract and the concentration of anthocyanins from each sample were the response factors used. In order to describe the responses, mechanical and phenomenological equations were used with a global performing fitting analysis from a multivariable perspective. The results showed that the three analyzed variables exert a direct influence on the responses obtained. It has been found that increasing pH and T values cause an exponential increase in anthocyanin degradation. In the overall analysis of all variables, it was concluded that the optimum conditions of anthocyanins stability were verified at pH <3.5 and T <30 ºC for a period of at least 72 h.

At the industrial level this type of studies is indispensable, in order to guarantee the production of functional extracts in the production of high-quality new foods. Therefore, it is essential to find the optimum conditions of its stability and processing.

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Caracterização química de óleos de grainha de uva, sementes de melão e sementes de abóbora

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A grainha de uva e as sementes de melão são dois subprodutos agroindustriais que permitem obter óleos vegetais. Pelo contrário, o óleo de sementes de abóbora é o principal produto desta cultura [1, 2, 3]. A utilização destes óleos nas indústrias farmacêutica, alimentar e cosmética pode responder à procura do consumidor por produtos naturais e sustentáveis.

O objetivo deste estudo foi a caracterização química do óleo de grainha de uva (OGU), óleo de sementes de melão (OSM) e óleo de sementes de abóbora (OSA). Foram determinados o perfil de ácidos gordos (GC-FID), o perfil de vitamina E (HPLC-DAD-FLD), os teores de clorofilas e carotenoides totais, compostos fenólicos totais (CFT), flavonoides totais (FT) e atividade antioxidante pelos métodos de FRAP e inibição do DPPH$^{\bullet}$ (métodos espetrofotométricos).

Os ácidos gordos maioritários determinados foram o ácido linoleico (OGU: 68,7%; OSM: 71,3%; OSA: 51,4%), o ácido oleico (OGU: 18,5%; OSM: 15%; OSA: 29,7%), o ácido palmítico (OGU: 7,1%; OSM: 8,6%; OSA: 12,2%) e o ácido esteárico (OGU: 4,9%; OSM: 4,5%; OSA: 5,7%). O vitâmero maioritário do OGU foi o α-tocoferol (209 mg/kg óleo), enquanto no OSM e no OSA foi o γ-tocoferol (439 e 703 mg/kg óleo, respetivamente). Os teores de clorofilas, carotenoides, CFT, FT e atividade antioxidante são apresentados na Tabela 1.

Baseado no perfil de ácidos gordos e vitamina E, estes óleos podem ser considerados para utilização na indústria cosmética e/ou para consumo alimentar, nomeadamente como ingrediente ativo no desenvolvimento de novos produtos.

Tabela 1. Teores de clorofilas, carotenoides, compostos fenólicos totais (CFT), flavonoides totais (FT) e atividade antioxidante (DPPH e FRAP).

	OGU	OSM	OSA
Clorofilas (mg/kg óleo)	0,41 ± 0,01^{b}	0,13 ± 0,01^{c}	1,6 ± 0,05^{a}
Carotenoides (mg/kg óleo)	0,14 ± 0,00^{b}	0,17 ± 0,01^{b}	13,65 ± 0,31^{a}
CFT (mg EAG/kg óleo)	7,68 ± 0,48^{c}	14,48 ± 0,44^{b}	35,5 ± 2,17^{a}
FT (mg EC/kg óleo)	1,12 ± 0,15^{c}	2,89 ± 0,12^{b}	16,14 ± 0,64^{a}
DPPH (μmol Trolox/kg óleo)	45,59 ± 4,97^{b}	20,93± 1,54^{c}	67,04± 6,66^{a}
FRAP (μmol ESF/kg óleo)	186,86 ± 2,44^{c}	278,59 ± 22,43^{b}	879,87 ± 56,48^{a}

Resultados expressos como média ± desvio padrão (n=3). Letras diferentes para cada linha significam diferenças significativas ($p<0,05$). EAG: equivalentes de ácido gálhico; EC: equivalentes de catequina; ESF: equivalentes de sulfato ferroso.

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Otimização da extração e estabilização de um aditivo natural à base de catequina, a partir de frutos de *Arbutus unedo* L.

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Arbutus unedo L. é uma espécie ornamental nativa da região do Mediterrâneo que produz frutos ricos em compostos fenólicos, em particular as catequinas [1]. Catequinas são flavan-3-óis que apresentam alta capacidade antioxidante [2]. No entanto, os flavan-3-óis estão susceptíveis a degradação por diversos fatores ambientais [3,4] e a estabilidade destes compostos durante o processamento e armazenamento é crucial para a preservação das suas propriedades bioativas.

O presente trabalho teve como objetivo otimizar a extração de catequina a partir de frutos de *A. unedo* por maceração (ME), micro-ondas (MAE) e ultrassons (UAE), utilizando a metodologia de superfície de resposta para avaliar os efeitos das principais variáveis de extração de cada técnica (tempo, temperatura ou potência e mistura hidroetanólica) e determinar a estabilidade do extrato rico em catequina sob influência da temperatura, do tempo e do pH, durante o armazenamento (sistema em pó) e aplicação numa matriz alimentar (sistema aquoso). As respostas medidas foram o conteúdo de flavan-3-óis e catequina, determinados por HPLC-DAD. Foram utilizadas equações mecanicistas e fenomenológicas para descrever as respostas para a estabilidade dos compostos.

Dentre as técnicas de extração avaliadas, a ME e a MAE foram mais eficientes, capazes de produzir 1,38±1 e 1,70±0,3 mg catequina/g matéria seca, respetivamente. As condições ótimas para a ME foram 93,2±3,7 min, 79,6±5,2 °C e 23,1±3,7% de etanol, enquanto para a MAE foram 42,2±4,1 min, 137,1±8,1 °C e 12,1±1,1% de etanol. A UAE apresentou menor rendimento nas condições otimizadas (0,71±0,1 mg/g em 42,4 min, 314,9±21,2 W e 40,3±3,8% de etanol).

O extrato rico em catequina (60% flavan-3-óis e 22% catequina) obtido sob as condições ótimas para a ME apresentou maior estabilidade no armazenamento a -20ºC e pH 5,4 durante o período avaliado (30 dias), enquanto a estabilidade dos compostos em sistema aquoso permaneceu estável durante as 24h de aplicação a um pH<4 e T<30ºC. Os modelos matemáticos gerados permitem prever a perda de catequina em condições especificas de temperatura e pH nos sistemas em pó e aquoso.

Conclui-se que os frutos de *A. unedo* são fontes de flavan-3-óis, em particular a catequina e seus derivados, que apresentam boa estabilidade no armazenamento e em solução aquosa, o que potencializa o interesse da aplicação destes compostos na indústria alimentar.

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A methodology for assess the concentration of biogenic amines in food: an introductory study

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Biogenic amines (BAs) are nitrogenous organic bases of low molecular weight and can be found in a variety of food products including seafood, meat, dairy, fruits, vegetables, nuts, chocolates and fermented products [1]. The most important BAs occurring in foods are histamine, cadaverine, putrescine, tyramine, tryptamine, spermine, β-phenylethylamine, and spermidine [2, 3].

The presence of BAs in food can be considered an indicator of microbiological contamination and deterioration [4] which when consumed may give rise to gastric and intestinal problems, headaches, pseudo-allergic responses, urticarial, nausea, vomiting, changes in blood pressure and allergies [5].

Chemiluminescence is an indirect method for detection and quantification of BA. Because BA do not have chemiluminescence properties, hydrogen peroxide (H_2O_2), which is a side product of its degradation by the enzyme such as, diamine oxidase, is used to obtain luminescence when reaction with 5-amino-2,3-dihydrophthalazine-1,4-dione ($C_8H_7N_3O_2$) occurs [6].

It is present an introductory study for the detection and quantification of BA by measuring the concentration of H_2O_2 using a chemiluminescence technique. A small low-cost hydroxyethyl cellulose based planar sensitive membrane combined with a photodetector is used to detect small H_2O_2 quantities and estimate the concentration of the BA in the food sample.

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Actividad citotóxica de fracciones de florotaninos obtenidas de *Bifurcaria bifurcata*

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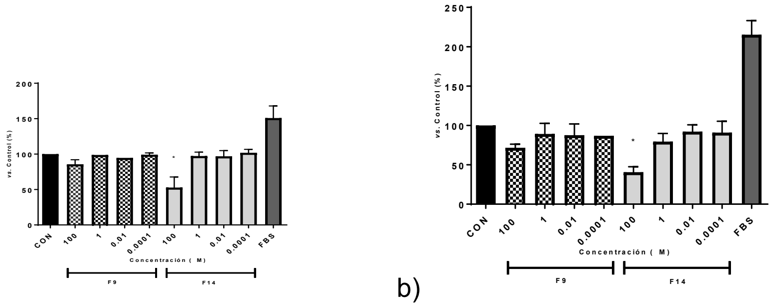
Se obtuvieron fracciones de florotaninos obtenidas mediante extracción con acetona/agua en las condiciones recomendadas [1] fueron preconcentradas en Amberlite XAD-16 y posteriormente, evaporadas, liofilizadas y separadas en fracciones empleando una columna semipreparativa de fase reversa C18 (12x250 mm), empleando un gradiente lineal de 5% a 95% de etanol en agua. Se separaron fracciones de oligómeros de florotaninos que eluyeron a los 9 y 14 min que fueron concentradas, filtradas y disueltas en medio (DMEM). Las fracciones se incubaron con la línea celular ATDC-5 de condrocitos de ratón (Raiken Cell Bank, Japón) en medio DMEM sin suero (control, CON). Se empleó el ensayo de viabilidad celular por reducción del compuesto MTT para determinar la citotoxicidad de las fracciones F9 y F14.

Se encontró una diferencia significativa en la actividad citotóxica entre las fracciones F9 y F14 (Tabla 1), siendo la menos polar y de mayor tamaño más citotóxica, a una concentración equivalente a 100 micromolar de floroglucinol, con una inhibición del crecimiento a 48 h del 60% aproximadamente (Fig. 1b). Este valor indica que esta fracción es interesante para analizar más en detalle su composición y analizar el/los florotaninos que determinan esta actividad, pues la concentración es suficientemente baja como para considerar una dosis terapéutica.



a) b)

Fig. 1. Efecto de la concentración de fracciones de florotaninos, expresados como equivalentes en floroglucinol, en la viabilidad celular a 24 (a) y 48 (b) h. FBS: control de medio con suero bovino fetal.

Tabla 1. Área de picos y equivalentes en floroglucinol de los principales picos con actividad citotóxica

Pico	RT (min)	Concentración (µM)	Volumen (mL)	Polifenoles (PT)[a] eqs. floroglucinol (µM)
1	9	109.11	1	1309.3
2	14	48.82	1.2	488.2

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Physicochemical characterization of wheat and rye flours

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Rye (*Secale cereale* L.) and wheat (*Triticum aestivum* L.) are widely grown cereals consumed as bread all over the word [1]. Cereals are processed by crushing using different types of mills and the force applied for cereals grinding reduce the particle sizes resulting in several types of flours [2]. Thus, the chemical composition of cereal grains affects their functional and technological characteristics. The present work evaluated the quality of wheat and rye flours according to the degree of refinement by determining the physicochemical parameters.

Seven flours were kindly donated by the Milling Company "Moagem do Loreto", Bragança, Portugal, in December 2017, namely T 55 and T 65 (wheat flours - refined samples), T 150 (whole wheat flour), T 70 and T 85 (rye flours - refined samples), and T 130 and T 170 (whole rye flours). Macronutrients and energetic value were determined according to official procedures of food analysis, while gluten was obtained by the addition of 2% NaCl solution and washed under stream of running water, and pH was determined by a calibrated digital pH meter.

The moisture content ranged from 9.3% to 14.7% in whole rye flour T 130 and whole wheat flour T 150, respectively. The protein content ranged between 6.93 g/100 g dw and 14.6 g/100 g dw in rye flour T 70 and in whole wheat flour T 150, respectively. The ash content in wheat flour presented lower values, namely T 55 (0.31 g/100 g dw) and T 65 (0.32 g/100 g dw). The fat content in wheat flours T 55 presented the lowest amount (0.76 g/100 g dw) while the rye flours T 170 presented the highest one (1.78 g/100 g dw). The different types of flour (wheat and rye) contained comparable amounts of total carbohydrates ranging between 82.4 to 91.3 g/100 g dw. The highest pH value was found in whole rye flour T 130 (6.44) and the lowest in wheat flour T 65 (6.04). Concerning dry and wet gluten, these were only detected in wheat flours. Dry and wet gluten ranged from 7.2% to 9.5% and 19.9% to 25.0%, respectively.

These results agree with the Portuguese legislation and with the information procedure in the field of technical standards and rules previewed by the European Parliament and Council. The physical chemical characterization of flours points to an important ingredient in the manufacture of bakery and pastry products.

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Chips industry by-products: isolation and chemical characterization of melanoidins

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The industrial processing of potato chips produces huge amounts of disposable by-products, which may include burned chips residues, a putative source of melanoidins. These are high molecular weight nitrogenous brown-colored compounds formed during food heat treatments, containing reducing sugars and proteins/amino acids. Melanoidins have been related with several health benefits, namely antioxidant, anti-microbial, and anti-inflammatory properties [1].

During frying, water evaporates due to the high temperature and potatoes constituents undergo several chemical reactions leading to the formation of chips flavor and aromas but also of melanoidins. On the other hand, due to the particular thermal treatment applied to potato chips, the frying oil fatty acids may suffer transesterification and may be incorporated into burned chips residues-melanoidins, as observed for organic acids in coffee melanoidins [2]. Despite the worldwide potato chips consumption, nothing is known about the melanoidins formed during frying. Thus, this study aims to isolate and characterize melanoidins in burned chips residues by using gas chromatography tools.

Taking advantage of melanoidins high molecular weight (HMW), they were isolated from the supernatant of burned chips residue by ultrafiltration using a set of 6 membranes. Because >100 kDa fraction was quantitatively dominant, an additional purification procedure, using a batch of C_{18} resin suspension for adsorption of hydrophobic material, was performed. This procedure allowed to obtain two fractions: AqHMW, which comprised the material not sorbed to the C_{18} resin and remained in the water solution; and MeHMW, which comprised the material retained in the C_{18} resin and recovered with acidic methanol. Both fractions were submitted to structural characterization by using sugars (determined by GC-FID as alditol acetates, after hydrolysis), methylation (identified by GC-MS after methylation, hydrolysis and acetylation), fatty acids (identified by GC-FID as fatty acid methyl esters, after transesterification), and oligosaccharide analyses (identified by GC-MS as alditol acetates). The AqHMW fraction is composed by 87% (w/w) of sugars and the MeHMW fraction is composed by 1% (w/w) of sugars (t-Glcp, 4-Glcp, and 4,6-Glcp are the most abundant linkages) and 0.2% (w/w) of fatty acids. Furthermore, according to the initial results of oligosaccharide analysis, the degree of polymerization seems to be three. These results allowed to conclude that potato chips melanoidins are composed by short chain oligosaccharides derived from starch and esterified with fatty acids.

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Desenvolvimento de cremes de barrar com adição de um processado de cogumelo *shiitake* (*Lentinola edodes*)

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Este trabalho enquadra-se no projeto *Agrio et Emulsio* (POCI-01-0145-FEDER-023583), com o objetivo de formular e conceber uma emulsão alimentar inovadora **à base de** um processado de cogumelo *Shiitake* (*Lentinula edodes*), para valorização de matérias-primas com potencial de aplicação em certos mercados como *gourmet*, *diet* e *vegan*, através de metodologias sustentáveis [1].

O cogumelo *Shiitake* é um fungo do filo *Basidiomycota* e do género *Lentinus*. É o segundo cogumelo comestível mais cultivado do mundo, representando atualmente cerca de 25% da produção mundial de cogumelos edíveis. A sua importância hoje em dia, deve-se a modos de vida e hábitos provenientes de países asi**áticos,** para além de várias aplicações na medicina tradicional chinesa. **É c**onsiderado um alimento de elevada qualidade, rico em proteínas, vitaminas e sais minerais e baixo teor em calorias e gorduras [2].

Uma emuls**ão** é um sistema multifásico termodinamicamente instável, constituída por duas fases imiscíveis, uma aquosa e outra lipídica, em que uma das fases se encontra dispersa na outra sob a forma de gotas esféricas. A estabilidade deste sistema depende da membrana que sustenta as gotas, e varia ao longo do tempo. Há dois tipos de emulsões: óleo-em-água e água-em-óleo. Os cremes de barrar são emulsões de água-em-óleo, cuja fase lipídica é uma mistura de óleos vegetais e/ou óleos e gorduras de origem animal contendo corantes naturais, estabilizantes, emulsionantes, aromatizantes, antioxidantes, lecitinas e vitaminas lipossolúveis. A fase aquosa inclui na sua constituição proteínas e leite desnatado, e pequenas quantidades de outros ingredientes como sal, conservantes, espessantes e vitaminas hidrossolúveis [3].

A metodologia utilizada implicou o desenvolvimento experimental com ensaios tecnológicos articulados com ensaios analíticos e sensoriais. Num ensaio preliminar, prepararam-se três concentrações diferentes de fase aquosa com o soro do leite de cabra, e em sequência, produziram-se três cremes de barrar de cogumelo *shiitake*, com incorpora**ção** dessas fases aquosas. Foram avaliados por um painel de provadores não treinado, que permitiu a seleção de um protótipo correspondente a uma das concentrações de fase aquosa. Após essa avaliação a fase aquosa mais pontuada foi produzida e sujeita a tratamento térmico – pasteurização, sob três condições diferentes. Com o objetivo de se comprovar a eficiência do tratamento térmico foram efetuada análise microbiológicas que permitiram a escolha do binómio tempo/temperatura mais adequado. Seguidamente, foram desenvolvidas oito formulações de creme de barrar de cogumelo *shiitake*, quatro delas *vegan* com fase aquosa de origem vegetal, e outras quatro lacto-vegetarianas com fase aquosa de origem animal, no caso, com o concentrado proteico de soro do leite de cabra. Foram avaliadas novamente por um painel de provadores não treinado, tendo sido selecionados dois protótipos, um deles *vegan* e outro lacto-vegetariano. Foi efetuada análise proximal, que permitiu verificar um teor de proteína mais elevado no creme de barrar lacto-vegetariano, conforme seria expectável. Prevê-se nos próximos meses, ensaios de estabilidade microbiológica, análise proximal e físico-química, assim como, ensaios de *food pairing & food design*.

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Nutritional characterization of *Cytinus hypocistis* L.

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The habit of eating wild plants in Europe is often associated with times of famine or food scarcity (although not exclusively). Most of the early studies on the use of wild food plants in Europe capture the memory of famine and the use of wild plants for survival, including the consumption of starvation foods that in normal times would be discarded by the community [1]. An example of such is the *Cytinus hypocistis* L.; the young plant can be cooked as an asparagus substitute; the nectar eaten as sweets, and the species is quoted as famine food in Portugal [2]. Despite these traditional uses, its chemical composition is largely unknown, and the active substances are not yet identified. To help start bridging this gap, and to explore alternative uses of this plant species, the present work reports the nutritional composition of *C. hypocistis w*hole plant and nectar.

Plant specimens were collected in June 2018 in Castro Daire, Portugal. After lyophilisation, the whole plant and the nectar chamber of flower were further analysed. The proximate composition was evaluated by AOAC official procedures (fat, proteins, ash, carbohydrates, and energy) [3], free sugars were determined using high performance liquid chromatography coupled to a refraction index detector (HPLC-RI), while organic acids were determined using ultrafast liquid chromatography coupled to a diode array detector (UPLC-DAD) [4].

The nutritional profile of the whole plant and the nectar chamber of the flower were very similar in terms of fat, ash and carbohydrate contents. Nevertheless, the protein content in the nectar chamber of the flower was almost 2-fold higher in comparison to the whole plant (9.4 and 4.9 g/100 g dw, respectively). Fructose, glucose, sucrose, and trehalose were the free sugars present in both samples. Although both parts presented similar concentration of trehalose, the sugar content was much higher in the whole plant (6.3 g/100 g dw versus 1.4 g/100 g dw) due to the higher levels of the other 3 sugars. Oxalic, malic, and citric acids were the identified organic acids in both samples, being citric acid the most abundant molecule. The nectar chamber of the flower also presented ascorbic acid (0.180 g/100 g dw), while the whole plant presented traces of shikinic acid.

This study allowed for a better understanding of the reasons behind the use of this plant in the past, but further investigation is needed in order to clarify C. *hypocistis* potential applications.

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Extrusão - um método viável no desenvolvimento de novas formulações sem glúten à base de leguminosas e arroz

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O cozimento por extrusão é um tipo de processamento alimentar de curta duração que se caracteriza pelo uso de alta temperatura. Prima também pelo controle automatizado, alta capacidade de produção, operação contínua, alta produtividade, versatilidade e alta adaptabilidade às condições de processamento, eficiência energética e baixo custo [1,2]. Esta tecnologia é útil para obter produtos tais como, salgadinhos, cereais matinais prontos para consumo, biscoitos, amidos modificados, proteínas vegetais texturizadas, massas, substitutos de carne e alimentos para animais de estimação [3].

Neste estudo, foram desenvolvidas seis misturas com diferentes proporções de arroz, feijão e alfarroba, avaliando-se as alterações induzidas pelo cozimento por extrusão na sua composição fenólica.

Para avaliação do perfil fenólico, as amostras foram submetidas a extrações hidroetanólicas (80:20, *v/v*) que foram, posteriormente, analisadas por HPLC-DAD-ESI/MS.

O perfil fen**ólico revelou** a ausência de compostos nas amostras de arroz e arroz comercial, contudo, evidenciou a presença de 5 e 28 compostos nas amostras de feijão e alfarroba, respetivamente. Na amostra de feijão destacou-se o derivado do ácido *p*-cumánico com um valor de 121 g/100 g massa seca (ms), ao contrário da amostra de alfarroba onde o composto maioritário foi um tetragaloil-glucósido, com 763 g/100 g ms.

Relativamente às misturas, verificou-se que a percentagem de leguminosas nas formulações foi uma variável que afetou significativamente a concentração de compostos fenólicos, uma vez que foi encontrada maior quantidade desses compostos nas misturas com maior concentração de feijão e alfarroba.

Tendo em conta os efeitos da tecnologia em estudo, a análise estatística mostrou uma diferença significativa entre todas as amostras, extrusadas e não-extrusadas, com exceção das formulações com 40% de feijão e 60% de arroz, onde o processo de extrusão não causou mudanças relevantes no conteúdo de compostos fenólicos.

Deste modo, foi evidente a presença de compostos bioativos nas farinhas de arroz-leguminosas (misturas de arroz, feijão e alfarroba), traduzindo-se numa ótima alternativa para o desenvolvimento de novos lanches sem glúten, fazendo frente a um mercado dominado principalmente por cereais.

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Extraction of bioactive compounds from pinus pinaster needles. optimization of the extraction stage

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Pinus pinaster is a traditional forest cultivar in Galicia (NW of Spain) occupying together with Pinus radiata an area of 620,000 ha. Pine wood is mainly used in the industrial sector of sawing and in the manufacture of wood panels. The potential of pine bark, cone or resin to obtain bioactive compounds, such as phenolic compounds, has been widely studied but not the pine needles [1].

In this work, the capacity of pine needles as a source of antioxidant compounds was evaluated. The extraction process was analyzed in order to find the operating conditions that lead to a high extraction yield together with a high antioxidant activity of the obtained extracts.

In a first stage, the influence of the solvent and solid-liquid ratio was studied. Extractions were carried out with ethyl acetate, acetone, methanol, ethanol and water. It was found that the results were improved when increasing the polarity of the solvent and aqueous solutions of ethanol, a generally recognized as safe (GRAS) solvent, were selected. Regarding the solid-liquid ratio, the highest tested, 1/5 g/mL, more favorable for the economy of the process, was chosen.

In a second stage, the experimental design and response surface methodology were applied to optimize the extraction of pine needles phenolics with aqueous ethanol. An incomplete Box-Benhken factorial design 33 was applied to study the influence of temperature (25, 50, 75ºC), time (30, 75 and 120 min) and ethanol concentration (10, 50 and 90% in vol.) on the yield and properties of the extracts (total phenols content and extract antioxidant capacity according to the FRAP, DPPH and ABTS methods). Temperature and ethanol concentration were found to be the most significant variables. Time only affected the ABTS antioxidant capacity. The response surfaces obtained for total phenol content and DPPH and ABTS assays showed a point of maximum response. Moving away from this point in any direction, the extracts properties decreased. The optimal extraction conditions selected were 60ºC, 30 min and 50% vol. of ethanol, with an extraction yield of 23.72%, 13.32 g GAE/100 g extract for the total phenol content, 816 nmol AAE/mg extract for FRAP antioxidant activity, 0.63 nmol TRE/g extract for the DPPH assay and 0.74 nmol TRE/g extract for the ABTS assay.

Finally, the aqueous extract and the ethanol/water extract selected as the optimal were analysed by RP-HPLC-ESI-TOF, which revealed the presence of (-)-epigallocatechin, (-)-gallocatechin, catechin hydrate, ellagic acid, epicatechin, ferulic acid, gallic acid, neochlorogenic acid, p-coumaric acid and quercetin-3-β-D glucoside in both extracts and, in addition, isorharmnetin, kaempferol and quercetin in the ethanol/water one. The major constituents of the aqueous extracts were p-coumaric acid, gallic acid and ferulic, in this order, whereas quercetin-3-β-D glucoside, ferulic acid and coumaric acid were the predominant ones in the ethanol/water extract.

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Caraterização química e nutricional de uma espécie de elevado interesse na indústria alimentar: *Ocimum basilicum* var. *purpurascens*

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O reino das plantas é composto por uma grande variedade de espécies de elevada importância para a alimentação dos seres heterotróficos, devido à sua composição em nutrientes e moléculas de elevado interesse [1]. O género *Ocimum* compreende mais de 150 espécies e é considerado um dos maiores géneros da família *Lamiaceae*, onde se inclui *Ocimum basilicum* var. *purpurascens*, conhecido como manjericão vermelho rubi [2]. Assim sendo, não só o manjericão é uma planta consumida mundialmente, tornando-se uma espécie de grande relevância, mas também as suas variedades, como é o caso do manjericão vermelho rubi.

O objetivo deste trabalho consistiu em caracterizar as folhas do manjericão vermelho rubi a nível nutricional (teor em humidade, cinzas, proteínas, gorduras, hidratos de carbono e energia) e a nível químico através do perfil em açúcares livres, ácidos orgânicos, tocoferóis e ácidos gordos.

O perfil nutricional foi avaliado utilizando metodologias oficiais de análise de produtos alimentares [3], os açúcares livres foram identificados através de um sistema de HPLC-RI, os ácidos orgânicos por UFLC-PDA, os tocoferóis por HPLC-fluorescência e os ácidos gordos por GC-FID.

Relativamente ao valor nutricional, destacou-se o teor em hidratos de carbono, como o macronutriente presente em maior quantidade, apresentando valores de 7,17 g/100 g de massa fresca (mf). De outro modo, a fração lipídica da amostra revelou apenas 0,36 g/100 g mf, sendo o macronutriente presente em menor quantidade e a energia total foi 41,22 kcal/100 g mf. Na avaliação dos compostos hidrofílicos, as folhas de manjericão vermelho rubi revelaram a presença de vários compostos, nomeadamente quatro moléculas de açúcares livres e sete ácidos orgânicos, destacando-se a glucose (0,040 g/100 g mf) e o ácido quínico (7,4 g/100 g mf), respetivamente. Relativamente aos compostos lipofílicos, particularmente os tocoferóis, foram detetadas as isoformas α-, β-, γ- e δ-tocoferol, sendo o γ-tocoferol a isoforma mais abundante (34,6 mg/100 g mf). No que concerne ao perfil de ácidos gordos, foram identificados vinte compostos, destacando-se o ácido α-linolénico (C18:3n3, 53,79%), seguido dos ácidos palmítico (C16:0; 16,75%), linoleico (C18:2n6; 6,6 %) e oleico (C18:1n9; 5,20%); todos os restantes apresentação concentrações inferiores a 5%.

Os resultados obtidos demonstram que esta variedade de manjericão vermelho rubi pode ser consumida como fonte de nutrientes, sendo também destacado o seu potencial como fonte de compostos de interesse naturais para aplicação na indústria alimentar e/ou farmacêutica.

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Comparative study of different techniques to extract rosmarinic acid from *Melissa officinalis* L.

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Due to the great demand of consumers for an increasingly healthy diet, the food industry has been interested in natural alternatives, namely from plant kingdom, in view of replacing artificial additives [1,2]. Thus, the development of these natural ingredients requires preliminary studies that evaluate the best extraction methodologies and conditions, in order to obtain the highest levels of the target compounds [3,4].

The aim of this study was to optimize the extraction of rosmarinic acid from *Melissa officinalis* L. (lemon balm), comparing three different techniques: maceration, microwave assisted extraction and ultrasonic assisted extraction. The response surface methodology was applied to obtain the conditions that maximize the extraction of rosmarinic acid, using a circumscribed central composite design with three variables and five levels, being the relevant variables time, temperature or power, and ethanol concentration. The amount of rosmarinic acid (obtained by HPLC-DAD) and the extraction yield were used as responses.

Ultrasonic extraction proved to be the most efficient technique, leading to 86 ± 4 mg of rosmarinic acid/g of plant (dry weight) under optimal extraction conditions: 33 ± 3 min, 372 ± 19 W and 40 ± 1% ethanol.

The results obtained highlight that *M. officinalis* species is a source of rosmarinic acid and reveal the best extraction conditions to obtain the highest levels of this molecule, with great interest for the food industry.

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Survey of aging key-compounds in Madeira Wine Blends towards the development of a new optical fiber for their detection

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The production of Madeira is distinguished from other fortified wines mainly by its singular aging process, which can include an artificial heating, usually at about 45°C for 3-4 months in stainless steel tanks – *estufagem* – before following aging, usually for 3 years in wooden casks. The wines with superior characteristics follow aging in *canteiro*, in which the wine remains in casks, usually kept in the upper floors of the wine cellars, exposed to higher temperatures (≈15 - 31 ° C) than usual, for a minimum period of 3 years. The oxidative operating conditions contribute to its typicality and exceptional longevity. Several compounds resultant from the aging process have been reported as wine aging key-compounds, namely 5-hydroxymethylfurfural (HMF) and sotolon [1]. Despite HMF usually occur at higher levels (milligrams per liter) than sotolon, it is not always relevant to the aroma (chamomile flowers) of these fortified wines but can be used as an aging/heat-treatment marker [2]. On the other hand, despite sotolon occurring as low as few micrograms per liter, it is a powerful odorant which may impart nutty, caramel or curry aromas, characteristic of Madeiras. The formation of both compounds is related to sugar degradation mechanisms [3].

Considering that the aging process is vital to the Madeira wine production, new challenging research issues are becoming eminent nowadays. Particularly, the development of sensors for the intelligent monitoring of the ageing process, which can become an important tool for the in loco measurements and decisions. In this sense, the present study aimed to survey the content of HMF and sotolon in 3-, 5- and 10-year old Madeiras towards the development of a new optical fiber, for the Madeira wine aging process control. Thus, 89 samples (Blends) from 4 Madeira wine producers were analyzed through LC-MS/MS to determine the sotolon contents and LC-DAD to determine the HMF contents.

The results showed that HMF contents in 3- to 10- years old blends varied between 3.9 to 155 mg/L, while sotolon levels varied between 2.0 to 516 µg/L. Despite no linear correlation was found between their levels and the corresponding sweetness degree, both increase with the age as expected, which confirms their choice for further process control. This information is essential to establish the best strategy for the sensor development.

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Evaluation of the intra- and interday variations on the amines and phenols content in biological samples of a lactating dairy cow

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In ruminants, the end-products of rumen fermentation have distinct functions in animal metabolism. A vast group of volatile compounds is formed and can be related to the feed composition, acting as biomarkers to evaluate the feed conversion rate based on the analysis of rumen content, feces, urine and milk. Moreover, these volatile markers might enable the diagnosis of digestive and metabolic upsets.

In this work, the profile of amines and phenols in biological samples (rumen content, feces, urine and milk) obtained from a fistulated Holstein cow was studied. The amines were derivatized with dansyl chloride (DNS-Cl) and analyzed by reversed-phase high performance liquid chromatography with fluorimetric detection (HPLC-FLD) [1]. The identity of the chromatographic peaks was confirmed by mass spectrometry analysis. The phenols were extracted from the samples by a salt-assisted liquid-liquid extraction (SALLE) protocol and analyzed by HPLC-FLD [2].

The samples were collected in 3 periods per day, twice a week, for 4 weeks, to evaluate the intra- and interday variations in the amines and phenols content. The major compounds identified in the samples were methylamine, ethylamine, butylamine, 2-phenylethylamine, iso-pentylamine, putrescine, cadaverine, tyramine, spermidine, spermine, phenol, cresol and 4-ethylphenol. The conclusions obtained in this work will help to understand the variations on the amines and phenols contents related to the digestion and metabolism of dairy cows, aiming the identification of potential biomarkers to be used for diagnose purposes.

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Human health risks associated with brominated flame retardants through contaminated smoked fish products

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The recognized health benefits of a seafood rich diet made it one of the most important food commodities worldwide. However, food safety is continuously threatened by numerous contaminants including those originated from environmental pollution, such as PolyBrominated Diphenyl Ethers (PBDEs). Moreover, as a result of their biotransformation, methoxylated PBDEs (MeOPBDEs) have been found in biotic samples and present identical toxic effects.

The aim of this study was to contribute with novel data on emerging contaminants, as PBDEs and MeO-PBDEs, in commercially relevant smoked fish products (N = 30) and the corresponding human exposure to assess their potential risk. In addition, the influence of products inherent features on the contamination status was evaluated.

Chemical analyses were performed by an environmental friendly method comprising a “Quick, Easy, Cheap, Effective, Rugged, and Safe” (QuEChERS)-based extraction followed by gas chromatography (tandem) mass spectrometry.

Almost all tested samples (*ca.* 80%) showed signs of PBDEs and/or MeO-PBDEs contaminantion. All smoked cod liver samples presented the highest degree of contamination, where a 100 g portion represented 12% of the PBDEs provisional tolerable weekly intake, as defined by the European food safety authority. Additionally, all tolerable daily intake percentages were below 0.2%, thus indicating no cause for concern for individuals exposed to PBDEs through consumption of smoked seafood products. In addition, a successful multivariate partial least squares regression model showed that sample fraction (especially liver), followed by lipid content and packaging type (canned products, in particular) were the variables that caused greater impact on PBDEs contamination level of smoked products.

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Citrus hystrix L. condimentary leaves: proximate composition, fatty acids and sugars profile

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Citrus hystrix L., commonly known as kaffir lime, is a plant belonging to the citrus family (Rutaceae). It is native to South Asia and Southeast Asia, mostly occurring in Indonesia, Malaysia, the Philippines, Laos, Thailand, and Vietnam. Its leaves and fruit have been widely used for culinary and traditional medicine purposes. Contrarily to the fruit juice and pulp, which present a pungent taste and therefore are not directly consumed, the leaves are considered as the most important spice in these regions, being added to almost every dish, besides ginger and lemon grass [1,2]. Thus, given the wide application of kaffir lime leaves as condiment, the present study intended to assess its nutritional value, namely its proximate composition in carbohydrates, protein, ash, and fat, as well as its fatty acids and sugars profile by GC-FID and HPLC-RI, respectively.

Regarding the nutritional composition of the condimentary leaves, carbohydrates were the most abundant macronutrients (64.7±0.2 g/100 g), followed by protein (17.98±0.03 g/100 g), and ash (12.96±0.06 g/100 g). In what concerns fatty acids, twenty-two compounds were detected, among which polyunsaturated fatty acids were prevalent (71.5±0.1%), with considerable percentages of linolenic (55.6±0.2%) and linoleic (15.02±0.07%) acids. This spice also presented palmitic (15.1±0.2%) and stearic (3.6±0.2%) acids as the most abundant saturated fatty acids (26.29±0.05%); and oleic (1.243±0.003%) and palmitoleic (0.74±0.05%) acids as the main monounsaturated fatty acids (2.05±0.05%). In terms of free sugars, three molecules were identified, with sucrose (3.5±0.1 g/100 g) being detected in higher concentrations than fructose and glucose (0.98±0.04 and 0.72±0.03 g/100 g, respectively).

Through the results obtained in the present study, it was possible to verify that kaffir lime presents an equilibrated nutritional profile, which valorizes its use as condiment, beyond its so appreciated taste.

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Gomphrena globosa L. e *Amaranthus caudatus* L. como fontes alternativas de compostos corantes

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Na última década, e devido à crescente preocupação dos consumidores, várias matrizes naturais têm sido utilizadas na procura de ingredientes corantes, alternativos aos artificiais, que têm sido associados a alguns efeitos tóxicos. As betacianinas são um grupo de compostos naturais com capacidade corante e têm sido amplamente utilizados na indústria alimentar, não só por causa do seu elevado poder de coloração, mas também devido às suas reconhecidas propriedades bioativas [1]. A principal fonte deste tipo de compostos é a beterraba, mas existem outras matrizes naturais, ainda pouco exploradas, que possuem na sua composição esta classe de moléculas. Exemplos disso são as espécies Gomphrena globosa L. e Amaranthus caudatus L., duas plantas da família das Amaranthaceae que apresentam flores com uma coloração viva, entre o rosa e o violeta, sendo as betacianinas os compostos responsáveis pelo seu efeito corante [2].

Assim, este trabalho teve como objetivo a obtenção de extratos ricos em pigmentos a partir das flores de G. globosa e A. caudatus, de forma a serem utilizados como corantes alimentares, oferecendo alternativas para a indústria alimentar que, para além de conferir cor, são ainda capazes de oferecer propriedades bioativas. Os extratos foram obtidos através de uma maceração dinâmica assistida por calor, sendo posteriormente caracterizados quanto ao seu perfil em betacianinas por cromatografia líquida de alta eficiência acoplada a um detetor de díodos e espetrometria de massa (HPLC-DAD-ESI/MS). A capacidade antimicrobiana foi determinada utilizando um painel de microrganismos Gram-negativo, Gram-positivo e fungos, utilizando um método colorimétrico de deteção rápida com cloreto de p-iodonitrotetrazolio (INT) e os resultados obtidos foram expressos em concentrações mínimas inibitórias do crescimento dos microrganismos (MIC).

Pela análise cromatográfica dos extratos foi possível identificar quatro compostos em cada uma das amostras. Em G. globosa os compostos maioritários identificados foram a gonfrenina III (17.9 ± 0.8 mg/g extrato) e a isogonfrenina III (13.5 ± 0.7 mg/g extrato), e os minoritários a gonfrenina II (8.6 ± 0.5 mg/g extrato) e a isogonfrenina II (6.9 ± 0.5 mg/g extrato). O extrato de A. caudatus apresentou como compostos maioritários a amarantina (171 ± 1 mg/g extrato) e a isoamarantina (38 ± 1 mg/g), enquanto que a betanina (1.6 ± 0.1 mg/g extrato) e a isobetanina (1.3 ± 0.1 mg/g extrato) foram encontrados em menor concentração. Na avaliação da atividade antimicrobiana o extrato de G. globosa apresentou MICs na ordem dos 0,15-0,35 mg/mL, enquanto que o extrato de A. caudatus revelou MICs na ordem dos 10-20 mg/mL.

Apesar de apresentarem diferenças no que diz respeito aos compostos que as constituem, estas espécies apresentam capacidade corante, pelo que ambas as plantas podem ser consideradas como fontes alternativas para obter ingredientes corantes de origem natural.

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Determinação do teor de histamina em pescado fresco, conservas e patês

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A intoxicação escromboide **é uma** intoxicação alimentar associada ao consumo de peixe com elevados teores de histamina [1]. O termo deriva de Scrombidae, família que inclui várias espécies de peixes (e.g. atum, cavala e agulhão), que se caracterizam por um elevado nível de histidina livre nos tecidos musculares [2]. As condições de conservação do pescado após a captura (e.g. temperatura) são determinantes para evitar a presença de elevados níveis de histamina, que se forma por descarboxilação bacteriana da histidina [1,3]. A utilização de peixe de má qualidade no fabrico de conservas, bem como o maneio incorreto do mesmo são as principais causas da elevada concentração de histamina nestes produtos [4].

O objetivo deste trabalho foi avaliar o teor de histamina em peixe fresco, conservas e patês, com vista a avaliar o potencial risco do consumo destes alimentos.

A amostragem incluiu 16 amostras de pescado e 40 amostras de conservas e patês provenientes de **várias superfícies comerciais,** na região de Coimbra e Aveiro, de forma a garantir a representatividade dos produtos disponíveis no mercado. A caracterização das amostras foi obtida através dos respetivos rótulos da embalagem. Todas as amostras se encontravam dentro do prazo de validade.

A determinação da histamina foi efetuada de acordo com as instruções inclusas no kit de ELISA (de competição) comercial utilizado (RIDASCREEN® Histamin, R-Biopharm AG, Darmstadt, Alemanha), o qual estava dentro do prazo de validade (limite de deteção para peixe fresco e conservas de peixe 2,5 mg/kg e patês 100 mg/kg).

No presente estudo, das 16 amostras de peixe fresco analisadas foram encontradas 4 amostras positivas (25%), em que nenhum dos resultados positivos ultrapassava o limite máximo de 200 mg/kg, sendo que o valor mais elevado (11,28 mg/kg) é 18 vezes inferior ao limite máximo e o valor mais baixo é inferior a 2,5 mg/kg. Estas amostras revelaram valores máximos inferiores aos observados nos estudos realizados na Grécia [3] e Brasil [4].

A histamina não foi detetada em nenhuma das 40 amostras de produtos à base de patês e conservas de peixe analisados. Nestes produtos, os resultados diferem dos reportados em estudos anteriores [3, 4, 5], nos quais foram detetados valores até 383,41 mg/kg.

Os resultados obtidos indicam que a produção das conservas e patês analisados parece ser segura, no que diz respeito à prevenção da contaminação por histamina. Em relação **às amostras de** peixe fresco os resultados sugerem uma conservação adequada que não deverá por em risco o consumidor deste alimento, contudo a incidência de resultados positivos justificam a realizaç**ão de** estudos adicionais.

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Caracterização do perfil fenólico de *Ocimum basilicum* var. *purpurascens* e avaliação do seu potencial bioativo

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As plantas possuem na sua composição vários compostos de interesse, particularmente compostos fenólicos, que se classificam como moléculas bioativas, exercendo funções benéficas para a saúde humana [1]. *Ocimum basilicum* var. *purpurascens* (popularmente conhecido por manjericão vermelho rubi) é uma planta anual, pertencente **à** família das *Lamiaceae*, resultando a sua cor púrpura da elevada concentração em compostos antociânicos. Esta variedade de *O. basilicum* **é** usada como planta ornamental, embora o seu óleo essencial seja utilizado na medicina popular [2].

O objetivo deste trabalho consistiu em avaliar o conteúdo em compostos fenólicos, bem como as propriedades bioativas (atividade antioxidante, citotoxicidade e atividade antimicrobiana) de um extrato hidroetanólico (80:20, *v*/*v*) de manjericão vermelho rubi.

A determinação do perfil fenólico foi realizada através de um sistema de HPLC-DAD-ESI/MS, a atividade antioxidante foi avaliada através de três ensaios *in vitro* (atividade captadora de radicais DPPH, poder redutor e inibição da descoloração do β-caroteno), a citotoxicidade foi determinada com recurso a linhas celulares tumorais (HepG2, NCI-H460, MCF-7 e HeLa), e a uma cultura de células primárias não tumorais (PLP2), aplicando o ensaio da sulforrodamina B e, por fim, a atividade antimicrobiana foi analisada através do método de microdiluição em bactérias Gram-positivo e Gram-negativo, e em fungos.

No extrato de manjericão vermelho rubi foi evidente a presença de 26 compostos fenólicos, dos quais 13 foram identificados como compostos fenólicos não antociânicos, destacando-se o ácido rosmarínico como composto maioritário, e 13 compostos antociânicos, no qual a cianidina-3-(6,6′-di-p-cumaroil)-soforosil-5-glucósido foi o composto mais abundante. Relativamente ao potencial bioativo desta espécie, o extrato revelou atividade antioxidante, evidenciando-se o ensaio da atividade captadora de radicais DPPH com valores de EC_{50} = 60 μg/mL. Foi também notório, no ensaio da atividade citotóxica, a ausência de capacidade antiproliferativa em todas as linhas celulares testadas mas, também, ausência de toxicidade do extrato para células não tumorais (GI_{50} >400 μg/mL). Relativamente **à atividade** antimicrobiana, os resultados obtidos foram satisfatórios para a maioria das bactérias testadas, mas também nos fungos; apresentando estes últimos valores de MIC (concentração mínima inibitória) inferiores, comparativamente **às** bactérias estudadas.

Os resultados obtidos neste estudo permitem concluir que o manjericão vermelho rubi é uma planta rica em moléculas bioativas, nomeadamente compostos antociânicos e não-antoci**â**nicos, que suscitam elevado interesse ao nível de vários setores industriais, tal como o farmacêutico e o alimentar.

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Application of a Codex Alimentarius method (Type I) for the survey of gluten in baby and infant foods

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The use of wheat flour and gluten in foodstuffs is extremely common because of their heat stability and useful effects on e.g. texture, moisture retention and flavour. Gluten is a mixture of prolamin and glutelin proteins present in wheat, rye and barley. Coeliac disease is a permanent intolerance to gluten that results in damage to the small intestine and is reversible when gluten is avoided by diet. According to the Codex Alimentarius (Alinorm 08/31/26) and European Union Regulation (No 828/2014) two categories for labeling of food according to the gluten content now exist: 1.) Food products which contain less than 20 mg/kg can be labeled as "gluten free"(GF). 2.) Food products labeled as "very low gluten" can have a gluten content above 20 and up to 100 mg/kg [1].
For such purpose, 42 commercially available baby and infant food samples were survey through a sandwich enzyme immunoassay (R5 ELISA RIDASCREEN® Gliadin, R-Biopharm, Germany) for the quantitative analysis of prolamins from wheat (gliadin), rye (secalin) and barley (hordein) in raw products like flours (buckwheat, rice, corn, oats, teff) and spices as well as in processed food, like noodles, ready-to-serve meals, bakery products, sausages, beverages and ice cream. This immunoassay is certified as a Codex Alimentarius Method (Type I), and an AOAC approved Official Method of Analysis Final Action OMA 2012.01 and an AACC International Approved Method (38-50.01). The manufactures instructed were followed and all samples were extracted with a patented Cocktail (official R5-Mendez method, R-Biopharm, Germany).
In total, 42 different baby and infant food samples (including cereal flours and flakes, as well as processed/ready-to-eat food and dairy drinks) were divided into 2 groups: "Gluten-free (GF) labelled foods" (n=21) and "non-GF labelled foods" (n=21). The analysis of the "Gluten-free labelled foods" (i.e. samples that according to the regulations in force should present a level below 20 mg/kg) revealed levels of gluten below the detection (3 mg/kg) and quantification (5 mg/kg) limits, with the exception of one (4.8%) sample of corn flour produced in Portugal (16.987 mg/kg). Given that this sample only contained a naturally free-gluten cereal (corn) this was probably the result of cross-contamination during processing. Considering the "non-GF labelled foods" it was observed that all samples ranged between 18.541 and 68.928 mg/kg, with an average value of 43.00±11.505 mg/kg. To the authors' knowledge this is the first reported market survey on the labelling compliance regarding gluten in baby and infant foods. This type of studies is important given that consumers rely on the food claims/labels to purchase foods with or without a specific ingredient and also because some studies ranked wheat as the second major food allergen, following milk, responsible for food allergen recalls [2].
In conclusion, in both "Gluten-free (GF) labelled foods" and "non-GF labelled foods", the labeling information complied with the legislation in force regarding the requirements for the provision of information to consumers on the absence or reduced presence of gluten in food. In addition, all the "non-GF labelled foods" samples, could be marked and commercialized as "very low gluten", given that none contains more than 100 mg/kg of gluten.

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Frutos de Rubus ulmifolius Schott como uma fonte de compostos fenólicos e propriedades bioativas

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O interesse em espécies silvestres tem vindo a aumentar gradualmente devido à sua rica composição nutricional e moléculas de interesse bioativo, fundamentais para o bom funcionamento do organismo. Esta diversidade de compostos, para além de ser benéfica a nível alimentar, estabelece vantagens para futuras aplicações em diversos setores industriais, particularmente, alimentar, cosmético e farmacêutico [1,2]. A espécie Rubus ulmifolius Schott (vulgarmente denominada por silva-brava ou amora-silvestre) pertence à família Rosaceae e é essencialmente conhecida pelos seus frutos. O seu perfil químico evidencia compostos bioativos, nomeadamente, compostos fenólicos, que lhes confere propriedades antioxidantes, anti-inflamatórias, antimicrobianas, antitumorais, entre outras [3,4].

Neste trabalho, foi determinado o perfil fenólico dos frutos da espécie R. ulmifolius, assim como, avaliado o seu potencial como agente bioativo, estudando a atividade citotóxica e antimicrobiana.

Os compostos fenólicos foram determinados através de um sistema HPLC-DAD-ESI/MS, enquanto que o potencial citotóxico das amostras foi avaliado em linhas celulares tumorais MCF-7 (adenocarcinoma da mama), NCI-H460 (carcinoma de pulmão), HeLa (carcinoma de cervical) e HepG2 (carcinoma hepatocelular), e numa cultura de células primárias não-tumorais (PLP2), pelo método da sulforrodamina B (SRB). A atividade antimicrobiana foi avaliada através do método de microdiluição usando bactérias Gram-positivo e Gram-negativo, bem como fungos.

Tendo em conta os resultados obtidos, R. ulmifolius evidenciou um perfil fenólico com 11 compostos não antociânicos (salientando-se o pentósido do ácido elágico) e 5 compostos antociânicos (destacando-se a cianidina-3-O-glucósido) com potencial corante. No que concerne às suas propriedades bioativas, os extratos hidroetanólicos preparados a partir dos frutos não revelaram qualquer capacidade antiproliferativa em nenhuma das linhas celulares testadas, mas também não manifestaram toxicidade nas células não-tumorais (GI50>400). No entanto, quanto à atividade antimicrobiana obtiveram-se resultados favoráveis, tendo os extratos revelado um efeito bacteriostático, com valores de MIC (concentração mínima inibitória) entre 5 e 20 mg/mL.

Assim, este estudo mostrou que os frutos de R. ulmifolius são uma boa fonte de compostos fenólicos e que exibem propriedades antimicrobianas, sendo possível a sua aplicabilidade não só como fonte de nutrientes, mas também como agentes bioativos.

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Determinação do perfil químico e nutricional dos frutos de Rubus ulmifolius Schott

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Nos últimos anos, o consumidor tem demonstrado uma elevada preocupação em relação à segurança e qualidade dos alimentos, o que resultou na crescente procura de alimentos saudáveis [1]. Deste modo, deve ser aplicada uma abordagem interdisciplinar a fim de promover a valorização de espécies silvestres, incentivando novos projetos ligados a uma extração ecologicamente sustentável de compostos bioativos e, consequentemente, a futuras aplicações no setor industrial [2]. O fruto de R. ulmifolius (amora silvestre) é bastante apreciado pelos consumidores, não só pelo seu agradável sabor, mas também porque é uma fonte de nutrientes e moléculas que interferem beneficamente na saúde do consumidor [3].

No presente estudo foi realizada uma avaliação nutricional (através da determinação do teor em proteínas, cinzas, gorduras, hidratos de carbono e energia) e do perfil em açúcares, ácidos orgânicos, tocoferóis e ácidos gordos dos frutos de R. ulmifolius.

O perfil nutricional foi avaliado aplicando metodologias oficiais de análise de produtos alimentares, os açúcares livres foram identificados/quantificados utilizando um sistema de HPLC-RI, os ácidos orgânicos por UFLC-PDA, os tocoferóis por HPLC-fluorescência e os ácidos gordos por GC-FID.

Os frutos de R. ulmifolius revelaram um perfil nutricional rico em hidratos de carbono (26,17 g/100 g mf (massa fresca)), assim como mostraram um valor energético de 125,25 kcal/100 g mf. Ainda no estudo nutricional, as proteínas evidenciaram uma concentração de 2,4 g/100 g mf, seguidas do teor em gorduras, e cinzas com valores de 1,22 e 0,58 g/100 g mf, respetivamente. Relativamente à avaliação da composição química, foram detetadas as moléculas de frutose, glucose e sacarose no perfil de açúcares livres (evidenciando-se a frutose como o composto presente em maior concentração) e os ácidos oxálico, quínico, málico, xiquímico, ascórbico e fumárico no perfil de ácidos orgânicos. Na avaliação dos ácidos gordos, foram identificados 25 compostos, exibindo o ácido linoleico (C18:2n6) a maior concentração, com um valor de 58%. Além disso, os frutos apresentaram todas as isoformas de tocoferóis, α-, β-, γ- e δ-tocoferol, destacando-se o γ-tocoferol com uma concentração de 2,80 mg/100 g mf, seguido de α-, δ- e β-tocoferol.

Tendo em conta os resultados obtidos, os frutos de R. ulmifolius mostraram ser uma boa opção para enriquecer a dieta diária, devido à sua composição nutricional e química.

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Transferencia de macronutrientes a *Lolium perenne* en suelos tratados con purín de vacuno

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Los residuos de origen animal, entre ellos el purín de vacuno, constituyen fuentes de nutrientes para las plantas. Al mismo tiempo su aplicación al suelo supone un aporte de materia orgánica. En Galicia el purín de vacuno se utiliza habitualmente en suelos de pradera en zonas ganaderas. Los nutrientes aportados por el purín se complementan comúnmente con nutrientes de origen mineral. La aplicación excesiva de purín o el desequilibrio entre las concentraciones de diversos nutrientes en el mismo pueden dar lugar a contaminación de aguas superficiales o subterráneas, en particular por nitrógeno y fósforo.

En este trabajo se realizan ensayos en macetas en invernadero, para estudiar la transferencia de macronutrientes a la vegetación y la producción de *Lolium perenne* L. en suelos tratados con purín de vacuno. Se aplicó una dosis conocida del mismo purín a muestras de horizontes superficiales de suelos de tres zonas ganaderas de Galicia en los que se sembró *Lolium perenne*. En las macetas que sirvieron como control se aplicó, en lugar de purín, el mismo volumen de agua destilada. La cantidad de purín aplicada equivale a 166 m^3/ha, dosis que puede considerarse elevada en relación con la aplicada habitualmente en el campo. Durante 10 semanas se aplicó agua (equivalente a un total de 246 mm) a las macetas y se recogieron y analizaron los lixiviados. Transcurridas 10 semanas desde la aplicación del purín, se cortó, pesó y analizó la vegetación. El suelo se analizó al principio y al final del ensayo.

Al final del ensayo, la concentración de potasio de cambio fue significativamente mayor en los suelos tratados con purín. Las concentraciones de fósforo total y asimilable, amonio, nitrato y magnesio de cambio fueron mayores en el tratamiento con purín solo en uno de los suelos estudiados.

La producción de materia fresca y materia seca fue significativamente mayor en los suelos tratados con purín. La absorción por la planta de nitrógeno, fósforo, potasio, calcio y magnesio fue significativamente mayor en los suelos tratados. Las concentraciones de macronutrientes en algún caso fueron menores en los suelos tratados, debido a un efecto de dilución (mayor crecimiento). Se pone de manifiesto, por tanto, la transferencia a la vegetación de estos macronutrientes aportados por el purín. Las cantidades absorbidas de los distintos macronutrientes variaron entre 19% (nitrógeno) y 66% (potasio) de la cantidad aportada con el purín.

Las concentraciones de calcio, magnesio y fósforo en la vegetación estuvieron por encima de los valores críticos para *Lolium perenne* [1] en suelos tratados y control. Las concentraciones de potasio estuvieron por debajo del valor crítico en suelos control y por encima en los suelos tratados. Las concentraciones de nitrógeno estuvieron por debajo del valor crítico en los suelos control y muy próximas al valor crítico en los suelos tratados. Raramente se encontraron correlaciones significativas entre las concentraciones o contenidos de macronutrientes en la vegetación y las concentraciones en el suelo en forma asimilable.

Las concentraciones de macronutrientes en los lixiviados de los suelos tratados fueron altas en las tres primeras semanas del ensayo y disminuyeron progresivamente hasta igualarse con los lixiviados de las macetas control. La lixiviación de P, K, Ca, Mg, NH_4^+ y NO_3^- fue mayor en los suelos tratados con purín y varió entre 4,5% (P) y 99% (NH_4+NO_3) de la cantidad aportada con el purín.

Conclusión: La aplicación de purín de vacuno a suelos de pradera da lugar a aportes considerables de macronutrientes, que se traducen en un mayor crecimiento vegetal. La lixiviación de nitrato es elevada tras la aplicación del purín.

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Hydrochlorothiazide cocrystals screening: A vibrational spectroscopy study.

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Pharmaceutical cocrystals are crystalline solids constituted by an active pharmaceutical ingredients (API) and a coformer, bonded together by noncovalent bonds in a define stoichiometric ratio [1]. Cocrystals can improve API properties, such as solubility, dissolution, bioavailability, stability and processability. Pharmaceutical industry has a growing interest in these forms since low solubility of APIs is a bottleneck in the production of new drugs. Among the different stages of cocrystal production, high throughput screening methods are of upmost important in order to design the appropriate form for subsequent industrial production [2]. The aim of this work was to develop a high throughput screening method based on the analysis of the cocrystallization product by vibrational spectroscopic techniques, namely, mid infrared spectroscopy (MIRS), near infrared spectroscopy (NIRS) and Raman spectroscopy. An ultrasound-assisted slurry cocrystallization was performed in a 96-well plate. Hydrochlorothiazide (HTZ) was the API used along with six coformers (all considered safe for human consumption) in the API:coformer ratio of 1:1 and 1:2. Seven solvents with different polarity were added to each predefine well (Figure 1). The cocrystallization final products were characterized by MIRS, NIRS and Raman spectroscopy.

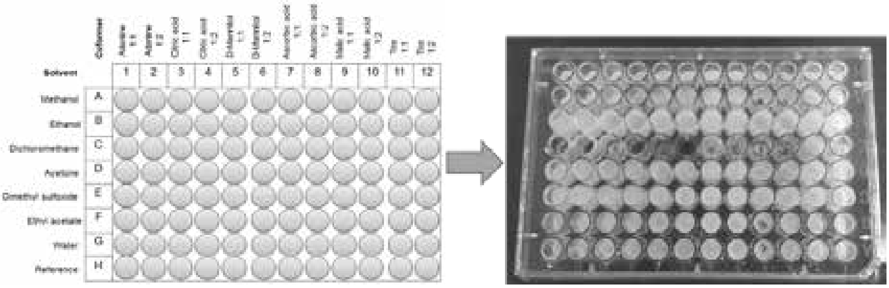

Figure 1: 96-well plate used ultrasound assisted cocrystallization.

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Comparative study of basic and acid transesterification for assessment of total 3MCPD in oil samples by GC-MS.

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3-monochloropropane-1,2-diol (3MCPD) is the primary compound of a group of contaminants denominated chloropropanols and due to its genotoxic activity have been classified as “possibly carcinogen to human” (category 2B) by IARC and a TDI have been set up at the level of 0.8 and 2 µg·kg of b. w. per day for both it free and esterified forms. [1-3] 3MCPD fatty acid diesters have been reported recently in various vegetable oil and oil-based foodstuff from Spanish market [4]

In order to provide data of the total 3MCPD occurrence, two new transesterification procedures have been developed. As a first step, 3MCPD is liberated from its fatty acid esters under either acid or basic conditions, two LLE with hexane are performed to remove all remains of the matrix, the aqueous phase is transfer, and a simultaneous HFBI derivatization and 3MCPD-HFBI complex extraction is performed by a DLLME for GC-MS analysis.

Factors such as acid and basic solution concentration, time of reaction, the temperature of reaction, and others were studied by experimental design, both methods have been validated following FDA guidelines of validation and have been applied to the same sample for comparative purposes.

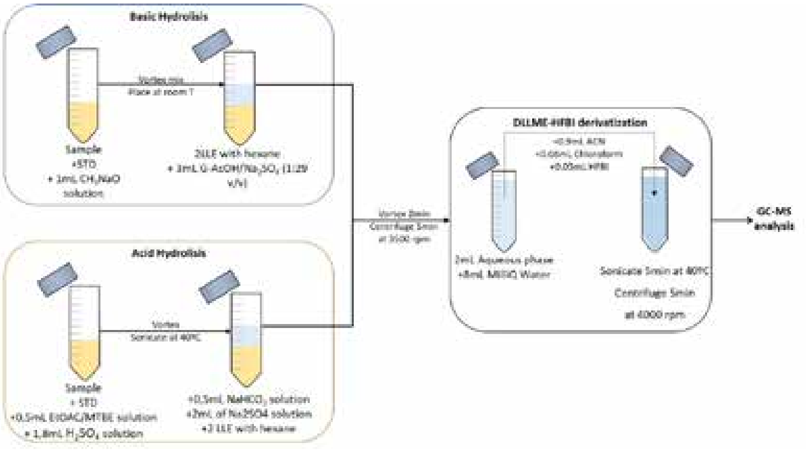

Fig.1. basic and acid transesterification scheme

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A miniaturized chip in a multi-syringe flow system for spectrofluorimetric determination of iodide in urine samples

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Iodine is essential for human growth and development, being a nutrient and a component of the thyroid hormones [1]. The determination of iodine status is based on the concentration of iodine excreted in urine [2]. Most of the methods used for urinary iodine concentration measurement are based on the Sandell-Kolthoff reaction [3]. In this study, a fluorometric detection approach of the Sandell-Kolthoff reaction is proposed. The catalytic effect of the redox reaction between Ce(IV) and As(III), with indirect determination of iodide, is miniaturized in a chip-based flow manifold. The idea was based on a previous work using an advanced three-dimensional (3D) printing features as a chip for the reaction [4]. The urine samples can be analysed in the developed system without any pre-treatment (ex. digestion). This advantage, combined with the fluorometric reaction, makes this method simpler, faster and more sensitive than the classic approach of the Sandell-Kolthoff reaction method. The manifold implemented, allowed to determine iodide within a range of 25 - 100 μg/L in urine. If an in-line dilution process is implemented, a 100-500 μg/L range can be potentially attained. The method was validated with international interlaboratory validation study samples, provided by the Center for Disease Control, USA.

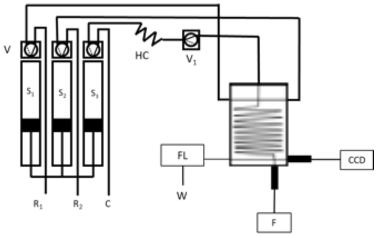

Fig.1. Flow diagram of the chip multi-syringe flow injection analysis for iodide determination in urine. S1–S3: syringe pumps; Vi: three-way solenoid valves; R1: Ce(IV) solution and R2: As(III) solution both in H2SO4; C: carrier (water); HC: 300 cm holding coil; F: irradiation from a D2 light source; CCD: optical fiber connected to the multi-channel spectrometer for fluorescence measurement; FL: Fluorimeter; W: waste.

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Looking for beer aging markers using gas-chromatography-mass spectrometry

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The main quality problem of beer are the chemical changes that occur during storage. A vast variety of flavours may arise, depending on the beer type as well as the storage conditions [1]. Beer flavour is mainly originated by the formation of aldehydes, esters, higher alcohols, ketones and other some compounds that are formed during the fermentation stage, in beer production [2].

The main goal of this work is to investigate the impact of storage conditions, mainly the temperature and time, on beer flavour stability. The profile of some compounds like phenylacetaldehyde, ethylphenyl acetate, phenylethyl acetate as well as some Strecker aldehydes, responsible for the development of sweet and honey like flavours [2], has been monitored throughout natural (20°C) and forced aging (37°C). Some other beers were maintained at 4°C which have been used as controls. The impact of storage temperature and time on these compounds has been evaluated.

Beers have been analysed during an extended storage period (six months), as well as after forced aging (1 and 2 weeks at 37°C). Phenylacetaldehyde, phenylethyl acetate, ethylphenyl acetate and some Streker Aldehydes content have been determined by gas chromatography-mass spectrometry (chromatographic profile and *m/z* pattern of fragmentation), after extraction with dichloromethane using 3-octanol as internal standard.

Phenylethyl acetate has been shown as the better analytical marker of beer aging induced by heat, among the studied compounds. An increase has been observed for phenylethyl acetate content for beers maintained at 37°C during 1 and 2 weeks. It has further been observed that the content of Streker aldehydes (2-methylbutanal and 3-methylbutanal) remained apparently constant in beers maintained at natural (20°C), forced aging (37°C) and 4°C (controls).

SPSS was used to statistically validate the significance of these findings. ANOVA and F tests have been used to compare the differences in the concentration of the compounds over the time. Significant differences have been observed in the concentration of phenylethyl acetate for forced aging samples (37°C), concluding that this is the better analytical marker of beer aging induced by heat than another studied compounds. The results were analysed at a significant level of 5%.

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Aplicación de la microextracción en la preparación de muestras de interés toxicológico

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De acuerdo con el Informe Europeo sobre Drogas emitido cada año por el Observatorio Europeo de las Drogas y las Toxicomanías (EMDCCA), la continua aparición de nuevas sustancias psicoactivas (NPS) sigue aumentando. Estos compuestos tienen efectos similares o más potentes que las drogas ilícitas, como el MDMA (éxtasis). Además, debido a que tienen una escasa fiscalización o ésta es inexistente, son vendidos como sustitutos de las drogas más conocidas y consumidas. De igual modo, el informe pone de manifiesto el aumento en el consumo de drogas ya conocidas como el cannabis, la heroína o la cocaína, provocando un mayor número de muertes por sobredosis [1].

En Toxicología es necesario el uso de métodos analíticos rápidos y fiables para poder extraer e identificar este tipo de compuestos en las distintas muestras biológicas de las que se dispone. Una de las técnicas novedosas utilizadas es la microextracción con adsorbentes empaquetados (MEPS) [2]. MEPS es una miniaturización de la extracción en fase sólida (SPE) que emplea los mismos principios que la técnica clásica, en la que el adsorbente se empaqueta en el cuerpo de una jeringa. Esta técnica de microextracción ofrece la ventaja de que reduce volúmenes, tiempo de análisis y costes en la preparación de muestra.

En objetivo de esta comunicación es presentar la aplicación de esta técnica de microextracción en el preparación de muestras biológicas para la determinación de diferentes drogas de abuso, entre las que se incluyen nuevas sustancias psicoactivas [3, 4].

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Enantioresolution, chiral recognition mechanisms and binding of xanthone derivatives on immobilized human serum albumin by liquid chromatography

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Chiral stationary phases based on human serum albumin (HSA-CSPs) exhibit a broad chiral recognition ability and high enantioselectivity for a variety of analytes due to the multiple binding sites [1]. Information about the interactions may be a valuable tool in design and optimization of chiral separations, as well as predicting how drugs will behave in human body, and understanding drug-drug interactions [2].

Thirteen enantiomeric mixtures of chiral derivatives of xanthones (CDXs) synthesized "in house" [3,4] were separated by liquid chromatography (LC) on an HSA-CSP. These enantioseparations were optimized using different mobile phases, under reversed-phase elution mode. Several chromatographic conditions, such as mobile phase pH, buffers and, ionic strength, organic modifiers and temperatures were explored. High enantioselectivity and resolution were obtained with α and R_S ranging from 1.55 to 8.16 and from 1.81 to 6.41, respectively.

LC protein binding affinity of each enantiomer of CDXs was also determined under chromatographic conditions that mimic the physiological environment. A fast and reliable method of affinity screening to HSA for this class of compounds is proposed. For the majority of the CDXs, high affinity was observed, with bound percentage values ranging from 79.02% to 99.99%.

Considering the importance of understanding the chiral recognition mechanisms associated with chromatographic data, computational studies by molecular docking were carried out. The docking calculations were in accordance with the experimental chromatographic parameters regarding enantioselectivity and enantiomer elution order, with a success rate of 77%.

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Potentiometric detection in liquid chromatographic systems

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The analytical techniques are extensively used to assess the quality control and safety patterns in various fields of analysis. The main technique used in the laboratories is based on liquid chromatographic systems, where electrochemical detection has not been widely used as much as spectroscopic methods. However, its importance cannot be overlooked. Electrochemical detectors are generally versatile analytical tools with great potential that offers high sensitivity and precision in a short time of analysis, using simple and low cost instruments. Detection limits in the nanomolar and even picomolar range have been achieved, making possible the analysis of extremely low levels of biological compounds. Besides, electrochemical sensors are favourable for analysis of complex samples, once no sample pre-treatment is required, and can be successfully used in the determination of analytes without absorption of UV-vis radiation. [1].

Therefore, the coupling of liquid chromatographic systems to a simple, selective, low-cost and sensitive detector can give a solution either for pre-screening or determination of single or multiple species in complex mixtures. Particularly, potentiometric detection with ion-selective electrodes (ISEs) have been extensively exploited in small benchtop laboratory apparatus as well as in automated flow equipment [2]. Determination of electrolytes in blood samples, heavy metals in natural water samples and pharmaceutical drugs in bulk drug materials are some of the examples where ISEs have been successfully applied.

Despite the broad range of applications of potentiometric sensors and the well-known use for determination of ionisable substances, references to their use as detectors in liquid chromatographic procedures are scarce. Contrarily to amperometric, coulometric and conductimetric detectors, which already have commercially available cells designed to accommodate chromatographic columns, potentiometric sensors still are in an embryonic stage.

So far, the potentiometric detection coupled to liquid chromatographic systems has been based in the search of the most favourable indicator electrodes as well as in the extension of the target analytes [3]. The results showed that potentiometric detection in HPLC have great potential development. On the one hand, ionic compounds similar to the target analyte can be readily detected following chromatographic separation. On the other hand, separation methods offer new targets to potentiometric detection, such as bioorganic compounds, which are available in very small quantities only and often in admixture with other substances.

Herein, it is intended to present an overview about the development of this hyphenated technique and discuss its great potential concerning new analytical applications.

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Electrochemical genosensors applied to cardiovascular pharmacogenetics

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Pharmacogenetic studies search for heritable genetic polymorphisms that influence responses to drug therapy. Pharmacogenetics has many possible applications in cardiovascular pharmacotherapy including screening for polymorphisms to choose agents with the greatest potential for efficacy and least risk of toxicity. Pharmacogenetics also informs dose adaptations for specific drugs in patients with aberrant metabolism [1]. Each year, around 32.4 million people suffer a myocardial infarction and strokes worldwide [2]. Despite advances in management, the high number of patients is indicative of the importance to optimize treatment strategies.

Warfarin is the most commonly prescribed oral anticoagulant for the treatment and prevention of thrombotic disorders and requires intensive monitoring and dosage adjustments to avoid drug-related complications [3,4]. In fact, because of its narrow therapeutic index, it is one of the most common causes of emergency room visits for adverse drug reactions [3]. Several factors have been reported to influence therapeutic warfarin dose requirements, including age, vitamin K intake, as well as genetic variants [4]. Two key enzymes involved in warfarin pharmacogenetics are the CYP2C9 (*CYP2C9* gene) and the C1 subunit of the vitamin K 2,3 epoxide reductase complex (*VKORC1* gene) [3]. Recently, pharmacogenomics studies indicated that single-nucleotide polymorphisms (SNPs) in the *CYP2C9* and *VKORC1* genes contribute to interindividual differences in patient´s responses to warfarin [4]. Thus, it is crucial to develop methodologies to predict the individual dosage of warfarin.

In this work an analytical approach based on electrochemical genosensor technique is under development to create a low-cost genotyping platform able to genotype SNPs related with the therapeutic response of warfarin. The design of this genosensor consists on the ssDNA immobilization onto gold surfaces that act as the SNPs complementary probes. The hybridization reaction is performed in a sandwich format of the complementary ssDNA, using an enzymatic scheme to amplify the electrochemical signal. Preliminary studies indicate that differences in the electrochemical answers were obtained depending of the hybridization reaction format. In fact, higher electrochemical intensities were measured when the hybridization reaction was performed with a complementary DNA (without SNPs). These results suggested that the sensor is able to discriminate between the complementary DNA and single base mismatch targets having a great potential for the DNA polymorphism analysis.

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Interferences minimization using solid phase extraction in a multiparametric sequential injection system

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Micronutrients are essential for the normal functioning of living organisms, consequently, supplements containing these micronutrients are often used in agriculture, resulting in their leaching into ground water. In this scenario, a multiparametric sequential injection system with a spectrophotometric detection for the determination of copper, zinc, and iron was developed (Fig. 1). To conduct all determinations using a single manifold, a non-selective reagent, such as 4-(2-pyridylazo) resorcinol (PAR), was chosen as the colour reagent for the determination of copper and zinc. As PAR is a non-specific reagent, solid phase extraction using two different sorbent materials was used to allow the determination of the individual metal ions. The materials used to separate the copper and zinc ions were Chelex 100 and a PVC-based polymer inclusion membrane (PIM) containing di-(2-ethylhexyl)phosphoric acid (D2EHPA), respectively. As a strategy for the iron determination, 3-hydroxy-4-pyridinone (MRB13) was considered as a highly selective iron chelator.

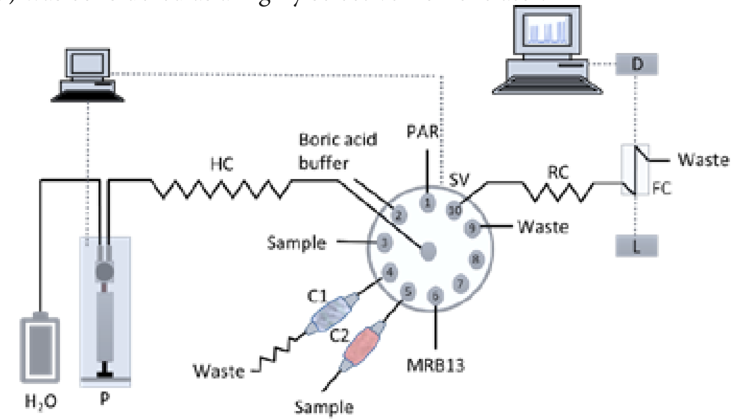

Fig.1. Sequential injection manifold for micronutrients determination. C1 – PIM column; C2 – Chelex 100 column; P – Syringe pump; HC – holding coil; SV – selection valve; RC – reaction coil; L – light source; FC – flow cell; D – Spectrophotometer;

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Dual-Emission ratiometric probe for H_2O_2 determination

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Hydrogen peroxide is a strong oxidant regularly used in numerous applications as cleaning agent, namely H_2O_2 is used for contact lens disinfection. However, H_2O_2 can be dangerous to the ocular epithelium and cornea being necessary to perform a carefully monitoring of its concentration to guarantee the safety of its utilization [1].
Semiconductor quantum dots (QDs) have demonstrated an enormous capability as reliable fluorescent probes for assessment of distinct analytes [2]. Carbon dots (CDs) are a recent class of fluorescent nanomaterials that have collected a deep attention, not only due to their low toxicity and high biocompatibility, but also because they are easily prepared by using cost-effective processes [3].
In the present work, two distinct photoluminescent nanoparticles were exploited to implement a ratiometric assay for the determination of H_2O_2. This dual-emission nanosystem involved the combination of a blue-emitting N-doped carbon dot (N-Cds) and a red-emitting CdTe QDs capped with 3-mercaptopropionic acid (MPA). Due to their inert behavior the former acted as internal reference while the later was accountable for analyte recognition and measurement. Simultaneously, a RGB-type probe based on color modulation of the different nanomaterials was also studied. The PL variations and color intensity were used for the detection and quantification of H_2O_2 in contact lens care solutions.

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Searching for the most variable *m/z* values in grape development in a Portuguese vineyard

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Each vineyard is known to have a strong impact on the metabolic compounds of grapes due to its external factors, named *terroir* [1]. Furthermore, knowledge on the metabolic behavior of vines in response to the *terroir* effect can help to assess, in advance, the optimal maturity of grapes. The aim of this work was to obtain a metabolic profile of vines in different locations and consequently associate it with the external conditions present during grapes' development using an untargeted approach.

Samples were collected in eight sites of a Portuguese vineyard during different developmental stages and analyzed using a metabolomic protocol based on liquid chromatography coupled to tandem mass spectrometry [2]. Briefly, samples were grounded and extracted using a mixture of water/methanol/chloroform (20:40:40, v/v/v). The aqueous methanol fraction was used for further analysis. An Agilent Eclipse plus C18 column (RRHD 1.8 µm, 2.1 mm × 100 mm) was used for chromatographic separation and elution was achieved in gradient mode. Water and acetonitrile both containing 0.1% (v/v) formic acid were used as mobile phase. Mass spectrometry analysis was performed in positive and negative ionization mode and data were acquired in scan mode to maximize the number of detected *m/z* values. MZmine software was chosen for data analysis due to its robustness in fragment selection. A baseline correction was applied to equalize baselines and an alignment algorithm was used to equalize retention times aiming to compare *m/z* values from different samples. Statistical and chemometric tools were used to exclude *m/z* values attributed to blanks and to establish a metabolic profile, respectively.

Preliminary results confirm that the methodology chosen for data analysis is fast and accurate for the viable selection of the most significant *m/z* features. Regarding currently analyzed samples, the proposed methodology allowed the identification of several *m/z* features presenting a statistically significant variation among sampling points, which will be further investigated as indicators of the maturity state.

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Desenvolvimento e aplicação de um método fluorimétrico para a quantificação de zinco em alimentos para cães

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Atualmente, uma dieta equilibrada é tão importante para os seres humanos quanto para os animais. Um alimento composto completo deve assegurar as necessidades alimentares dos animais que dependem, entre outros, da sua idade e do seu porte. O zinco é um oligoelemento essencial para vários processos biológicos, nomeadamente para a produção de energia. O zinco ingerido pelos animais provém das matérias-primas utilizadas na formulação de alimentos compostos, bem como pela sua fortificação com fontes inorgânicas e/ou orgânicas de zinco. Daqui decorre a necessidade de conhecer o teor em zinco quer dos vários ingredientes, de modo a ser avaliada a necessidade de fortificação, quer do alimento composto final para garantir a cobertura das necessidades dos animais neste elemento.

Neste contexto, o presente trabalho teve por objetivo avaliar uma metodologia simples, rápida e de baixo custo para determinação do teor em zinco de alimentos compostos para cães baseada na determinação fluorimétrica com o uso de sondas fluorescentes, nomeadamente: 5-((4-(bis(piridin-2-ilmetil)amino)fenil)carbamoil)-2-(2-cloro-7-fluoro-6-oxido-3-oxo-3*H*-xanten-9-il) benzoato de potássio (Newport Green DCF) e ácido 2,2'-((4-(2,7-difluoro-3,6-di-hidroxi-4a*H*-xanten-9-il)-3-metoxifenil)azanodiil)diacético (FluoZin-1), em formato de microplaca. Vários aspetos foram estudados, nomeadamente, a estabilidade da fluorescência da sonda ao longo do tempo, a concentração da sonda usada e o pH do meio reacional. Após selecionar a sonda FluoZin-1 como mais indicada para a aplicação alvo, foram fixadas as condições reacionais, definindo-se o tempo de leitura da fluorescência após adição dos reagentes em 5 min, a concentração da sonda fluorescente em 2,5 μM e o pH do meio reacional em 7,0. Os alimentos compostos foram analisados após digestão ácida por microondas [1].

A metodologia desenvolvida apresentou um limite de deteção de 13 **μ**g/L e um limite de quantificação de 39 **μ**g/L em amostras após digestão ácida, correspondendo a um limite de deteção de 5 mg Zn/kg de alimento. A repetibilidade intra e inter-dia foi avaliada para soluções contendo 100 **μ**g/L em Zn(II), fornecendo valores de desvio padrão relativo <3,7 e <7,1%, respetivamente.

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Desenvolvimento e caracterização de um sensor potenciométrico para a determinação da atropina

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A atropina é um alcaloide extraído das folhas da *Atropa belladonna* com uma importância significativa para fins clínicos e analises farmacêuticas. Trata-se de um agente anticolinérgico e um antagonista das ações de outros agonistas muscarínicos. É uma substância ativa com enumeras aplicações nomeadamente em casos de disritmia cardíaca, asma, bloqueio cardíaco, anestesia geral, massagem do seio carotídeo e no tratamento de intoxicação por organofosforados [1].

Dada a sua ampla utilização, são descritos diversos métodos analíticos para o seu controlo de qualidade, nomeadamente espetrofotometria, quimiluminescência, cromatografia gasosa e cromatografia líquida de alta eficiência. A potenciometria com elétrodos seletivos de iões (ESIs) pode constituir uma alternativa já que apresenta algumas vantagens relativamente aos métodos referidos [2] . A utilização de moléculas de reconhecimento adequadas faz com que este tipo de sensores se destaque quer pela seletividade quer pelos limites de deteção que alcançam. Entre os diferentes materiais usados na construção de membranas sensoras, surgem os cucurbiturilos como promissores.

Assim, o objetivo deste trabalho consistiu no desenvolvimento e avaliação de um elétrodo seletivo de iões para a determinação da atropina em formulações farmacêuticas. O sensor otimizado é constituído por uma membrana polimérica que incorpora 30.1%(m/m) de cloreto de polivinil carboxilado, 1.1%(m/m) de cucurbit[6]uril como iónoforo, 68.5%(m/m) de 2-nitrofenil octil éter como solvente mediador e 0.3%(m/m) de tetraquis (4- clorofenil) borato de potássio como aditivo. Numa solução tampão de MES-NaOH a pH 6, o desempenho do sensor de atropina é caracterizado por um declive de (58.7±0.6) mV dec^{-1}, com um limite prático de deteção de (6.30±1.62) $\times10^{-7}$ mol L^{-1} e um limite inferior de resposta linear de (1.52±0.64) $\times10^{-6}$ mol L^{-1}. Os coeficientes de seletividade potenciométricos foram determinados para diferentes iões (possíveis interferentes na matriz em estudo), verificando-se uma boa seletividade do sensor para a atropina. A análise potenciométrica da atropina em amostras de formulações farmacêuticas injetáveis mostrou precisão e exatidão estatística quando comparada com a análise cromatográfica, proposta pela Farmacopeia Britânica.

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Avaliação de métodos analíticos para determinação de teobromina em presença de cafeína

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O grupo das metilxantinas são alcalóides purínicos encontrados em plantas como chá e café, representados pela cafeína (1,3,7-trimetilxantina), teobromina (3,7-dimetilxantina) e teofilina (1,3-dimetilxantina). A cafeína, principal constituinte do café, é biosintetizada à partir da xantosina com três passos de metilação e uma hidrólise, incluindo a teobromina como intermediário [1]. A teobromina é também gerada no metabolismo da cafeína em plantas ou bactérias e por ensaios biocatalíticos [2].

Estruturalmente elas diferem em um grupo metil, seja em posição ou substituições, sendo difícil analisá-las quando em conjunto. Existem vários métodos analíticos aplicados a determinação de xantinas [2, 3]. A cromatografia líquida de alta eficiência (HPLC), utilizando fase reversa e detecção UV, separa adequadamente as xantinas por diferença de interações proporcionando uma quantificação precisa. A espectroscopia de infravermelho (IR) geram bandas de absorção características dos grupos funcionais presentes na molécula, possibilitando a distinção entre as xantinas.

No intuito de realizar análises quali e quantitativas de ambas xantinas cafeína e teobromina, alguns métodos analíticos foram testados. A execução da análise TLC foi comprometida devido a baixa solubilidade da teobromina, dificultando a aplicação da amostra e comprometendo a formação de mancha. A avaliação dos espectros de UV não distingue as moléculas, inclusive com mesmo máximo de absorção em 272 nm, mesmo variando a faixa de pH. A análise por FT-IR possibilitou a determinação de cafeína e teobromina mesmo em conjunto, já que a ausência de um grupo metil na teobromina gera espectro com bandas de absorção diferentes como a banda em 3158 cm^{-1}, característico de N-H. A quantificação é obtida pela área da banda, podendo-se empregar a técnica de deconvolução de modo a separar bandas sobrepostas.

Foram realizadas análises quantitativas, por HPLC e FT-IR, de teobromina e cafeína em mistura à partir de concentrações conhecidas. Os resultados por FT-IR são aproximados às concentrações teóricas podendo ser utilizado para monitorar a concentração de teobromina. A técnica FT-IR proporciona quantificação de teobromina em presença de cafeína, sendo uma alternativa vantajosa à técnica cromatográfica (HPLC) por ser simples, de baixo custo, sem necessidade de preparo de amostras e sem consumo de reagentes.

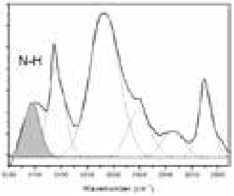

Fig.1. Deconvolução de banda FT-IR.

Tabela 1. Valores de teobromina obtidos por FT-IR.

Amostra	Conc. Real %	Conc. Medida %
Caf-Teob 1:9	90	86
Caf-Teob 1:1	50	61
Caf-Teob 9:1	10	4

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Ionic liquid-embedded C18 for solid phase extraction

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Ionic liquids (IL) have been widely used due to their intrinsic characteristics. They present low melting points, high thermal stability, selective dissolvability, negligible vapour pressure, non-inflammability, and the tunability, that results from the possibility to generate new species resulting from the variation of the organic cation, the inorganic or the organic anion and the length of the side chain attached to the organic cation [1, 2]. In this work a imidazolium based ionic liquid was used to be embedded in the octadecyl silica. The imidazolium group from the IL, promotes the possibility of this solid phase to exhibit ion-dipole interactions, hydrogen-bonding, electrostatic interactions and π-π interactions with analytes, apart from the hydrophobic effect usually used with the conventional C18.
The developed solid phase results from two reactions. The first one happens between the 1-allylimidazole and 1-bromooctadecane in acetonitrile, stirred at 60 °C for 72 hours, that results in 1-allyl-3-octadecylimidazolium bromide ionic liquid [3]. This compound is than grafted onto 3-mercaptopropyltrimethoxysilane-modified silica. This last reaction happens at room temperature in methanol, by irradiation with a UV-lamp (365 nm) using 2,2-dimethoxy-2-phenylacetophenone (DPAP) as a radical initiator [4]. The obtained solid phase was characterized by elemental analysis and nuclear magnetic resonance spectroscopy.
The final intuit is to package the developed solid phase in cartridge to be used in solid phase extraction processes.

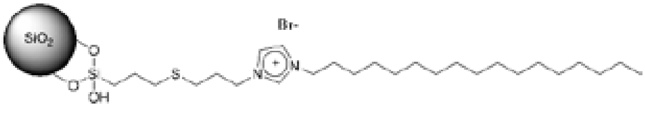

Fig.1. Octadecylimidazolium-modified silica

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¿Es la filtración un problema en la determinación de compuestos orgánicos en aguas?

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La filtración es una etapa típica de los métodos analíticos de determinación de compuestos orgánicos en muestras acuosas. Mediante esta etapa se eliminan las partículas presentes en la muestra, para, o bien, analizar sólo los contaminantes en la fase disuelta, o bien analizar por separado ambas fases para así determinar el fraccionamiento de determinadas sustancias entre la fase disuelta y la fase adsorbida a la materia orgánica y el particulado presente. Sin embargo, se ha visto que en ocasiones esta filtración puede llegar a producir retenciones de algunos compuestos en el filtro que pueden dar lugar a errores en la determinación [1,2].

En este trabajo se ha llevado a cabo el estudio de la etapa de filtración para la determinación de pesticidas, estrógenos y fragancias. Se han testado los filtros habitualmente utilizados para el filtrado de muestras acuosas (celulosa, fibra de vidrio, fibra de cuarzo), pero además, se han ensayado otras alternativas de filtración no tan habituales como el uso de filtros de acero o nylon y el filtrado a través de frita de teflón.

El estudio se ha llevado a cabo con agua de mar sintética preparada en el laboratorio para evitar interferencias debidas a la adsorción de los compuestos a la materia orgánica o el particulado. La misma muestra sobrecargada se analiza sin filtrar y después de someterla a la filtración por los distintos métodos ensayados comparándose los resultados.

Con los filtros habituales se han observado pérdidas importantes de los compuestos estudiados, quedando en algunos casos totalmente retenidos en el filtro, o con pérdidas que llegan al 50%.

Los mejores resultados en el caso de las fragancias se han obtenido utilizando filtros de acero de 20 micras de tamaño de poro, con pérdidas menores al 30%. En el caso de los pesticidas y los estrógenos, los mejores resultados se han obtenido filtrando las aguas mediante jeringas de vidrio con frita de teflón de 20 micras de tamaño de poro, con porcentajes de pérdidas del 3% para los pesticidas y del 20% para los estrógenos.

Por todo ello se constata que en ocasiones la filtración puede llegar a ser un problema en el desarrollo de un método analítico, y es necesario estudiar cuidadosamente esta etapa con el fin de evitar dar resultados erróneos o asignar de modo incorrecto el fraccionamiento de compuestos.

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Efecto de la presión aplicada al análisis de gases por FT-IR

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La espectroscopía FT-IR es una herramienta de gran relevancia para el control de calidad del gas natural gracias a su rapidez, ausencia de tratamiento de la muestra y posibilidad de miniaturización para uso *in situ*. Sin embargo, los espectros de muestras complejas pueden ser difíciles de interpretar (p.ej., gases de combustión, gas natural, etc.) debido a los solapamientos de los picos espectrales [1].

Por eso, es importante visualizar todas las bandas espectrales, incluidas las menos intensas, para realizar el análisis cualitativo. Para ello se aprovecha el efecto de ensanchamiento por presión ("*pressure broadening effect*") que proporciona un gas inerte añadido a la muestra. Este consiste en que, cuando la presión aumenta dentro de la celda de gas, las colisiones entre partículas son más frecuentes, lo que restringe parcialmente los movimientos de rotación y de vibración de las moléculas y degenera sus niveles energéticos nominales. Si la resolución instrumental es más grande que el ancho del pico espectral (lo que es frecuente en los equipos instrumentales habituales), la señal de absorbancia puede ser demasiado baja (por el efecto policromático). Cuando se introduce gas inerte, algunos picos espectrales incrementan su señal relativa gracias al ensanchamiento de sus bandas [2]total absorption across a band per mole of absorber increases with pressure. A. Non-overlapping line approximation Full description of an absorption band is complex, but approxi-mate expressions can be used over limited ranges of absorber mole fraction, pressure and pathlength. It can be shown that the \" non-overlapping line approximation \" applies at ambient pres-sure and CO 2 mole fraction over the short pathlengths found in LI-COR infrared gas analyzers (Wolfe and Zissis, 1978.

Clásicamente se ha utilizado N_2 aunque algunos autores han probado también el uso del H_2 y He [2], [3]total absorption across a band per mole of absorber increases with pressure. A. Non-overlapping line approximation Full description of an absorption band is complex, but approxi-mate expressions can be used over limited ranges of absorber mole fraction, pressure and pathlength. It can be shown that the \" non-overlapping line approximation \" applies at ambient pres-sure and CO 2 mole fraction over the short pathlengths found in LI-COR infrared gas analyzers (Wolfe and Zissis, 1978. En este trabajo se evalúa el efecto de magnificación de la señal que producen tres gases inertes habituales: N_2, He y Ar. Los resultados sugieren que, mientras que el He y N_2 provocan un aumento general en la absorbancia en todos los picos espectrales, el Ar potencia más los picos de menor intensidad.

En la Fig. 1 se ilustran las absorbancias de dos picos de intensidades muy diferentes (alta: 3863 cm^{-1}; y baja: 3750 cm^{-1}) de una muestra de gas natural. Se puede observar que el menor pico, 3750 cm^{-1}, aumenta claramente su intensidad cuando se utiliza Ar como gas inerte, mientras que en la banda más intensa el incremento es ligeramente menor al obtenido con los otros gases.

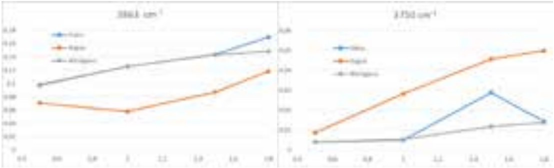

Fig.1. Absorbancias de una muestra de gas natural a dos números de onda en función de la presión.

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Técnicas analíticas para la identificación y caracterización de plásticos de juguetes

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Las autoridades tienen la responsabilidad de controlar las mercancías que están disponibles para los consumidores, para asegurar que se comercializan productos seguros. Ciertos productos como juguetes y artículos de puericultura, utilizados por la población más vulnerable, incluyendo a los bebés o recién nacidos, pueden contener compuestos tóxicos como metales, compuestos orgánicos volátiles (VOCs) o ftalatos. Para estos últimos su concentración está limitada por la entrada 51 del anexo XVII del Reglamento (UE) 1907/2006 [1].

La mayoría de juguetes dirigidos a niños están hechos de plástico. La identificación del tipo de material que los componen, así como el análisis de compuestos orgánicos e inorgánicos presentes en ellos puede resultar un reto analítico debido a la gran abundancia de constituyentes químicos que conforman estos materiales. Algunas de estas sustancias químicas, de estar presentes, podrían suponer un riesgo para la salud [2,3].

En este trabajo se utilizan distintas técnicas analíticas sencillas y rápidas con las que obtener una identificación y una primera aproximación de los principales compuestos presentes en juguetes.

Así se utilizó el FT-IR para identificar el material con el que están hechos los juguetes, la fluorescencia de RX como técnica semicuantitativa que nos indica los principales metales que contienen los juguetes, y HS-GC-MS para el análisis de 49 compuestos orgánicos volátiles.

Se analizaron 7 muestras de juguetes obtenidos en una tienda local. Los resultados muestran presencia de algunos compuestos tóxicos demostrando la idoneidad de estas técnicas para la caracterización de dichas muestras.

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Pharmaceutical cocrystallization techniques: advances and challenges

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Active pharmaceutical ingredients (API) with inappropriate properties and interesting pharmaceutical activity are one of the actual problems in pharmaceutical industry. Cocrystallization have been surged as method capable of improve API properties, such as solubility, bioavailability and stability, maintaining the pharmacological activity. Cocrystals are homogenous (single-phase) crystalline structures composed by two or more components in a definite stoichiometric ratio bonded together by noncovalent bonds.[1] The necessity for high-throughput screening methods and scalable methods still hinders the use of cocrystals by the pharmaceutical industry. The aim of this poster is to present an overview of the already reported cocrystallization methods, focusing in the specificities of each technique. Methods advantages and disadvantages are also reported. The cocrystallization methods are classified as solvent-based and solvent-free methods (Figure 1), and also they are indicated as more appropriate for screening, laboratory or industrial scale.[2]

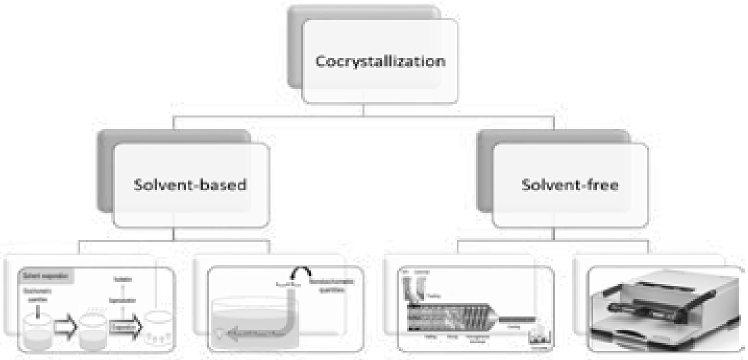

Figure 1: Scheme representing the classification of the cocrystallization methods.

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Histamine detection by electrochemical sensors employing commercial and non-commercial instrumentation

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The concentration of histamine is a widely recognized indicator of fish safety and quality. Due to its toxicity, histamine is the only biogenic amine of which the maximum concentration is legally established (according to European Regulation, fish samples cannot exceed 200 mg·kg^{-1}) [1]. Conventional methods for histamine analysis, that mainly involve chromatographic techniques, are time consuming and require expensive and complex instrumentation [2]. Electrochemical sensors are an interesting alternative since they offer a simple, low cost and user-friendly solution. Therefore, in this work, an enzymatic sensor coupled with a small-size potentiostat was developed with the aim of creating a portable device that allows the monitorization of histamine in fish along the whole food chain, from fishing to costumer. The electrochemical sensor was based on miniaturized electrodes (screen-printed carbon electrodes) and diamine oxidase. For signal transduction a platform capable of performing amperometric and voltammetric measurements was developed. This platform was designed and assembled as a compact-size prototype with a complete software package for data acquisition. The results obtained with the developed platform were compared with those obtained by a commercial potentiostat/galvanostat.

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QA21

Development of a genoassay for the transgenic soybean detection using a surface response methodology

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The production of genetically modified (GM) food that is resistant to insects and viruses has alarmed the public on the potential health risks with resulting DNA recombinant technology [1]. The security of GM food consumption and its impact towards environment and health are still not known until the present time [2].

To protect consumers, the traceability of GM products (food or feed) on the EU market is regulated by mandatory labelling rules (Regulation EC nº1830/2003). Consequently, the application of electrochemical biosensors in the field of food analysis represents a promising technique to explore because it answers to the demands of high sensitivity, specificity, and fast analysis. Moreover, these devices have potential to be used by food processors and regulatory authorities in order to verify and insure the compliance of the legislation.

In this work, an electrochemical genoassay for detection of an 84-mer DNA sequence encoding part of the transgenic soybean was developed. This genoassay is based on a sandwich format, which allows shortening the capture probe and improving the selectivity, while avoiding the labelling of the target. Superparamagnetic core/shell iron oxide/gold (Fe_3O_4@Au) nanoparticles were used as a platform for the design of the genoassay. Briefly, the construction of the assay involved four steps: i) Fe_3O_4@Au surface modification via binary self-assembled monolayers (SAMs), ii) covalent immobilization of aminated DNA capture probes, iii) hybridization of the complementary DNA sequence by using a sandwich format assay, and iv) chronoamperometric signal detection.

The optimization of the composition of the sensing phase is critical to get the best analytical performance. Considering that the Design of experiments approach has proved to be a powerful tool in Analytical Chemistry, this study was focused on the optimization of all genoassay phase construction using a sequential Response Surface Methodology to achieve a reliable and low-cost technology for the transgenic soybean detection. First, a 24-run Plackett-Burman design with two blocks representing each DNA target concentration was carried out. After detecting the most influential control factors that produce the biggest impact on the response (steady-state current intensity), a 4-factor Box-Behnken design with 6 blocks varying 2 factors each block and 4 center points was conducted. The purpose was to predict possible quadratic terms that may provide curvature to the surface response model. The data was fitted to a polynomial equation using stepwise multiple linear regression and the optimal factor values were obtained by numerical optimization.

It was concluded that the conditions that maximized the performance of this assay was: DNA capture probe concentration at the low level (0.25 μmol·L^{-1}), homogeneous hybridization temperature at the low level (22 ºC) and DNA target concentration at the high level (10 nmol·L^{-1}).

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Exploring the acetylacetone derivatization for the GDME extraction and determination of formaldehyde

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Since a long time ago, when it was first described by Nash and co-workers [1], the acetylacetone reaction has been one of the best options for formaldehyde derivatization. The reaction of formaldehyde with acetylacetone, in the presence of excess ammonium salt, forms 3,5-diacetyl-1,4-dihydrolutidine (DDL), which has a yellow colour that can be spectrophotometrically determined at 412 nm. Acetylacetone is mostly used due to its high selectivity towards formaldehyde. This procedure is present in different European and international standard procedures for the determination of formaldehyde in wood-based products, such as in EN 717-3 and ISO 12460-5 [2]. Usually, a derivatization period of one hour is used before the spectrophotometric analysis, with the solution sheltered from light, as the derivatization product DDL decomposes on exposure to heat or light.

In gas-diffusion microextraction (GDME) [3, 4] experiments, the presence of a derivatization reagent in the acceptor solution, which can be chosen according to the desired analyte and detection technique, increases the selectivity, sensitivity and the enrichment factors of the extraction with GDME. Moreover, the derivatization can be performed simultaneously with the extraction, which simplifies the overall procedure.

In this work, we assess the stability of the formaldehyde-acetylacetone derivative (DDL) over a defined period of time. Kinetic studies were performed by continuously measuring the absorbance at 412 nm over extracts obtained from the GDME extraction of wood-based panels. Different parameters and its influence on the derivatization reaction were evaluated, such as the temperature of extraction or the spiking of the sample.

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QA23

Modificación de electrodos con dispersiones de nanotubos de carbono en polivinilpirrolidona y su aplicación a la evaluación del contenido de polifenoles en vino

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En esta comunicación se describe el desarrollo de un nuevo método para la evaluación rápida del contenido de polifenoles en vino. Está basado en la modificación de electrodos de carbono vítreo con una capa de nanotubos de carbono (NTC), los cuales permiten obtener la señal analítica debida a la oxidación electroquímica de los polifenoles a potenciales moderados. La presencia de nanotubos de carbono en la interfase de transducción tiene un efecto beneficioso en la electroquímica del proceso electródico que permite la detección de los polifenoles, mejorando claramente el funcionamiento observado en el electrodo sin modificar.

La capa de nanotubos de carbono se obtuvo a partir de dispersiones acuosas del nanomaterial. Para ello se toma un volumen adecuado de las mismas, se deposita sobre la superficie del electrodo de carbono vítreo y se deja evaporar el disolvente. El polímero de polivinilpirrolidona (PVP) se empleó para ayudar en el proceso de dispersión de los nanotubos de carbono mediante tratamiento ultrasónico. El procedimiento óptimo para obtener una dispersión adecuada consistió en: *1)* 2,0 mg de NTC se dispersaron en 4,0 ml de disolución de PVP al 0,10% (p / p) mediante tratamiento ultrasónico, aplicando 2000 J de energía; *2)* las dispersiones se centrifugaron a 2500 rpm durante 40 minutos; y *3)* se recogieron los sobrenadantes conteniendo el nanomaterial disperso.

Los electrodos modificados con la capa de NTC se acoplaron a un Sistema de análisis por inyección en flujo (FIA), mostrando excelentes propiedades analíticas en la detección de diferentes polifenoles encontrados habitualmente en el vino, destacando su buena sensibilidad, amplio intervalo de respuesta lineal (típicamente de 2 a 200 mM) y excelente estabilidad. Este comportamiento permitió la estimación del contenido total de polifenoles en múltiples muestras de vinos blancos (30 muestras por hora) gracias a la notable estabilidad de la señal durante las mediciones, sin observar pérdidas de señal ni efecto "memoria". Además, la metodología propuesta posibilitó la detección de diferentes grupos de polifenoles simplemente ajustando adecuadamente el potencial de detección.

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Determinación de microplásticos en mejillones

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El plástico constituye uno de los contaminantes más comunes y persistentes en el medio marino, pudiendo representar entre el 60 y el 80% de la basura marina total. La fracción que en la actualidad preocupa más son los microplásticos –MP- (partículas plásticas menores de 5 mm) ya que pueden causar daños en la cadena trófica. El principal riesgo asociado a los microplásticos es su biodisponibilidad para los organismos marinos que los pueden ingerir [1]. Diferentes estudios han demostrado los efectos potenciales sobre la biota, como el bloqueo intestinal, la disminución de la movilidad o la muerte [2]. Además, los MP pueden adsorber compuestos tóxicos persistentes presentes en el agua de mar, introduciendo contaminantes en los organismos. Tales contaminantes pueden ser aditivos de la producción del plástico y/o contaminantes hidrofóbicos presentes en el medio marino.

Los mejillones son candidatos excelentes para evaluar la presencia de microplásticos en el medio marino ya que filtran grandes volúmenes de agua cuando se alimentan. La extracción de los microplásticos de bivalvos, en particular en mejillones, se suele realizar mediante digestiones químicas empleando uno o más reactivos (KOH, H_2O_2), pudiendo causar daños en las partículas de plástico y dificultar su medición mediante microespectroscopia infrarroja [3].

Por este motivo, se ha propuesto el uso de digestiones enzimáticas para eliminar la materia orgánica y no dañar a las partículas de microplásticos. El objetivo de este trabajo es, por tanto, implementar un procedimiento para la determinación de microplásticos en muestras de mejillones mediante digestión enzimática (usando proteasa y lipasa). La identificación y caracterización de los microplásticos se realizó mediante μFTIR**.**

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Merging zones approach in a flow-based platform for the determination of the total protein content in microbiological samples

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Lactic acid bacteria (LAB) can produce bacteriocins, that are a portion of the total protein content produced during fermentation. Bacteriocins are peptides or proteins synthesized by bacteria and archaea with a bacteriostatic or bactericidal activity over principally closely related species (e.g., *Listeria monocytogenes*) [1]. These bacteriocins have a wide variety of applications. From the food industry, where bacteriocins can be incorporated in food products susceptible to microbial contamination, reducing the probability of consumer's infection by some of the most prominent pathogenic bacteria; to pharmaceutical industry, where these peptides can be used as a viable alternative to antibiotics due to the emergence of multiple antibiotic-resistant bacteria [2]. Thus, it is important to have a tool to monitor the production of the protein content that is being produced in the fermentation process.

Flow-based methods are well known for their efficiency in the execution of several analytical steps. These systems have started as automation tools for wet chemical analysis and further used in biochemical assays [3]. In this context, an automatic methodology in a flow injection analysis (FIA) platform based on a Lowry assay for the determination of the total protein content produced by lactic acid bacteria (LAB) was developed. This methodology is based in two steps: i) binding of Cu2+ to the protein, resulting in the reduction of the Cu^{2+} to Cu(I); and ii) oxidation of Cu(I) by the Folin-Ciocalteu reagent (FCr). In the last step, the FCr is reduced producing a colour change that can be monitored at 750 nm [4,5].

With the developed methodology it was possible to establish a linear relationship up to 0.5 g/L of BSA (model protein) with a limit of detection of 0.05 g/L. A low consumption of sample and reagents was also achieved by using a merging zones approach with a determination rate of about 90 determinations per hour.

Since the matrix of interest, fermented culture media, is very complex, the possible interferences from the compounds of the chemically defined culture medium will be evaluated and the system will be applied to the quantification of the total protein content produced in a chemically defined media.

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construction and evaluation of a *vicia villosa* biosensor for cancer-associated tn antigen

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Classical methods used in the clinical field for detection of antigens, like ELISA, are time-consuming, tedious, and often require extra care and expensive instruments [1]. Biosensors are a simple and rapid technology platform, useful for the detection of specific structures or molecules, particularly adequate for clinical analysis [2-4].

Lectins have been widely used as tools for the study of glycoconjugates, glycoproteins and glycomes, for histochemistry and cytochemistry techniques and for the study of physiological and pathological processes including cell differentiation and cancer.

This work describes the development of a label-free biosensor for selective detection and discrimination of the cancer-associated Tn antigen, using *Vicia villosa* agglutinin (VVA) as the recognition element. The VVA biosensor was constructed by immobilizing the lectin on screen-printed gold electrodes. Formation of complexes between VVA and Tn-containing glycoproteins (asialo-bovine submaxillary mucin and asialofetuin) were monitored by electrochemical impedance spectroscopy, measuring the impedance increase of the biosensor after incubating the sample.

The biosensor response was related to the glycoprotein amount applied on the sensor surface and asialofetuin amounts down to 2.5 ng still caused an increase in impedance of 5.9%. Albumin, the most abundant serum protein, did not interfere in the detection of the Tn-carrying glycoproteins up to a concentration of 0.01 mg ml^{-1}. The developed lectin-based biosensor was used to evaluate the Tn-expression in serum samples and allowed to discriminate samples from healthy individuals and patients with different types of carcinomas, where the increased expression of Tn aberrant glycans is well established.

The advantage of this approach is that no labeled molecules are required to detect the binding event, which simplifies the biosensor design [5]. The construction procedure is simple, does not require any sophisticated equipment and demonstrated to be reproducible. Therefore the biosensor can be easily constructed in any laboratory. Furthermore, it consumes minute volumes of reagents, including the biorecognition element, minimizing the cost per biosensor. After the construction, the biosensor can be stored at 4ºC for three days without losing the sensing performance.

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Preparação e caracterização de membranas com base em biopolímeros

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Nos últimos anos, houve um decréscimo nos recursos naturais, bem como um aumento no impacto negativo que os resíduos das empresas nos processos produtivos têm sobre o meio natural, pelo que levou ao surgimento da "economia circular e sustentável". Os elevados desperdícios da indústria pesqueira e afins representam um grave problema ambiental e social, pelo que, dentro deste tema, o objetivo do presente trabalho é o aproveitamento de componentes extraídos de desperdícios ou sub-produtos desta indústria de modo a explorar a sua potencial aplicação na área dos sensores de metais pesados com base em membranas.

A preparação das membranas baseou-se na utilização de biopolímeros chamados glicosaminoglicanos (GAG) ou outros polissacáridos sulfatados, tais como, quitosano, sulfato de condroitina e fucoidano, extraídos dos desperdícios, nomeadamente de crustáceos, peixes e algas castanhas, respetivamente.

Diferentes membranas foram sintetizadas com base em dois biopolímeros, otimizando uma síntese já descrita na literatura e adaptando-a para outros biopolímeros.[1] Foram ainda sintetizadas membranas com base em biopolímeros e siloxanos, ajustando o método já descrito e recriando para outros biopolímeros.[2] Devido às estruturas químicas flexíveis destes biopolímeros **é** possível recorrer à impressão molecular para melhorar a selectividade e capacidade destas membranas para um determinado catião metálico, tendo sido aplicado esta técnica a estas membranas. Esta técnica é algo ainda não muito presente na literatura para este tipo de membranas, existindo apenas um artigo sobre a impressão de um catião metálico em membrana de quitosano.[3] Diferentes técnicas de caracterização foram utilizadas, entre as quais, FTIR e TGA, que permitiram determinar o sucesso da incorporação dos biopolímeros e as alterações no espetros na presença de catião, possibilitam a confirmação da presença deste catião.

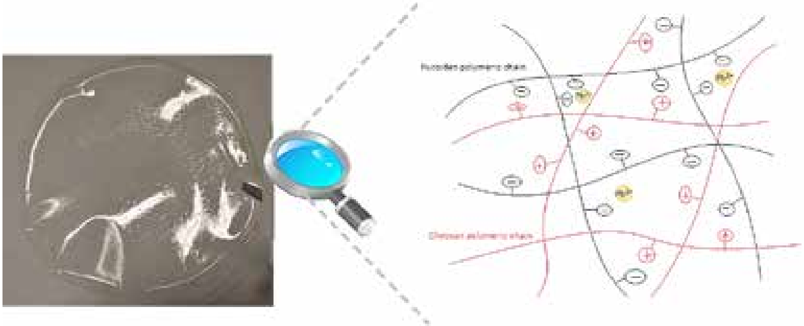

Figura 1 – Imagem de uma membrana com esquema de reticulação e exemplo de interações entre cadeias e catião metálico

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Metabolic evaluation of coffee beans cultivated in different plant densitied

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Coffea arabica is cultivated in monoculture and agroforestry systems. One important agronomic aspect that characterizes different planting systems is the number of plants per hectare.The aim of this study was to verify if different planting densities in coffee cultivated in monoculture influence the metabolomic profile of coffee beans. Coffee plants were cultivated under two high planting densities (10,000 - R10 and 6000 - R6 plants ha^{-1}). The metabolites were extracted according to a simplex-centroid design consisting of ethanol (e), acetone (a), dichloromethane (d) and hexane (h). The crude extracts were analyzed by FTIR (4000-675 cm^{-1}). Principal Component Analysis (PCA) was applied to FTIR spectra for fingerprint evaluation, as well as to explore the spectroscopic differences of chemical compositions for different densities and extraction solvents.

Figure 1 shows the score plot for PC1 vs. PC2. PC1 discriminated between sample extracts with ethanol (on the positive side) and without ethanol (on the negative side) for their extracting solvent compositions. The loading values indicated that bands around 2924; 2854; 1745 cm^{-1}, were important for extracts prepared containing ethanol. PC2 differentiated the samples according to the planting density; on the negative side the R10 extracts were grouped with the R6 extracts the positive side. The negative loading values for PC2 showed that the bands at 2934, 2858, 1752 and 1472 cm^{-1} contributed to the low values of the R10 extracts whereas those at 2915; 2847 and 1735 cm^{-1} with positive loading values to the higher R6 extract values. Bands around 2924 and 2855 can be assigned to asymmetrical C–H stretching (CH_2) and symmetrical C–H stretching (CH_2) with a weak shoulder at 2954 cm^{-1} caused by the methylene asymmetrical stretching band. Already bands around 1745 and 1472 cm^{-1} may correspond the C=O stretching of aliphatic ester and the symmetrical angular deformations of methylene groups, respectively. These groups may be present in the fatty acids already studied in coffee [1,2]. The adjacent bands provided by the loadings indicate the possibility that different fatty acids could discriminate the grain extracts from different planting densities. Thus the FTIR fingerprints associated with PCA showed spectral differences between grain extracts of coffee plants cultivated at two planting densities and extracted by extractive solvents with or without ethanol.

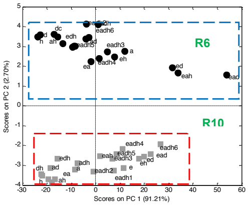

Fig.1. PC1 x PC2 score plot for FTIR

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An automatic evaluation of the β-Galactosidase activity

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The implementation of biocatalytic procedures in flow systems, namely SIA, as an alternative to conventional batch assays, assures a strict control of the reaction conditions, allowing the maximization of enzyme activity [1]. These features are a consequence of the minimization of operator intervention, and of the high reproducibility of the small sample volumes aspirated with a precise timing for mixing and detection, essential for kinetic measurements. Besides, one can obtain simplicity, robustness, and minimization of effluent produced which all contributing to a green chemistry [2].

The main goal of this work is to evaluate the activity of the enzyme β-galactosidase by an automated methodology with use of sequential injection analysis (SIA). β-Galactosidase (β-gal) is a glycoside hydrolase enzyme responsible for the hydrolysis of β-galactosides into monosaccharides by breaking the glyosidic bond. β-galactosidase is important for organisms as it is a key provider in the production of energy and a source of carbons through the breakdown of lactose to galactose and glucose. This enzyme has been used as a biochemical marker in different fields as environment to identify sources of pollution [3] or in biology to study health problems [4].

In our work the substrate is 4-methylumbelliferyl-β-d-galactopyranoside (4-MUG) that after hydrolysis, results in a fluorophore that is monitored at an emission/excitation wavelength of 365/460nm, allowing to measure the enzyme activity in different conditions [5].

To estimate the best conditions for the biocatalytic action of the enzyme several parameters on the assay are assessed, namely media composition, pH, temperature, the residence time of the sample in the system, substrate and enzyme concentrations.

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Determinación indirecta de ésteres de 3-mcpd mediante hidrólisis enzimática y gc-ms

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Durante el procesado de alimentos a altas temperaturas se generan compuestos potencialmente tóxicos, como los ésteres de ácidos grasos de cloropropanoles, que disminuyen el valor nutricional del alimento, tienen una incidencia negativa en la salud de los consumidores y representan una constante preocupación de agencias como la FDA, la EFSA y AECOSAN [1]. Destaca el 3-MCPD (3-monocloropropano-1,2-diol) y sus ésteres, que se forman a altas temperaturas durante la etapa de desodorización en el proceso de refinado de los aceites. La International Agency for Research on Cancer (IARC) ha clasificado el 3-MCPD y sus ésteres como potencialmente cancerígenos [2]. Al entrar al organismo, los ésteres de 3-MCPD sufren una hidrólisis enzimática en el tracto intestinal y finalmente se libera 3-MCPD libre. Por ello, es importante investigar la presencia de estos contaminantes en los aceites comerciales [3].

En este estudio se ha optimizado nueva metodología analítica para evaluar el 3-MCPD y sus ésteres con diferentes ácidos grasos mediante GC-MS. Se ha estudiado la idoneidad de una hidrólisis enzimática (Amano Lipasa de *Burkholderia cepacia*) de los ésteres, seguida de una microextracción líquido-líquido dispersiva (DLLME) incluyendo la derivatización del 3-MCPD con N-Heptafluorobutirilimidazol (HFBI). Se evaluaron diferentes temperaturas de sonicación (20°C, 37°C y 50°C), diferentes pH (pH 5 y pH 7) y tiempo de ultrasonidos (2, 5 y 10 min). El método se ha aplicado al análisis de diferentes muestras de aceites comerciales para evaluar el alcance real de dichos compuestos en los consumidores.

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Development of a MIP-based sensor for ecstasy

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In the present study, an electrochemical sensor based on molecularly imprinted polymers (MIPs) to selectively quantify 3,4-methylenedioxymethamphetamine (MDMA, also known as ecstasy in biological samples was developed. The sensor was constructed through electrochemical polymerization of *o*-phenylenediamine (*o*-PD), in the presence of the analyte MDMA, thus forming a MIP, on the surface of a portable screen-printed carbon electrode (SPCE).

The step-by-step construction of the SPCE-MIP (Figure 1) was studied by cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS) and scanning electron microscopy (SEM). The analytical quantification of MDMA was performed by directly measuring the anodic current of its oxidation signal through square-wave voltammetry (SWV).

Experimental parameters that affected the performance of the SPCE-MIP sensor were optimized, such as the monomer/template ratio, the number of electropolymerization scanning cycles, and the incubation period. Optimized sensors exhibited suitable selectivity in comparison with endogenous and non-endogenous compounds with similar chemical structures, namely epinephrine, norepinephrine, dopamine, tyramine, amphetamine and methamphetamine. Moreover, sensors showed good repeatability (2.6%) and reproducibility (7.7%) as well as a stable response up to one month. A linear range of up to 0.2 mmol L^{-1} was achieved with an r^2 of 0.9990 and a limit of detection (LOD) and quantification (LOQ) of 0.79 and 2.6 μmol L^{-1}, respectively. The proposed sensor was successfully applied to biological samples, namely human blood serum and urine samples, showing its potential for application in medicine and in forensic sciences.

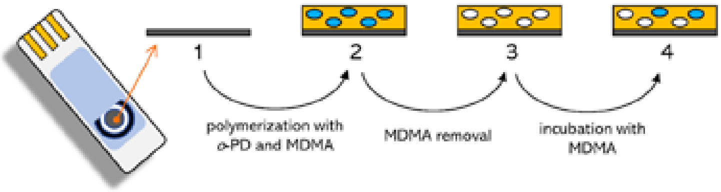

Figure 1 – Schematic illustration of the construction of the MIP-SPCE sensor.

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Automatic methodology to perform loading of 5-fluorouracil from mesoporous silicon nanoparticles

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An automatic methodology based on sequential injection analysis (SIA) was developed to perform the loading of the anticancer drug 5-fluorouracil (5-FU) from porous silicon (PSi) nanoparticles (NPs).

The most common loading method is the immersion method, although other methods can be used to incorporate drugs into mesoporous silicon (PSi) NPs, such as impregnation or covalent attachment. Thereby, this drugs may be efficiently loaded, although the adsorption of the drug on the surface is difficult to control and it usually requires some time to complete [1].

The loading assay was conducted with the purpose of reducing the time to load 5-FU into the PSi NPs, not affecting the reproducibility and the %-drug loading normally obtained in batch procedures. The assay was made in strictly aqueous media and the parameters optimized were: the sequence and number of 5-FU and PSi NPs aliquots, as well as the aspiration and propulsion flow rates of them in the SIA system.

Four different functionalized PSi nanoparticles were used for drug loading and the conditions procedures were studied in the SIA system.

About the results, the time spent to perform SIA assays is much smaller (4 min) than the time spent in batch procedure (2 h). Batch and SIA methods were tested and compared for the different behaviours of the PSi nanoparticles towards both methodologies and comparing the results obtained in loading SIA system with the ones obtained using batch procedure by Student's t-test, for a 95% confidence interval, showing that there are no significant differences between Besides its environment friendly due to the low volumes spent and effluents produced.

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Modificação da química de superfície de pontos quânticos de CdTe para a determinação de iões metálicos

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Os pontos quânticos semicondutores (do inglês quantum dots, QDs) são nanomateriais adequados para o desenvolvimento de metodologias analíticas baseadas em fotoluminescência para a deteção e quantificação de iões metálicos devido às suas notáveis propriedades óticas, que incluem i) altos rendimentos quânticos garantindo maior sensibilidade; ii) bandas de absorção amplas que permitem a fotoexcitação simultânea de múltiplos QDs de tamanhos distintos, cada um emitindo luz num comprimento de onda específico; iii) bandas de emissão estreitas minimizando a sobreposição e simplificando consideravelmente a discriminação da resposta ao analíto [1].

Tendo em conta que a química da superfície dos QDs assim como a natureza do agente estabilizador (capping ligand) afeta a reatividade dos QDs em termos de seletividade e sensibilidade, foram avaliados o uso de uma variedade de ligandos orgânicos com grupos funcionais distintos no estudo da interação dos pontos quânticos de CdTe com diferentes iões metálicos, tais como, Hg^{2+}, Cu^{2+} e Ag^{+}. Parâmetros como constantes de Stern-Volmer, constantes de ligação de equilíbrio e os valores do tempo de semi-vida de fluorescência foram estudados de forma a aferir a reatividade de cada um dos agentes estabilizadores testados em relação ao Hg^{2+}, Cu^{2+} e Ag^{+}.

Devido à grande reatividade demonstrada pelos QDs, a seletividade pode tornar-se um grande problema na aplicação de pontos quânticos semicondutores em análises químicas. Sendo assim, neste trabalho foi estudada a combinação na mesma análise de múltiplos QDs, estabilizados com ligandos distintos e emitindo em diferentes comprimentos de onda, de forma a obter um perfil específico de resposta a um determinado analíto. Adicionalmente foram utilizadas ferramentas quimiométricas para análise e processamento de dados, permitindo assim aumentar significativamente a seletividade, exatidão e precisão da metodologia proposta. Os resultados obtidos de todos os modelos PLS demonstraram a possibilidade de realizar previsões exatas e precisas de Hg^{2+} e Cu^{2+} (R^2_{CV} próximo de 1, RMSEC e RMSECV a variar entre 0,0094-0,15 e 0,013-0,19 mg L^{-1}, respetivamente). Além disso, a sensibilidade dos modelos desenvolvidos também foi calculada e foi possível concluir qual a combinação de QDs assegurou uma quantificação mais sensível do Cu^{2+} (sensibilidade = 653 L^{-1} mg para sonda conjugada MPA/MPA) e do Hg^{2+} (sensibilidade = 14017 L^{-1} mg para sonda conjugada com GSH/MPA).

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Evaluation of analytical potential of fluorescence resonance energy transfer (FRET) sensing combining CdTe quantum dots and Au nanoparticles for chemical analysis

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The focus of this work is the study and analytical exploitation of the fluorescence resonance energy transfer (FRET) process between mercaptopropionic acid (MPA)-capped CdTe quantum dots (QDs) and cysteamine (CS)-capped Au nanoparticles. In the developed system, selected target analytes were capable of interacting with either the CdTe QDs, acting as energy donors [1], or the Au nanoparticles (AuNPs), behaving as energy acceptors [2], yielding a concentration-related modulation of the FRET efficiency between both nanoparticles. Distinct mechanisms, involving modification of the QDs quantum yield (QY), AuNPs agglomeration, nanoparticles detachment, etc, could be proposed to explain the referred FRET modulation. The proposed approach confirmed a great prospective for implementing rapid, simple and reliable sensing methodologies for the monitoring of relevant pharmaceutical, food and environmental species. Moreover, it shows a great analytical versatility since it is possible to easily adapt the surface chemistry of both QDs and AuNPs to the chemical nature of the target analyte.

POSTER

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Aplicación de microextracción líquido- líquido dispersiva asistida por ultrasonidos a la determinación de catinonas sintéticas y drogas de abuso en saliva

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El Informe Europeo sobre Drogas de 2018 del Observatorio Europeo de las Drogas y las Toxicomanías (EMCDDA) ofrece una revisión de las últimas tendencias y pautas de consumo de drogas en Europa en 2018. La oferta y consumo de nuevas sustancias psicoactivas (NSP) es un problema creciente y un riesgo para la salud pública, cuyo control supone un reto multidisciplinar que incluye el desarrollo de metodológias bioanalíticas rápidas y eficaces [1]. Las catinonas sintéticas están relacionadas químicamente con la catinona, un estimulante natural procedente de la planta *Catha edulis*, cuyos efectos son parecidos a los de drogas estimulantes ilegales comunes como la anfetamina, la cocaína y la MDMA. Las catinonas sintéticas constituyen el segundo grupo de nuevas sustancias psicoactivas (NSP) vigiladas por el EMCDDA; en Europa se ha detectado un total de 130, de ellas 12 por primera vez en 2017 [1].

El objetivo de este trabajo es incrementar y mejorar la investigación de NSP, para evaluar su consumo y afrontar su prevención y tratamiento. Para ello, se propone el desarrollo y validación de estrategias analíticas para la determinación rápida de NSP (20 drogas ilícitas incluyendo catinonas y escopolamina) en fluidos biológicos como saliva. La metodología de análisis se basa en la miniaturización de la etapa de preparación de muestra utilizando la técnica de microextracción líquido-líquido dispersiva (DLLME) asistida por ultrasonidos [2, 3]. Tras la optimización de variables que afectan a la microextracción (pH, volumen de muestra, disolventes de dispersión y extracción, volumen de disolventes y salting-out) el método fue validado y aplicado al análisis de muestras de fluido oral.

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Free malondialdehyde analysis in oil samples using a new gas-diffusion microextraction by HPLC-FLD-UV

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Under the influence heat, temperature, light, time of exposure, and others, oil and oil-based foodstuff are submitted to a series of chemical and structural change giving rise to undesirable contaminants such as malondialdehyde (MDA) which is the primary and more stable lipid peroxidation product, and its toxicity is due to its reactivity with nucleic acids. [1-3]

A new effective, rapid and easy method is proposed using a gas-diffusion microextraction (GDME) procedure for the extraction of MDA from oil samples and in situ Thiobarbituric acid (TBA) derivatization for HPLC-FLD-UV analysis. [4]

The extractive device is placed in a flask containing the sample, which is heated to enhance the pass of MDA to headspace and the transfer through a microporous hydrophobic membrane to the acceptor solution containing TBA derivative reagent, then MDA-TBA adduct is analyzed by HPLC-FLD-UV.

Factors such as TBA concentration, sample amount, reaction time and temperature have been studied using a symmetrical factorial design $3^4//3^2$. GDME-HPLC-FLD-UV has been validated regarding linearity, repeatability, reproducibility and was applied to various oil samples to assess MDA presence.

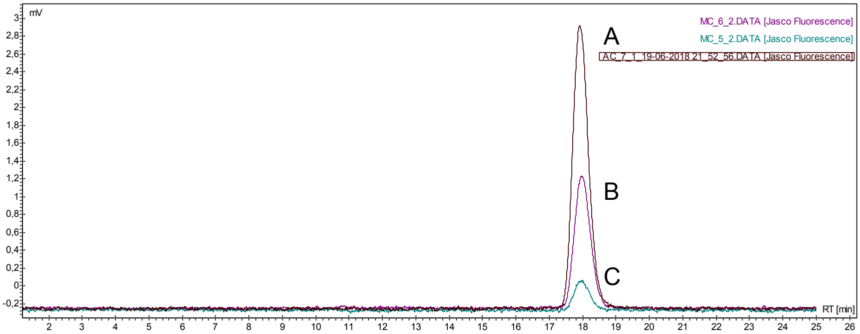

Fig.1. MDA in oil samples A. 10µg·g-1 MDA spiked sample, B. Refined peanut oil, C. Virgin sesame oil

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Validación dun analizador automático para a determinación de ácidos orgánicos en viños

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Os ácidos orgánicos son os responsables do carácter ácido que posúen os viños e constitúen un dos elementos máis importantes na elaboración dun viño xunto cos azucres, xa que son os metabolitos primarios relacionados coa calidade do viño. Algúns están presentes de forma natural no zume da uva coma o ácido tartárico, ácido málico e ácido cítrico. Outros orixínanse durante a fermentación do zume da uva e durante a conservación do viño, que son o ácido láctico, ácido acético e ácido succínico. O perfil e os niveis de concentración dos ácidos orgánicos son moi importantes, posto que teñen grande influenza na estabilidade química e no pH así coma no aroma e sabor do viño. O contido de ácidos orgánicos no viño está relacionado coa variedade da uva, coa rexión xeográfica e coas condicións climáticas durante o crecemento e colleita da uva, asemade coas técnicas de vinificación [1].

A acidez dun viño pódese clasificar en dúas categorías: a acidez volátil, que está representada polo ácido acético, e a acidez total, que se expresa en forma de ácido tartárico. A acidez é un dos parámetros que debe ser avaliado en tódalas etapas da elaboración do viño (Regulamento CE Nº 607/2009) [2]. Para a acidez volátil o límite máximo permitido é de 1.08 g/L para viños brancos e 1.2 g/L para viños tintos, expresados en ácido acético. Para a acidez total, expresada en ácido tartárico, a cantidade non debe ser inferior a 3.5 g/L. Con respecto ao ácido cítrico, a Organización Internacional do Viño e da Viña (OIV) establece un contido máximo de 1 g/L [3].

Neste traballo levouse a cabo a validación dun analizador automático para a determinación de ácidos orgánicos en viños. O procedemento baséase nunha serie de reaccións químicas (ácido tartárico) e enzimáticas (ácidos acético, cítrico, láctico e málico) para unha posterior lectura fotométrica no propio rotor de reacción. Os métodos enzimáticos baséanse no uso de enzimas deshidroxenasas en presenza de NADH para formar NAD^+, cuxa absorbancia se mide a 340 nm. No caso do ácido tartárico a determinación realízase mediante reacción cunha sal de vanadio en medio ácido para xerar un complexo coloreado que absorbe a 520 nm.

Os métodos validáronse en termos de linealidade, sensibilidade, precisión e exactitude, empregando mostras procedentes de ensaios colaborativos (BIPEA), obténdose resultados satisfactorios. Ademais os métodos foron aplicados **á** análise de diferentes tipos de viños, tanto tintos coma brancos de diferentes anos, procedencias e variedades. Cumpre salientar que este equipo permite múltiples configuracións, gran rapidez de análise, emprego dun reducido volume de mostras e reactivos, o que unido a un mantemento mínimo supón unha redución notable nos custos do laboratorio.

AGRADECEMENTOS: J.F. Campo-Martínez agradece ao Laboratorio Agrario e Fitopatolóxico de Galicia polo seu acollemento para a realización de prácticas e poñer a súa disposición tódolos recursos posibles para a realización deste traballo.

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Optimization of microextraction by packed sorbent (meps) for new psychoactive substances and z-drugs in human plasma samples by uplc-ms/ms.

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New psychoactive substances (NPS) market is constantly growing. These compounds are not covered by drug controls, so they are marketed as "legal" drugs replacements for illicit drugs. Designer benzodiazepines (DBZD) have recently emerged as medicines in some countries (such as phenazepam in Russia), in "self-medication" cases (for insomnia or daily stress) or as drugs in recreational environment [1]. In addition, non-medical consumption of prescription benzodiazepines is becoming a serious threat to public health throughout the world [2]. Because of the limited legislation issues and the limited biological information available for these NPS, it is necessary the development of new analytical methodology, as microextraction by packed sorbent (MEPS), capable of extracting and identifying them in human biological fluids [3].

The optimization of a microextraction by packed sorbent (MEPS) method has been carried out for 5 designer benzodiazepines (clonazolam, deschloroetizolam, nifoxipam, flubromazolam and meclonazepam) and 3 Z-drugs (zolpidem, zaleplon and zopiclone) in human plasma samples. The extracts were analyzed by ultra-performance liquid chromatography coupled to tandem mass spectrometry (UPLC-MS/MS). A chemometrics tool, such as experimental designs, was used to perform extraction parameters, for example: the type and volume of elution solvent, pH, number of extraction cycles, volume of washing solvent and type of sorbent.

AGRADECIMIENTOS**:** The authors would like to thank the Dirección General de Tráfico (Ministry of Interior, Spain), Project SPIP2015-01838, for their financial support.

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Thermal properties and molecular interactions of alginate/gelatin hydrogel microparticles

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Hydrogels are attractive materials for several engineering applications. They can be obtained, for example, from the combination of alginate and gelatin, and have been widely used in microencapsulation processes. In this work alginate/gelatin hydrogel microparticles were prepared based on the enzymatic crosslinking of gelatin (transglutaminase, TGase), and alginate gelation induced by calcium chloride ($CaCl_2$). The evaluated conditions to study thermal properties, and molecular interactions between microparticle's components where: gelatin amount (%wt, polymeric mixture-basis), TGase amounts (active units/$g_{gelatin}$) and contact time with $CaCl_2$ (min). Four samples were obtained. For sample 1 the evaluated conditions were: gelatin amount 25 %wt; TGase amounts 10 U/g and contact time with $CaCl_2$ 81 min. For samples 2, 3 and 4: gelatin amount 75 %wt, 75 %wt and 75 %wt; TGase amounts 10 U/g, 30 U/g and 30 U/g and contact time with $CaCl_2$ 81 min, 21 min and 81 min, relatively. One formulation composed only by alginate (MAlginate) was also produced for comparison. The contact time with $CaCl_2$ was 240 min.

Fourier transform infrared spectroscopy (FTIR) and differential scanning calorimetry (DSC) confirmed that the studied variables influence both, thermal properties and the developed molecular interactions between the two polymers (alginate and gelatin) (fig.1). FTIR results show that a higher contact time with $CaCl_2$ led to an increased level of alginate crosslinking. The use of TGase results in the increasing of the hydrogen bounded N-H groups. According to DSC results the use of TGase increases the thermal stability of crosslinked microparticles.

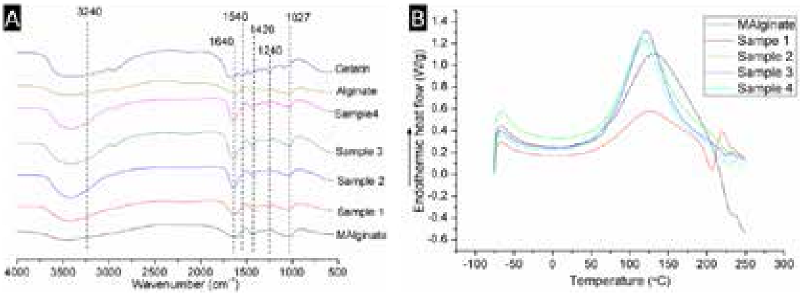

Fig.1. (A) FTIR spectra of pure gelatin, pure alginate, alginate microparticles (MAlginate) and gelatin/alginate microparticles (Samples 1, 2, 3 and 4); (B) DSC thermograms of MAlginate, and samples 1, 2, 3 and 4.

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Study of polymer additives migration on coated wires

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In normal operation conditions, coated wires are subjected to various types of stress, which can be electric (voltage and operating frequency), heat (room temperature variations, and operating temperature), mechanical (vibration, torsion) and environmental (moisture and contamination by chemical agents)[1]. Stress accelerates the aging process that can cause irreversible changes in the material damaging the required performance. In advanced cases of aging or from the manufacturing process defects, begins the process of degradation that can lead to rupture of the coating [2,3].
To understand the behavior of materials used as coating of wires, study was done using three different materials: PVC, XLPE and ETFE and materials were submitted to different working conditions, PVC is widely used as coating due to it chemical resistance [4] but working temperatures cannot exceed 125ºC. XPLE is an alternative to PVC that have seen the increase on the usage due their reusability, recyclability and recoverability. ETFE have been tested before as coating material for power cables and did not show changes in the polymeric structure [5,6,7]. It was mainly used as a standard in terms of material degradation. ETFE is used in small scale and it is mainly used due to his special thermal characteristics [8,9].
Microscopy and spectroscopy techniques were chosen to analyse materials and as conclusion it was seen that PVC gave worst results as some additives migrated to the wire cores creating some interactions on production processes.

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Micro-structured Fluorescent Powders for Detecting Latent Fingerprints on Different Types of Surfaces

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Benzazole dyes are known for their excellent photophysical properties, such as high fluorescence emission and large Stokes shift (ΔλST),[1] and have been widely applied in various fields of science.[2,3] However, their potential applications in forensic science, especially for latent fingerprint detection, are still poorly explored.

In this study, we developed micro-structured fluorescent powders based on benzazole dyes and a silica matrix using a simple procedure and evaluated the powders for fingerprint detection on different types (porous and non-porous) and colors (dark, white, and multi-colored) of surfaces.

To assess the efficiency of these proposed powders, comparisons were performed with commercially available black, white, and fluorescent powders (Sirchie®) for different types of surfaces. The developed micro-structured powders showed intense fluorescence emission in the blue-green region and created a sharp contrast with the fingerprint residues when exposed to long wavelengths of UV light (365 nm), producing distinct ridge details on all examined surfaces.

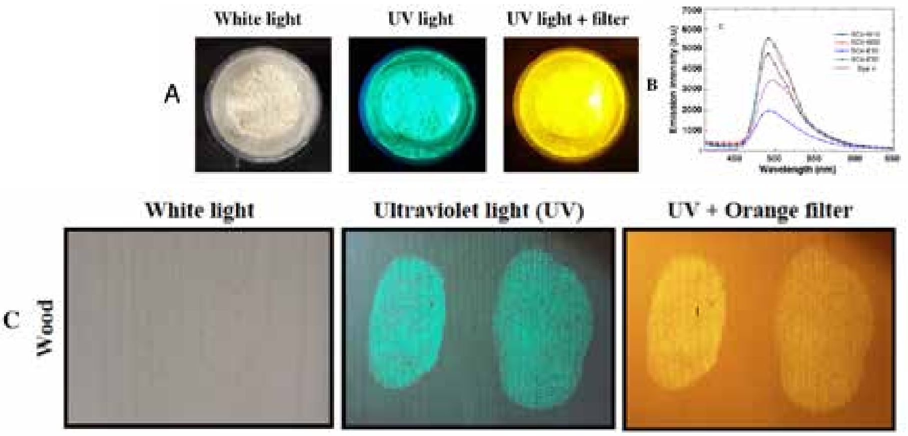

Fig.1. Images of fluorescente micro-powders under white and UV light (365 nm) with and without orange filter (A), fluorescence emission spectra (B), and latent fingerprint processed with proposed fluorescent micro-powders on porous surfaces (C).

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Selective capture of beta-pinene by molecularly imprinted polymers: freundlich isotherms obtained by gc-ms.

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Beta-pinene minus (CAS# 18172-67-3, C10H16, MW 136.23) is an important starting material for flavor and fragrance synthesis [1], that is usually distilled from turpentine (Leiria, Portugal) with its plus enantiomer. Further purification is costly and difficult. We were supplied with a molecularly imprinted polymer (MIP, code name "BP-MIP0005") specifically designed to capture beta-pinene-minus enantiomer and its corresponding non-molecularly imprinted polymer (NIP, code name BP-NIP0005) produced under the same experimental conditions in the absence of the target molecule. These MIP and NIP are polyurethanes that were produced by a new "bulk" technology and reduced to powder under pestle-and-mortar. The volatile target molecule was released from the MIP under reduced pressure, at room temperature.

Gas-Chromatography coupled with Mass Spectrometry (GC-MS) in Electron Impact mode (EI^+) was used to simultaneously identify and quantify the major terpenes present in 1/100000 (v/v) diluted turpentine (mixtures of alfa and beta-pinene, and limonene in two enantiomeric forms each, total of 6 enantiomers), before and after exposure to known amounts of MIP and NIP. Solutions of various pure enantiomers of the 3 chemicals in question were also used against MIP and NIP in known amounts. The amounts in solution above MIP and NIP were estimated by GC-MS, after 1 minute of vortex and centrifugation at 2500 rpm for 5 minutes. The difference in amount measured (NIP-MIP) was adjusted to a Freundlich isotherm [2].

Preliminary results obtained so far show that the MIP in question is capable of capturing beta-pinene-minus when it is exposed to it and is incapable of capturing alfa-pinene-minus and limonene-minus. Results with plus enantiomers are pending.

The results using turpentine dilutions show that beta-pinene is captured into the cubic picometer-sized pockets of the MIP, but GC-MS can not distinguish the minus and plus enantiomers. However, when the turpentine is further diluted the Freundlich isotherm shows no capture of beta-pinene in spite of the GC-MS detection of its presence. That constitutes a "smoking gun" that points to the possible enantiomeric selectivity of the MIP under investigation vis-à-vis beta-pinene-minus, a minor component when compared with beta-pinene-plus (<10%, v/v).

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Análise de Componentes Principais aplicada ao estudo da oxipropilação do resíduo da semente da *Araucaria angustifólia*

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A casca do pinhão brasileiro é um resíduo lenhocelulósico da semente da Araucaria angustifólia, uma espécie de conífera nativa da América do Sul. Esta semente é consumida após sofrer um processo de descasque, resultando na produção de uma quantidade significativa de resíduo sem valor comercial. Tendo por objetivo o desenvolvimento de aplicações para a valorização da casca do pinhão (PFS), este trabalho foca a produção de biopolióis a partir desta fonte lenhocelulósica através do processo de oxipropilação. O trabalho compreendeu o estudo da relação entre as variáveis do processo e as propriedades dos biopoliois, utilizando a metodologia de Análise de Componentes Principais (ACP). No que respeita à oxipropilação, selecionaram-se três razões PFS/óxido de propileno (PO) (30/70, 20/80 e 10/90; m/v). Testaram-se ainda quatro níveis de catalisador: 5, 10, 15 e 20%, (m/m, base biomassa). A oxipropilação ocorreu em condições moderadas de temperatura, pressão e tempo, resultando na produção de poliois líquidos. Numa segunda etapa, procedeu-se à caracterização dos biopoliois, no que respeita ao teor de homopolímero (POO), teor de grupos hidroxilo (IOH), viscosidade (V) e biomassa por reagir (UR) no biopoliol. Posteriormente, através da Análise de Componentes Principais, efetuou-se a avaliação das interações estabelecidas entre as variáveis do processo de oxipropilação e as propriedades dos poliois obtidos. A análise de ACP (Fig. 1) clarificou as interações estabelecidas, provando ser uma ferramenta útil para descrever e visualizar o processo de oxipropilação, com possibilidade de ser estendida a outros tipos de biomassa ou integrando diferentes variáveis de entrada.

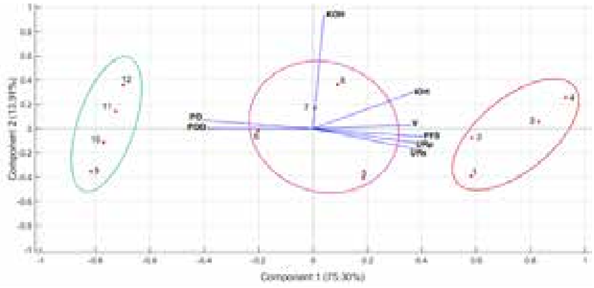

Fig.1. Biplot da ACP: óxido de propileno (PO), casca do pinhão (PFS), teor de catalisador (KOH), teor de homopolímero (POO), Teor de grupos hidroxilo (IOH), viscosidade (V), biomassa por reagir no poliol (UR).

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Freundlich isotherms: development of calculation models to determine adsorption of beta-pinene-minus from liquid solutions

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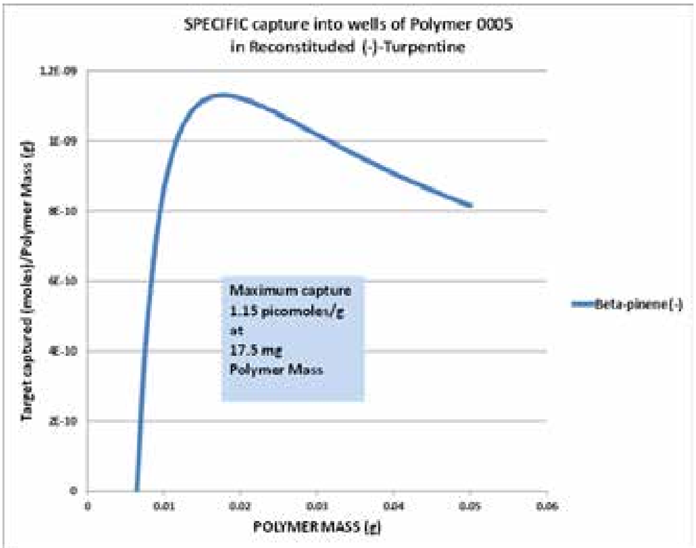
RAW DATA: two sets of concentrations (triplicates) of the major terpenes in turpentine (including beta-pinene) determined by GC-MS in supernatants after adsorption of liquid solutions to Molecularly Imprinted Polymer (MIP) and Non-Molecularly Imprinted Polymers (NIP), as a function of known amounts of insoluble polymer (0-50 mg scale). Calibration curves were prepared with the minus enantiomers of various terpenes.
SOFTWARE: Mathematical models were devised in Microsoft Excel spreadsheets, including the final graphs used for output.
ALGORITHM:
Step 1 - conversion of GC-MS signals to concentration averages;
Step 2 - adjustment of the two separate Freundlich [1] equations to the NIP and MIP amount adsorbed data sets, versus polymer mass;
Step 3 – The difference in amount measured (NIP-MIP) was adjusted to a Freundlich isotherm [1] as a function of polymer mass.
DATA OUTPUT:



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Evaluation of the removal of diclofenac sodium in water by electrocoagulation

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Emerging pollutants are potentially toxic substances with little knowledge about the effects on the environment, which are indispensable for today's society, such as pharmaceuticals, cosmetics and pesticides. These substances are introduced and distributed on a large scale to the environment and, in general, have significant potential to generate environmental impacts [1].

An emerging contaminant, diclofenac sodium is an anti-inflammatory drug. Its solubility in aqueous medium is insufficient to dissolve the entire dose in the gastrointestinal tract, with about 65% being excreted and taken by sanitary sewage into the environment. It presents great resistance to biological and chemical treatments, in addition to being bioaccumulative, and it is one of the most significant pharmaceutical active compounds present in the water medium [2, 3].

The objective of this work was to evaluate the efficiency of electrocoagulation in the treatment of water containing diclofenac sodium. The experiment was carried out in a 15x15x11cm acrylic vat, placed on a stirring plate under medium agitation. For the assembly of the monopolar reactor in parallel, 8 aluminum plates of 10x10 cm were placed in the tank, 1.0cm apart, with a total surface area of contact with the effluent of 0.880m². The electrodes were connected to a power supply and the pH was monitored. In the experiments performed in different combinations of pH values (3, 5, 7, 9 and 11), current density (12, 36 and 70 A/m²) and sodium chloride (1,0 and 2,0 g/L) and diclofenac sodium (0.03 a 0.07 g/L) concentrations, the removal varied between 27.83% and 56.50%. The best result was obtained with the experimental conditions of initial pH of 3, 1.0 g/L sodium chloride concentration, initially containing 0.05 g L of diclofenac and with current density of 12 A/m². The experiment showed efficiency in the removal of diclofenac sodium.

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As total y especies de As en arroz comercial en Ecuador y otros países de Latinoamérica y de la Península Ibérica.

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Es conocido que el Arsénico inorgánico es un compuesto tóxico, considerado por la Agencia Internacional de Investigación sobre el Cáncer como cancerígeno clase I. El arroz es una de las principales fuentes de exposición debido a que la bioacumulación de arsénico inorgánico (iAs) en el grano, aproximadamente 10 veces más alta que en otros cereales [1]. En los países de Latinoamérica (Ecuador, Brasil y Perú) el consumo percápita medio de arroz sobrepasa los 100 g/persona/día [2]. En España el consumo es netamente inferior (16 g/persona/día) [3], pero representa el 30% de la producción de arroz en la Unión Europea, mientras que Portugal solo representa el 6% de la producción en Europa [4], pero tiene el consumo percápita más alto de la Unión Europea de 16kg/persona/año[4].

Específicamente para el arsénico, hay dos mecanismos relacionados en la absorción de arsénico, el primero a través del transportador de fosfato, ya que el arseniato presenta una estructura similar a la del ion fosfato y el segundo cuando el arsenito (análogo al ácido silísico y especies metiladas de As no disociadas (ácido dimetil arsínico (DMA) y ácido monometil arsónico (MMA)) son tomadas por las raíces de la planta de arroz por las acuaporinas [5]. Las condiciones anaeróbicas de los cultivos de arroz y su fisiología única facilitan una eficiente absorción del arsénico por la planta [6].

En el presente estudio se analizaron muestras (54) de arroz comercial de Ecuador, Brasil y Perú y de la Península Ibérica, se determinó As total y especies arsenicales: As inorgánico (As(III) y As(V)) y As orgánico (ácido dimetil arsónico, DMA, ácido monometil arsínico, MMA y arsenobetaína). En paralelo se analizó el material de referencia certificado (CRM) harina de arroz 1568b del NIST USA. Para la determinación del contenido de As total las muestras fueron sometidas a una digestión ácida en una placa de calentamiento y el contenido de As total fue determinado en ICP-MS. Para la determinación de especies de arsénico la digestión se realizó en un horno microondas y la separación y cuantificación en un HPLC -ICP-MS.

La concentración de As total promedio en el arroz comercial del Ecuador fue de 0,1047 ± 0,0550 mg/kg, Brasil: 0,171 ± 0,046 mg/kg, Perú: 0,152 ± 0,039 mg/kg, España: 0,215 ± 0,112 mg/kg y Portugal: 0,191 ± 0,015 mg/kg, los valores más altos obtenidos corresponden al arroz integral. En los arroces de los países de Latinoamérica predominaron las especies inorgánicas y en los de la Península Ibérica el DMA.

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Iberian partnership on the study of platinum-group elements (PGE): the case of Tagus estuary

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Platinum-group elements (PGE) have increased in the environment over the past decades due to an increase of their applications, which are transverse to several technology-based industries. Anthropogenic emissions over the past decades have been attributed mainly to automotive catalytic converters (ACC). However, other sources may contribute significantly to the increase of PGE concentrations in aquatic systems, such as industrial activities, medicinal uses and jewellery. Thus, PGE are emerging contaminants in the environment, potentially bioavailable and posing hazardous impacts. Despite being well characterised in urban environments, PGE remain poorly understood in aquatic systems [1]. As a result of a collaboration between Portugal and Spain over the past years, this work presents the data collected so far in the Tagus estuary. This system is ideal due to active and historic anthropogenic pressures and its connection to the sea.

To improve the knowledge of PGE behaviour in a transitional environment, with particular emphasis on Pt and Rh, different types of samples have been collected and analysed by Adsorptive Cathodic Stripping Voltammetry [2]. All data were compared with ancillary parameters.

A set of 72 superficial sediment samples allowed to assess the pathways, spatial distribution, and the identification of potential different sources of Pt and Rh into the Tagus estuary. Concentrations ranged 0.18 – 5.1 ng Pt g^{-1} and 0.019 – 1.5 ng Rh g^{-1}. According to their spatial distribution, four distinct PGE areas are discussed: industrialised, motorway bridges, wastewaters (WWTP) and pluvial discharges and the natural background areas. Two main origins of Pt and Rh to the estuary were identified: historical and present day industrial activities and the ACC.

Three sediment cores were collected at the industrial sites of Tagus estuary: a dismantled area with a historical industrial variety of activities (BRR); a site where presently operates a chemical-complex unit; and one core distant from the other areas, located in the Natural Reserve. The highest Pt and Rh concentrations were found in the deeper sediments, in particular at BRR, evidencing a clear signature from the historical industrial activities that occurred previously to the implementation of ACC, in the early 1990s. In addition, the mechanisms responsible for PGE retention in sediments were also evaluated.

Ongoing work is focused on the transfer of Pt and Rh from the urban area to the estuary through the WWTP and the possible tidal effect on the recirculation of those elements within the estuary and the adjoining coastal area. Moreover, Pt and Rh dissolution from road dust and complexation experiments are being performed to further improve the understanding of PGE biogeochemistry in aquatic systems.

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EFEITO DE CATIÕES DE METAIS NA RESISTÊNCIA DE GEOTÊXTEIS À TERMO-OXIDAÇÃO

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Os geotêxteis são materiais poliméricos usados na construção de várias estruturas como: aterros de resíduos, estradas, ferrovias ou estruturas de proteção costeira, com funções de drenagem, filtragem, proteção, separação ou reforço. A oxidação é um dos principais mecanismos de degradação dos geotêxteis, podendo provocar quebras nas cadeias poliméricas e, consequentemente, a redução da resistência mecânica dos materiais. O processo de oxidação ocorre segundo um mecanismo de reação em cadeia relativamente complexo, que é iniciado pela formação de radicais livres, quer pela ação da radiação ultravioleta (UV) (foto-oxidação), quer pela ação da temperatura (termo-oxidação). Na ausência da radiação UV e à temperatura ambiente, o processo de oxidação dos geotêxteis é normalmente lento. Contudo, não pode ser desprezado, uma vez que, na maioria dos casos, os geotêxteis devem desempenhar as suas funções durante várias dezenas de anos.

Neste trabalho, estudou-se o efeito de catiões de metais, como o cádmio, cobre, cobalto, ferro, níquel, manganês e zinco, no processo de termo-oxidação de três geotêxteis de polipropileno estabilizados com diferentes teores dos aditivos Chimassorb 944 e negro de carbono. Para tal, os geotêxteis foram expostos, sequencialmente, a soluções de um dos catiões de metais (imersão a cerca de 20 ºC durante 100 dias) e à termo-oxidação (exposição a 110 ºC durante um período máximo de 56 dias). Os danos sofridos pelos geotêxteis foram avaliados pela monitorização do seu comportamento à tração.

Os resultados obtidos permitiram concluir que (1) os catiões cobre, cobalto, ferro, níquel, manganês e zinco aceleraram o processo de termo-oxidação dos geotêxteis; (2) o catião cádmio não teve influência na velocidade do processo de termo-oxidação; (3) o aumento da concentração dos catiões de metais deu origem a um aumento da velocidade do processo de termo-oxidação; (4) o aumento do teor de Chimassorb 944 (de 0,2% para 0,4%, *m/m*) retardou o processo de termo-oxidação catalisado pelos catiões de metais e (5) o negro de carbono (1,08%, *m/m*) não teve influência na velocidade do processo de termo-oxidação.

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Modelling the Absorption Spectra of Polycyclic Aromatic Hydrocarbons over Seoul, South Korea

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The effect of light-absorbing atmospheric particles on climate forcing has been integrated into climate models [1], but the absence of brown carbon (BrC) in these models has caused the existence of significant differences between model predictions and measured data on radiative forcing [2]. However, making quantitative predictions of the contribution of BrC has been a challenging task for experimental approaches, resulting in high uncertainties in the prediction and mitigation of BrC.

Herein, we have used a density functional theory (DFT) approach to generate models for the "real-world" absorption of BrC. Namely, we have used as case-study the absorption of polycyclic aromatic hydrocarbons (PAHs) found in the atmosphere over Seoul (South Korea). These models took into account the seasonal variation of the PAHs, as measured experimentally [3].

Our models were able to identify the more relevant UV and visible regions for the light absorption spectrum of the PAHs, and to decompose these relevant bands to contributions attributable to individual molecules. It allowed us also to determine and understand changes in the combined absorption spectrum of PAHs to the seasonal variation of their concentration, helping also to identify the most problematic season of the year for climate forcing.

This information is essential for developing global models able to predict the climate effects of BrC. It also shows the advantages that DFT calculations can bring to the study of the effects of light-absorbing atmospheric particles on climate forcing.

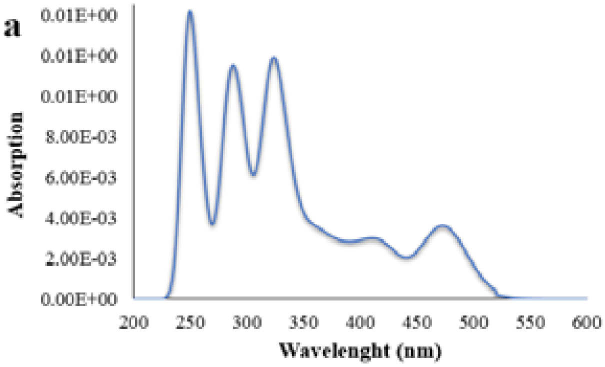

Fig.1. Combined absorption spectrum for PAHs found over Seoul.

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Variación temporal de las formas geoquímicas de P en sedimentos de la Laguna de Xuño (NO Península Ibérica, Galicia, A Coruña)

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La Laguna de Xuño presenta un sistema laguna-barrera de origen natural de escaso contacto con el mar. Es un humedal singular y de alto valor ambiental situado en la costa gallega. Además, se encuadrada dentro de una Zona de Especial Conservación (ZEC). En trabajos previos, se contribuyó al conocimiento de la dinámica espacio-temporal del comportamiento geoquímico y fraccionamiento del Fe, Mn y metales traza (Cu y Co). En este estudio, se llevó a cabo una extracción secuencial del P siguiendo el método propuesto por [1]the modification suggests isolation of P associated with aluminum (A1, [2]compared to 21:1 to 31:1 mol:mol in the saltmarshes, which is consistent with a trend toward P-limitation of primary production in freshwater and N-limitation in salt marshes. However, total P concentration, 24.7 +/- 11.1 mu mol P g dw(-1 y adaptado [3]NaHCO3-Pi, and NaHCO3-Po en muestras recogidas en dos periodos diferentes (agosto y octubre de 2011) en el centro de la laguna separando las siguientes fracciones: F1: P-adsorbido, F2: P-adsorbido a óxidos e hidróxidos de Fe, F3: P asociado a minerales de la arcilla e hidróxidos de Al, F3-B: P asociado a los ácidos húmicos, F4: P-apatito y F5: P asociado a la materia orgánica refractaria.

Los resultados muestran importantes cambios estacionales y con la profundidad en la distribución de las concentraciones de P en las distintas fracciones geoquímicas consideradas.

En el muestreo de agosto la fracción dominante fue la F5 (P asociado a la M.O. refractaria) cuyos valores máximos se obtuvieron en superficie (24 $\mu mol \cdot g^{-1}$), disminuyendo sustancialmente con la profundidad. A continuación, le siguen las fracciones F3-B (P asociado a los ácidos húmicos), con valores máximos en superficie (22 $\mu mol \cdot g^{-1}$); F3 (P asociado a minerales de la arcilla e hidróxidos de Al), con valores máximos en las muestras más superficiales (1,5 $\mu mol \cdot g^{-1}$); F4 (P-apatito), con valores máximos en la muestra más profunda (1,2 $\mu mol \cdot g^{-1}$); F2 (P adsorbido a óxidos e hidróxidos de Fe), con la máxima concentración en superficie (0,49 $\mu mol \cdot g^{-1}$) y la F1 (P adsorbido), cuyo valor máximo también se detectó en superficie (0,05 $\mu mol \cdot g^{-1}$).

En el muestreo de octubre, las concentraciones fueron en general mayores a las del muestreo anterior, excepto para la F4 (P-apatito), cuya concentración máxima también apareció en profundidad (1,2 $\mu mol \cdot g^{-1}$). El patrón de comportamiento para el muestreo de octubre mantuvo las dos mismas fracciones con las concentraciones más elevadas en agosto (F5 y F3-B). Sin embargo, los valores máximos se detectaron en muestras subsuperficiales (28 y 26 $\mu mol \cdot g^{-1}$, respectivamente). Las siguientes fracciones con mayores concentraciones máximas fueron la F2 en superficie (2,25 $\mu mol \cdot g^{-1}$), F3 en superficie (2 $\mu mol \cdot g^{-1}$), F4 en profundidad (1,2 $\mu mol \cdot g^{-1}$) y finalmente (como en agosto) la F1 en superficie (0,06 $\mu mol \cdot g^{-1}$).

Los resultados ponen de manifiesto la importancia en este sistema lacustre de las formas orgánicas de P, tanto refractarias como lábiles. En condiciones dulceacuícolas, los óxidos de Fe y Al formarían complejos con ácidos húmicos disociados (y cargados negativamente) y el fosfato que esté unido a dichos óxidos podría, de este forma, ligarse también a los ácidos húmicos. La Laguna de Xuño presenta un marcado carácter eutrófico asociado a la concentración elevada de formas de N y P en el agua de la laguna. Además, el riesgo de eutrofización por P puede ser mayor si se considera el P asociado a los ácidos húmicos de los sedimentos (fracción mayoritaria en los resultados obtenidos) porque son formas de P solubles que pueden ser exportadas y biodisponibilizadas por algas que dispongan de la enzima fosfatasa alcalina [4].

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Quantification of Fatty Acid Ethyl Esters in Biodiesel via ATR-FTIR

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Biodiesel, a mixture of alkyl esters produced from fatty acids is pointed out as a feasible renewable and low carbon substitute of fossil diesel for the transportation sector [1]. Biodiesel is mainly produced by catalyzed transesterification of vegetable oils, waste cooking oils and animal fats with methanol. To improve biodiesel sustainability the nowadays in use methanolysis (given FAME) must be replaced by ethanolysis (given FAEE). In fact, methanol is mostly obtained by fossil sources whereas ethanol can be obtained from agriculture leftovers [2].
Several techniques [3] can be used to control the transesterification reaction extend, and consequently biodiesel yields such as chromatography, ^{1}H RMN, thermogravimetry, and infrared spectroscopy among others. Some of these techniques despite the high accuracy, are expensive, not user friendly, time-consuming, and cannot be used inline with the process.
Biodiesel (FAEE) production was carried out by ethanolysis reaction of soybean oil over Ca-based heterogeneous catalyst obtained by calcination of calcium rich alimentary wastes. Attenuated Total Reflectance Fourier Transform Infrared Spectroscopy (ATR-FTIR) was used to quantify the FAEE yield in the reaction mixture. Quantification was carried out without previous purification. The FAEE content was computed considering the reflectance bands in the range 1780-1690 cm^{-1} (Fig. 1) being the band around 1735 ± 2 cm^{-1} attributed to biodiesel (FAEE) as reported by Zagonel et al [4]. The band centered at 1744 cm^{-1} was ascribed to oil species. FAEE yield was estimated by computing the surfaces ratio of both bands. Surfaces were computed considering gauss curves for IR bands. In order to check the accuracy of data obtained by FTIR-ATR, ^{1}H RMN and GC techniques were also applied.

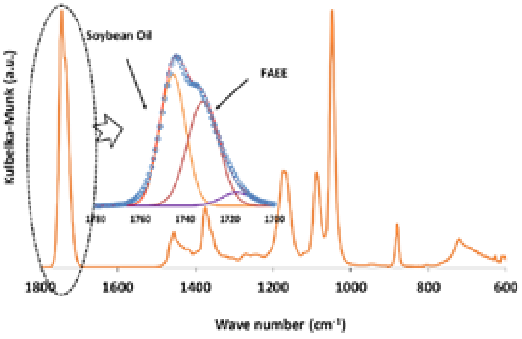

Fig.1. FTIR-IR spectra of FAEE and selected bands for esters quantification.

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Estudio del suelo rizosférico de la chuquiragua (*Chuquiraga Jussieui*) en un medio volcánico de clima frío (páramos del volcán Cotopaxi-Ecuador)

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Los páramos son ecosistemas naturales sobre el límite de bosque cerrado dominado por pajonales, arbustos, humedales y pequeños bosques, es un ecosistema de clima frio y es muy frágil a los cambios en el uso de la tierra [1]. Se extienden desde la línea de los bosques continuos (bosques andinos), hasta donde pueden existir plantas debajo de la nieve eternas. En Ecuador los páramos se ubican en la altitud de 3500 m como límite inferior, pero las condiciones climáticas y antrópica hacen que este límite varié mucho y que en algunos casos se encuentren a veces paramos desde los 2800 m hasta 4200m, especialmente en el sur del país y representan el 6 % alrededor de 1250000 ha. [2] del territorio nacional. El clima es la condición formadora de suelos en la mayoría de los páramos del Ecuador, diferenciándose por la roca madre entre el norte y sur del país. La mayor parte de los páramos son depósitos de cenizas, lapillis y piedra pómez, compuestos fundamentalmente por minerales del grupo de los piroxenos y anfíboles que liberan una gran cantidad de cationes útiles para las plantas [3]

Para el presente trabajo se determinó la movilidad de nutrientes en la rizosfera y suelo no rizosférico (bulk) de la especie Chuquiragua (*Chuquiraga Jussieui*), planta del Parque Nacional Cotopaxi (Cotopaxi-Ecuador), se muestreo la rizosfera (R) a profundidades de 0-10 cm (R_{10}) y 10-20 cm (R_{20}) y un suelo a granel cercano (Bulk) a 50 cm Fig.1, analizando pH, CIC, textura, macro y micro nutriente, disponibilidad de los mismos mediante extracción con Mehlich 3. Obteniendo una textura arenosa, con CIC < 1 cmol/kg, saturado en bases, con $pH_{(H2O)}$ entre 5.61 y 6.06 ligeramente acido, el $pH_{(KCl)}$ 4.86-5.36, inferior al pH(H2O) que indica la presencia de cationes ácidos en el complejo de intercambio catiónico(CIC) y muy bajo contenido del fosforo Mehlich (2.11-2.87) mg P/Kg en la rizosfera(R), observándose diferencias con el suelo a granel (bulk)

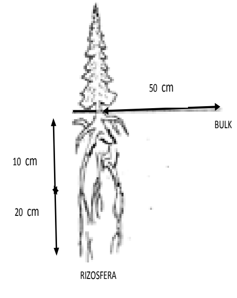

Fig.1. Esquema de muestreo.

AGRADECIMIENTOS: Al Laboratorio de Química Agrícola de la Universidad de Santiago de Compostela en especial a María Santiso y Paco Casás por su colaboración y asistencia en el laboratorio.

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Aplicação de argilas pilarizadas em processos de oxidação avançados para o tratamento de efluentes vinícolas

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A utilização de minerais argilosos, quer como adsorvente quer como suporte para catalisadores heterogéneos para reações catalíticas, é uma alternativa promissora para a descontaminação de efluentes industriais, uma vez que são abundantes, viáveis do ponto de vista ambiental e possuem um custo bastante reduzido em comparação com outros materiais utilizados. A esmectite (SMT) corresponde a um grupo de minerais argilosos que se caracteriza por um tamanho de partículas inferior a 2 µm e uma estrutura singular, o que lhe confere propriedades únicas, tais como, elevada capacidade de troca catiónica, elevada área superficial e elevada estabilidade **térmica**. Neste sentido, o presente trabalho apresenta como principal objetivo o desenvolvimento de catalisadores heterogéneos, utilizando esmectites pilarizadas com diferentes metais, incluindo Al, Fe e Cu, para aplicação em processos de oxidação foto-catalítica, com vista ao tratamento de efluentes vinícolas. A indústria vitivinícola representa uma fonte de geração de efluentes de elevada carga orgânica, que se caracterizam pela presença de compostos com elevado poder recalcitrante, sendo a descarga descontrolada dos mesmos um elevado risco para o ambiente.

No sentido de otimizar as condições experimentais para um maior grau de degradação de matéria orgânica, efetuou-se a variação das condições experimentais, nomeadamente a variação do pH, da quantidade de H_2O_2 adicionada, da massa de catalisador e da fonte de radiação adicionada ao sistema: uma fonte UV-A (365 nm) e uma fonte UV-C (254 nm).

Os resultados obtidos (Fig.1) demonstram a elevada atividade dos catalisadores heterogéneos nos processos de foto-catálise, o que se traduziu em percentagens de remoção de COT de 67% (Al-Fe-SMT pil.) e 79% (Al-Cu-SMT pil.), após 240 min de reação, utilizando uma concentração de H_2O_2 de 97.94 mM, 1.50 g de catalisador e uma fonte de radiação UV-C (254 nm). No que diz respeito às concentrações de ferro lixiviado, estas foram sempre inferiores a 0.50 mg/L.

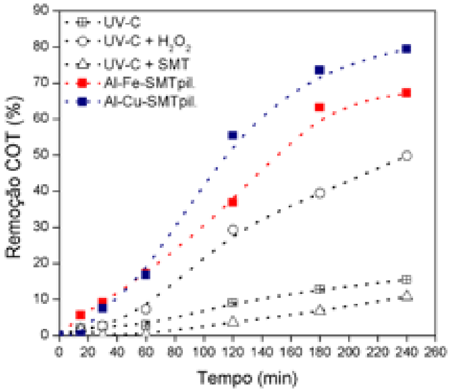

Fig. 1. Evolução do processo de degradação de matéria-orgânica ao longo do tempo. Condições experimentais: UV-A (254 nm), 1.50 g catalisador, [H2O2]0 = 97.94 mM, Vefluente = 500 mL, [COT-efluente]0 = 250 mg/L.

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Comparison of Advanced Oxidation Processes as a pre-treatment for *Sambucus Nigra* wastewater

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Sambucus nigra is commonly known as elderberry and it is possible to find it in Europe, North America, Asia and North Africa. The elderberry is characterized by their antioxidant, antibacterial and anticarcinogenic effects [1], which make them a profitable product for pharmaceutical, medicine and biotechnology applications [2]. Also, the berries are used in the production of juices, jams, jellies, for dietary supplement and in some cases, for fresh consumption. Putting aside the great properties of elderberries, this industry generates a huge volume of solid residues and wastewater that exhibit hazardous characteristics [3] making them unsuitable for conventional treatments.

The application of Advanced Oxidation Processes (AOPs), based on strong oxidants generation, are able to degrade recalcitrant compounds allowing a biological treatment afterwards and so reducing operating costs.

The aim of this study was to increase the biodegradability of this wastewater by performing a comparison between photo-Fenton, electro-Fenton and ozonation processes, at pilot plant scale. For each case it was checked different operational conditions, looking for the lowest treatment cost (Fig. 1).

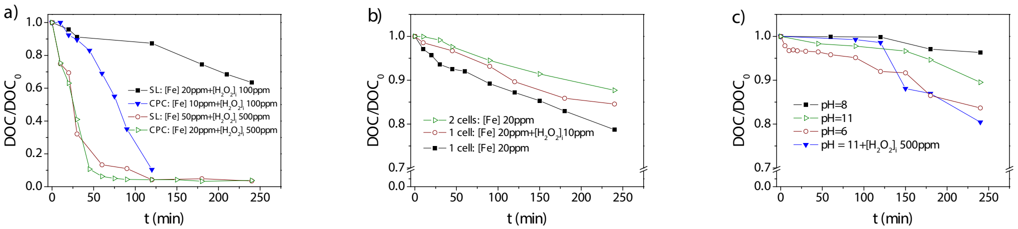

Fig.1. DOC removal versus time: a) Photo-Fenton; b) Electro-Fenton; c) Ozonation processes.

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Monitoring the impact of fertilizers on soil leachates using sequential injection analysis for multiparametric determination

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Forest fires are one of the most common environmental disasters in the Iberian Peninsula, with incidences increasing every year. In just two decades, the probability of a fire year in Portugal burning 100,000 hectares has increased from 30% to 61%, and the risk of a fire year burning over 500,000 hectares is expected to grow over the next decade [1]. The high temperatures that occur during these events seem to deeply affect the soil's physical properties, including soil permeability [2]. These changes may, therefore, affect the leaching of nutrients and other compounds.

The lack of nutrients in the soil in many geographic regions has led to an increased usage of fertilizers during the last decade. Excessive use of nitrogen fertilizers can lead to the contamination of the soil and, consequently, compounds can reach groundwaters through leaching, with potential environmental and agricultural consequences [3]. For these reasons, it has become a necessity to monitor the soil/water interface.

This work aimed to set up and monitor laboratory scale soil columns (LSSCs) using flow analysis methods for assessing nutrient and pH levels and characterizing soil leachates from both indigenous and burned soil. A flow analysis method was developed to determine calcium and magnesium concentrations (given these metal ions are common parameters in water analysis) and iron concentrations (since inorganic fertilizers are commonly supplemented with this metal ion), overcoming the disadvantages of conventional methods in terms of time consumption, waste production and cost. The LSSCs were set up with burned and indigenous soil cores from the same sampling site. Leachates were obtained through rain simulations with rain water and rain water with the addition of inorganic fertilizer.

Table 1. Features of the developed SI method for the multiparametric determination of calcium, magnesium and iron(III)

Me^{x+}	Dynamic range (mg/L)	Typical calibration curve[a] A = S x mg/L Me^{x+} + b	LOD[b] (µg/L)	LOQ[c] (µg/L)	Determination rate (h^{-1})	Effluent Production (mL)
Ca^{2+}	0.16 – 8.0	A = 0.12±0.01x[Ca] + 0.089±0.002	7	22	90	1.8
Mg^{2+}	0.16 – 8.0	A = 0.019±0.003x[Mg] + 0.222±0.003	8	28	86	1.8
Fe^{3+}	0.20 – 2.0	A = 0.018±0.004[Fe] + 0.008±0.002	7	23	82	1.9

[a] Total of three calibration curves; [b] Limit of detection; [c] Limit of quantification

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Viability of the conversion of leachate effluents, from a mechanical biological treatment plant for municipal solid waste, to fertilizers

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Disposal of municipal waste is a major environmental problem. Increased urbanization and industrialization, especially in developing countries, requires municipal authorities to handle larger amount of municipal waste than in the past [1]. Considerable attention has been paid to the land application of municipal solid waste composts and sewage sludge worldwide in recent years [2]. In this context, the main environmental issue associated with the compost manufacture process is the production of a waste liquid leachate very complex in terms of composition. However, compost leachates may also be considered as a source of nutrients and can be converted to fertilizers. Therefore, this study intends to assess if a particular raw effluent leachate, originated from a mechanical biological treatment plant for municipal solid waste, can be used as a potential source for fertilizers. For this purpose, physical and chemical properties of the waste leachate stream were determined to evaluate if it meets suitable requirements for using as commercial fertilizer according to the proposal of regulation of the European Parliament of 2016 [3]. Samples of leachate were collected from the open tank where the effluent is stored, before it is sent to the treatment process. The physical and chemical characterization procedures were developed in order to establish the main properties relating to the leachate samples regarding commercial fertilizer content specifications. The selected parameters measured were pH, conductivity, dry mass, ashes content, TOC and inorganic carbon content.

Table 1. Measured parameters for the original leachate and concentrated samples.

Samples	pH	Conductivity (mS/cm)	%Dry Mass	%Ash	%TOC	%IC
Original	7,95	22,00	2,76	1,37	1,22	0,18
3,19	6,40	46,00	8,26	4,31	3,64	0,31
3,23	6,43	45,50	8,21	4,23	3,63	0,31
3,33	6,49	45,50	8,58	4,39	3,46	0,27
4,23	6,44	53,80	11,19	5,65	4,65	0,28
4,39	6,47	53,60	11,26	5,81	4,63	0,27

As shown, the samples analyzed were the original leachate and concentrated samples obtained through simple distillation to fulfill the European legislation specifications. Each concentrated sample was labeled by its volume concentration factor. The samples show almost neutral pH, which is essential for plant growth and low values of conductivity reinforced by low values of inorganic carbon, which means low content of carbonates and bicarbonates. Dry mass and ash analysis exhibit low values of solids and inorganic content, respectively, below the relevant legislation requirements, which establishes values under 40%w/w.

The concentrated leachate has potential to be used as fertilizer after simple processing. It shows high TOC after concentration and low levels of inorganic content. Other analysis remains to be done like the quantification of heavy metals and nutrients such as P, K and N.

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Simultaneous removal of sulfamethoxazole and methyl paraben by electro-Fenton treatment

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The presence of organic compounds in wastewater has increased over the last years. Among them, compounds such as pharmaceutical and personal care products (PPCPs) are released into the environment because their uncontrolled consumption. Thus, it has become a social problem that needs to be tackled. These pollutants, currently, are not completely removed in the wastewater treatment plants due to their lack of adaptation of these pollutants, which makes it necessary that alternatives arise to efficiently eliminate these compounds.

Advanced oxidation processes (AOP) have demonstrated to be promising, efficient and environmental-friendly methods for the remediation of water and wastewater and, for this reason, are emerging as a sustainable technology for the elimination of organic compounds. Among them, electro-Fenton (EF) is one of the most employed AOP, in which the oxidation efficiency of the Fenton technique is enhanced by the simultaneous application of an electric field.

In this work, the application of EF in the degradation of two different PPCPs was tested. At the beginning, the degradation of the selected pollutants, sulfamethoxazole (SMX) and methyl paraben (MePa), was studied individually and combined. The obtained results showed a high efficiency in the removal of the pollutants in a short period of time (Fig. 1). Then, the operational variables affecting the process (intensities, pH, catalyst concentration, etc.) and other, as the kind of cathode material, were studied and the process was optimized. Almost complete removal of the pollutants was achieved in less than 50 min. Mineralisation studies were also performed to verify not only the removal but the degradation of the contaminants showing a TOC reduction of more than 70% in 240 min. Moreover, this fact was also confirmed by the screening of the generated carboxylic acids proving the total degradation.

Therefore, the results obtained in this study allowed to confirm the suitability of EF as a viable alternative in the treatment of the selected emerging contaminants.

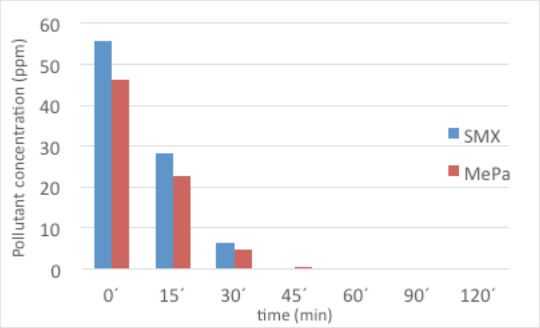

Fig.1. Removal profiles of a mixture of SMX and MePa by EF treatment

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Monitoring of several chiral drugs in the Douro river estuary by LC-MS/MS

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Chiral drugs (CDs) have been targeted as an environmental concern due to their different forms occurring in the environment. CDs can be administered as a mixture or enantiomerically pure. Their metabolism and degradation/biodegradation can be enantioselective. Therefore, CDs can be detected in the environment with different values of enantiomeric fraction (EF) [1]. Enantiomers can have different pharmacokinetics, pharmacodynamics and (eco)toxicity which may affect aquatic organisms in an enantioselective way [2]. Consequently, it is important to determine the EF of these compounds in environmental monitoring programs for accurate risk assessment. This work presents the development of an enantioselective method to quantify CDs in surface water of the Douro river estuary. Different classes of CDs, such as adrenergic beta-blockers, antidepressants, stimulants, non-steroidal anti-inflammatory drugs (NSAIDs) and some illegal drugs as cocaine and its metabolites were selected, accounting twenty three target compounds. The analytical method was based on solid phase extraction (SPE) followed by liquid chromatography tandem mass spectrometry (LC-MS/MS) with a triple quadrupole analyser. The enantioseparations were performed using Chirobiotic V® and Whelk-O® columns. Samples collected in five sampling points of the Douro river estuary were analysed for one week. Nine compounds were found every day, including illicit drugs, namely amphetamine and methamphetamine. Tramadol and its metabolites *N*-desmethyltramadol (NDT) and *O*-desmethyltramadol (ODT) were also found, being tramadol and NDT found at all sampling points, with NDT having a concentration about six times higher than tramadol.

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Aplicação do processo Fenton no tratamento de efluente gasoso contendo tolueno

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Nos últimos anos as principais agendas ambientais mundiais não têm poupado esforços para alertar sobre o perigo da geração e descarga no meio ambiente de diversos tipos de efluentes. As indústrias químicas, tais como as petroquímicas, têm um papel importante nesta temática com produções diárias de grandes quantidades de efluentes líquidos e gasosos. Estes efluentes contêm elevadas concentrações de substâncias perigosas, tóxicas e/ou recalcitrantes, tais como os compostos orgânicos voláteis (COVs). Os COVs apresentam riscos elevados para o meio ambiente e para a saúde humana [1], com destaque para os BTEX (benzeno, tolueno, etilbenzeno e xileno). Estes altos riscos têm impulsionado a busca crescente de novas tecnologias de tratamento alternativas, entre as quais os processos oxidativos avançados (POAs) [2]. Recentemente foi reportado um estudo que aplica um POA clássico, o processo Fenton (comumente utilizado para tratar efluentes líquidos), como alternativa de tratamento de correntes gasosas contendo BTEX [3]. Neste processo o efluente gasoso é alimentado continuamente a um reator de coluna de bolhas (RCB) ou a um reator descontínuo contendo placas perfuradas ou dispersor de gases, promovendo-se assim a transferência dos poluentes para a fase líquida, que contêm o reagente de Fenton (mistura de Fe^{2+} e H_2O_2), onde ocorre a oxidação, *in situ,* dos compostos por intermédio dos radicais hidroxilos ($HO^{\bullet}$) gerados durante a decomposição catalítica do H_2O_2. O princípio e eficiência deste processo está, portanto, dependente da transferência de massa dos poluentes presentes na fase gasosa contaminada para o líquido onde ocorre a degradação oxidativa (Fig. 1.), tal como foi aplicado no tratamento de correntes contendo NOx [4]. Contudo, ainda há muito para desenvolver nesta área. O objetivo deste estudo é tratar uma corrente gasosa contendo tolueno pelo reagente Fenton. Um estudo paramétrico está a ser realizado para avaliar o efeito das principais variáveis processuais (temperatura, caudal de gás, pH e concentrações de catalisador/oxidante), quer em termos de transferência de massa, quer da oxidação do poluente.

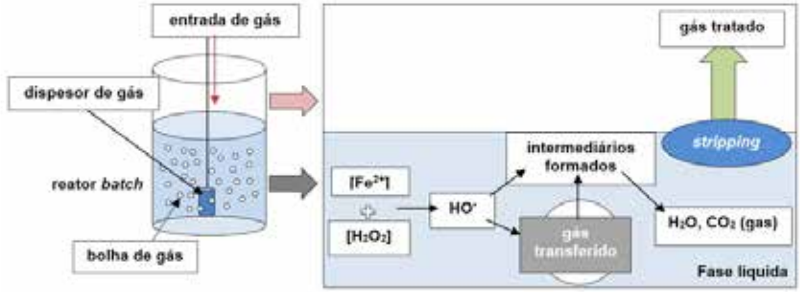

Fig.1. Esquema do tratamento de um efluente gasoso pelo processo Fenton (adaptado de [5]).

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EU multi-class organic micropollutants in Leça River: Spatiotemporal monitoring and fluorescence excitation-emission matrices assessment

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A wide range of micropollutants end up at trace concentrations in aquatic environments such as surface water, where they may cause several implications for public health [1]. In this context, the European Union recommended the monitoring of priority substances (PSs, Directive 2013/39) and contaminants of emerging concern (CECs, Decision 2018/840) in this matrix [2].

In the present study, a spatiotemporal monitoring of thirty nine multi-class organic micropollutants, including some PSs and CECs, was performed in Leça River, a stressed river located in the north of Portugal. The water samples were collected, during wet and dry seasons, at different locations and analyzed by an offline solid phase extraction follow by ultra-high-performance liquid chromatography coupled to tandem mass spectrometry method. In addition, the fluorescence excitation-emission matrices (EEM) were measured.

Twenty one out of thirty nine target micropollutants were found in the selected river. A widespread occurrence of micropollutants was verified at ng L^{-1} levels, with the highest concentration verified for tramadol in dry and wet season, 396 ng L^{-1} and 233 ng L^{-1}, respectively [3]. Regarding the results for EMM, the increase in fluorescence response profiles for specific locations of the Leça River were in agreement with the distribution trend of some target micropollutants along the river. Accordingly, preliminary EEM analysis may help to inform the design of future monitoring studies [3].

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Getting inspiration from the surface of plants leaves

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Natural materials exhibit unparalleled levels of sophistication and miniaturization, high degree of complexity, high hierarchical structuring (often ranging from the nano- to the macroscale), organic/inorganic hybrid strategy, functionality, adaptation and resistance [1]. The surfaces of natural materials offer unique examples of self-cleaning, antifouling, low, high or reversible adhesion, drag reduction, superhydrophobic/superhydrophilic, oleophobic/oleophilic or superomniphobic behaviour.

The field of biomimetics aims at mimicking Nature to develop materials, devices, and processes displaying properties of commercial interest [2]. Bio-inspired materials and surfaces have minimum human impact on the environment and may thus be considered as eco-friendly.

Green plants are characterized by a diversity of hierarchical surface structures [3] and can be employed as models for the development of biomimetic surfaces. Wettability results from the interplay between the leave's morphology and surface chemistry (wax composition) [4]. The most widely explored wettability effect is the so-called Lotus Effect observed in the leaves of the Lotus plant (*Nelumbo nucifera*), which are extremely water repellent [5] and present self-cleaning ability. Several examples of the application of superhydrophobicity can be found in the sector of coatings for the automobile, aeronautical, aerospacial, naval, textile and building industries. The air-roots of epiphytic orchids show an opposite behaviour: these are constructed for efficient water absorption through their surfaces [6].

The main goal of the current work has been to study in depth the surface of the *Prunus lusitanica* [7] leaf. The fresh plant material was collected at the Botanical Garden of the University of Trás-os-Montes e Alto Douro. *P. lusitanica*, an endemic species from the western Mediterranean basin, characteristic of ancient Laurel forests, is currently considered as a vulnerable taxon (category B2ab -http://www.iucnredlist.org/details/62857/1-).The wettability was quantified by means of static and dynamic contact angle (CA) measurements using the sessile drop method. The CA of different locations of the upper (abaxial) and lower (adaxial) sides of the leaves was measured regularly over a period of one year. The total amount of waxes and their composition were determined. The morphology was studied by Scanning Electronic Microscopy (SEM) and Atomic Force Microscopy (AFM) using a tapping mode.

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Quantification of enantiomers of psychoactive substances and β-blockers by GC-MS in wastewaters to estimate consumption

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Currently, consumption of illicit substances and pharmaceuticals used as drugs of abuse has increased dramatically [1]. After consumption, residues of these substances and their metabolites are excreted by the urine and feces and discarded into wastewater treatment plants (WWTPs). Initially, these substances were analyzed to investigate environmental contamination and risk assessment. However, since 2005, with the detection of cocaine in wastewater [2], a new epidemiological tool has been developed using untreated wastewater to study collective habits of consumption of pharmaceuticals or illicit substances by a population. This approach is known as wastewater-based epidemiology (WBE) and provides quantitative estimates in a non-invasive manner and in almost real-time [3]. As the majority of these substances are chiral and can be commercially available as racemates or enantiomerically pure, distinction of the enantiomers is essential for WBE because it can provide information regarding: evidence of the existence of chiral pharmaceuticals and illicit drugs in the environment; estimation of pharmaceuticals and illicit drugs consumption in a specific area/community; distinction of different traffic routes and synthesis processes; monitorization patterns of drug consumption; distinction between licit and illicit use of drugs; differentiation between consumption and disposal of unused drugs [2, 3]. The aims of this work were the development and validation of a gas chromatography–mass spectrometry (GC-MS) method for the quantification of 11 chiral substances of forensic interest (psychoactive drugs and β-blockers), based on the formation of diastereomers, using (*R*)-(–)-α-Methoxy-α-(trifluoromethyl)phenylacetyl chloride ((*R*)-MTPA-Cl) as chiral derivatization reagent. The method was applied to an influent of a WWTP and the prevision of consumption of the target chiral substances in a specific population were back-calculated.

Results showed the occurrence of amphetamine (AMP), methamphetamine (MAMP), 3,4-methylenedioxyamphetamine (MDMA), alprenolol (ALP), norfluoxetine (NFLX), fluoxetine (FLX), metoprolol (MET), propranolol (PHO) and sertraline (SER) at concentrations ranging from 19.1 ng L-1 (MAMP) to 4948.1 ng L-1 (FLX). The enantiomeric fractions (EF) were determined and showed differences in the enantiomeric composition of these drugs. The presence of nearly racemic form of AMP (EF = 0.42), ALP (EF = 0.49), FLX (EF = 0.48) and PHO (EF = 0.45) and single enantiomers for MAMP (EF ≅1), MDMA (EF ≅1), NFLX (EF ≅0) and MET (EF ≅1) were also observed, suggesting enantioselective processes in their formation.

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Desalination Technologies: an Energy Approach

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In the last decade, desalination has become one of the world's most important issues associated with unconventional water resources. The topic is especially relevant in areas where drinking water is scarce and salt water is available. The huge benefits of desalination (increase of water resources and improvement of water quality), there is still ample research and improvement opportunities, especially in those aspects related to energy consumption and efficiency [1].

There are available several desalination technologies [2, 3, 4]; that we can dividing it into two main groups: processes based on evaporation (Multistage Flash, Multi Effect Distillation and Vapor Compression Evaporation), and processes based on membranes (Reverse Osmoses, Electro-Dialysis and Membrane Distillation). One of the main barriers to disseminate desalination is their high operation cost, which is seriously influenced by energy consumption (representing 50 to 60% of total costs) [1]. The present work intends to evaluate some technological approaches of sea water desalination, namely: reverse osmosis (Fig.1), distillation and solar evaporation to accomplish a more efficient plant. Additionally, numerical simulation [5] will be used to model different technology setups and quantify their energy efficiency. The simulation tests allow to optimize the operation of each technological scenario and compare the performances of various technologies. An estimate energy consumption and operating costs in drinking water production according to a set of technologies will be handed over.

Fig.1. Laboratorial facility of reverse osmosis used in the experiments.

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E-waste: potential impact of yttrium and lanthanum on embryonic development of *Crassostrea gigas*

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In recent decades, global production of high-tech products (e.g. smartphones, computers, displays) has increased exponentially, a pattern that should continue. A wide range of electronic devices relies on rare earth elements (REE) such as yttrium (Y) and lanthanum (La). In addition to the shortage of raw materials, due to the limitation of REE sources in Nature [1], the increasing generation of electronic waste (E-waste) and the direct or indirect release of REE into the environment raises worldwide concern. Particularly, information about the ecotoxicity of Y and La and potential implications for the sustainability of ecosystems is very scarce.

In this study, a standardized embryotoxicity test on oyster *Crassostrea gigas* [2] was performed to assess the impact of anthropogenic Y and La (individually). Different concentrations in water (0, 2.5, 5.0, 10, 20, 40, 80 and 160 μg/L) were studied at salinity 30 and temperature 24ºC. REE levels in water were analysed by ICP-MS (Thermo X-Series). Embryo-larval development was visually investigated on an inverted microscope and camera (Leica: DMIL-1; MC170 HD).

Results showed that comparing to control condition (seawater in absence of REE), where a very high frequency of normally developed embryos was observed (D-shape, Fig.1 A), Y or La conditions had negative impacts, mainly characterized by retardation of embryonic development. Stronger toxic effects were noted for La in comparison to Y, which also included developmental defects and mortality (Fig.1 B, C and D.

Overall, this work brings new insights into the potential implications of the widespread use of Y and La in high-tech products and the rise of E-waste in the survival of the aquatic population and in the functioning of ecosystems, if proper management strategies are not implemented.

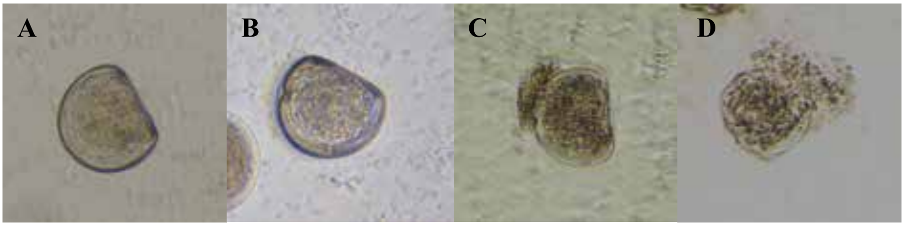

Fig.1. Photographs of some larval development types recorded for C. gigas after exposure to Y or La: A) D-shape; B) indented shell; C) protruded mantle; and D) dead larvae.

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Será possível extrair valor dos smartphones em fim de vida?

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Os smartphones são ferramentas essenciais ao nosso dia a dia, e na sua constituição, estes dispositivos utilizam pequenas quantidades de alguns elementos químicos, que são considerados as “vitaminas da tecnologia” (Fig. 1). Com o desenvolvimento tecnológico, a procura por estes elementos, aumentou, provocando uma diminuição nas reservas e na oferta, devido a restrições geopolíticas. A conjugação destes fatores levou a que estes elementos sejam considerados elementos críticos de tecnologia (ECT), e a sua recuperação de dispositivos em fim de vida é crucial para garantir a sua disponibilidade no futuro.

Neste contexto, nos últimos anos surgiu uma nova linha de investigação que procura encontrar novas fontes destes elementos, nomeadamente no desenvolvimento de processos eficientes para a recuperação e reciclagem destes elementos a partir de lixo eletrónico.

Nesta comunicação será realizada uma revisão bibliográfica desta temática e serão apresentados alguns resultados sobre a síntese e aplicação de alguns nano adsorventes magnéticos na recuperação e reciclagem de alguns desses elementos críticos. Um desses exemplos, é um compósito magnético preparado com nanopartículas de magnetite e grafite esfoliada, que apresenta capacidade para remover lantanídeos (La, Eu e Tb) de soluções aquosas, em baixas concentrações. Este adsorvente apresentou uma eficiência de remoção superior a 80% após 15 minutos de contacto (pH ca. 8), utilizando apenas 50 mg/L de material.

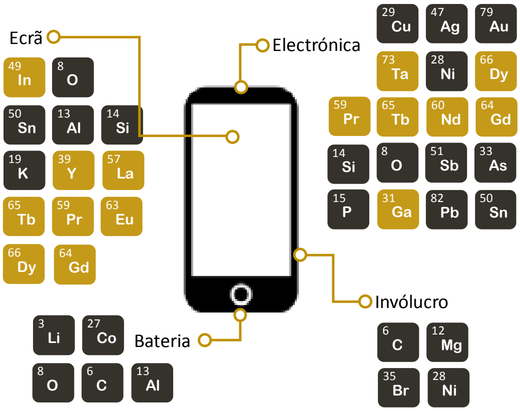

Fig.1. Composição química de um smartphone (adaptado de http://www.chemeurope.com)

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Tratamento de efluentes vinícolas mediado por microalgas

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As microalgas têm a capacidade de crescer em águas residuais, assimilando os nutrientes e compostos orgânicos aí presentes, removendo, assim, a carga poluente. Os efluentes são um meio de crescimento de baixo custo para a produção de biomassa algal que pode ser usada em diversos sectores, tal como alimentação animal, fertilizantes, produção de bioenergia e outros produtos como pigmentos, proteínas e lípidos [1].

Existem vários estudos de uso de microalgas para o tratamento de efluentes do sector agroalimentar, como por exemplo as indústrias de lacticínios e cervejeira [2]. No entanto, a aplicação de microalgas em efluentes da indústria vinícola ainda é limitada [3,4,5].

Este trabalho tem como objetivo estabelecer um processo de biorremediação de um efluente vinícola, usando quatro espécies: *Chlorella vulgaris*, *Chlorella protothecoides*, *Scenedesmus obliquus* (microalgas verdes) e *Spirulina maxima* (cianobactéria), avaliando o crescimento microalgal e a remoção de carbono orgânico total (TOC). As espécies foram testadas em condições mixotróficas (recorrendo a iluminação artificial) e condições heterotróficas (ausência de luz).

Os resultados mostram que este tipo de efluente pode ser usado como meio de crescimento para as quatro espécies testadas. Além disso, obteve-se uma remoção da maioria do carbono orgânico total (80 a 90%), geralmente ao final de 10 dias após inoculação, exceto usando a espécie *S. obliquus*, que mostrou resultados inferiores.

Em condições de heterotrofismo, apesar de a remoção de TOC ter sido bastante rápida e elevada (superior a 80% após 3 a 5 dias), a produtividade em biomassa foi bastante inferior ao obtido em condições mixotróficas. Apenas a espécie *C. vulgaris* mostrou produtividades semelhantes nas duas situações.

Combinando a produtividade em termos de biomassa e remoção da carga orgânica, a espécie *C. vulgaris* mostra-se a mais promissora no tratamento deste efluente.

Tabela 1. Produtividade de biomassa e remoção de TOC máximas para cada espécie.

	$P_{x, max}$ (mg L^{-1} dia^{-1})		**Remoção de TOC $_{max}$ (%)**	
	Mixotrofismo	Heterotrofismo	Mixotrofismo	Heterotrofismo
S. obliquus	24,2	2,41	18,5	37,6
S. maxima	36,2	6,49	79,8	81,0
C. protothecoides	43,8	14,90	89,8	92,5
C. vulgaris	48,8	38,18	91,2	93,7

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Aterros sanitários em Portugal - Energia

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A gestão integrada de resíduos urbanos (RU) é um dos grandes desafios para a atual e futuras gerações. Atualmente, os aterros sanitários são considerados como a última operação de eliminação de acordo com a hierarquia da gestão de resíduos. Nos últimos anos verificou-se um declínio acentuado da percentagem de RU enviado para aterro, em consequência da estratégia nacional de resíduos e do aumento de infraestruturas de tratamento mecânico e biológico.

O desenvolvimento sustentável promove o uso de fontes de energia renováveis. Os RU podem ser usados para produzir energia através do biogás obtido por digestão anaeróbica, em aterros sanitários e em estações de tratamento de resíduos e águas residuais, sendo que o biogás é considerado uma fonte de energia renovável [1 – 2].

O presente trabalho pretende realizar um levantamento da produção de biogás e energia a partir de aterros sanitários em operação e encerrados. Assim, foi realizada uma extensa revisão bibliográfica, em sites oficiais nacionais e europeus, artigos, teses e relatórios das 23 entidades gestoras (EG) de resíduos em Portugal para recolha de dados. Posteriormente foram enviados inquéritos para as 23 EG por forma a completar os dados recolhidos. Com as informações adquiridas foram realizados diversos cálculos, nomeadamente, produção anual de RU, quantidade de RU enviada para aterro sanitário, biogás e metano produzidos e a correspondente produção de energia.

A produção de RU e a energia produzida através do biogás de 2 das 23 EG analisadas, uma do sul (A) e outra do centro de Portugal (B) são apresentadas na Figura 1. A entidade A possui 2 aterros e a entidade B possui 1 aterro. Como se pode verificar a entidade A atinge o máximo de produção de energia em 2016, devido à diminuição de biogás num dos aterros em 2017. Para a entidade B a produção de energia pelo biogás só está disponível a partir de 2015, ano que coincide com o encerramento do único aterro da EG. Os resultados obtidos até ao presente indicam que os dados relativos aos aterros encerrados há mais anos são mais escassos, devido possivelmente à menor quantidade de metano produzido, o que geralmente inviabiliza a valorização energética do biogás.

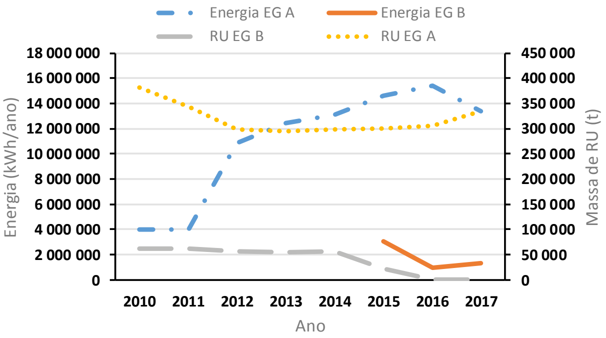

Fig.1. Produção de RU e energia nos aterros das EG A e B

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Caraterização Físico-Química de Amostras no Âmbito da Diretiva Quadro da Água

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A Diretiva Quadro de Água é o principal diploma legislativo da União Europeia relativo a água cujo objetivo fundamental é conservar e melhorar o ambiente aquático dos Estados Membro. O diploma estabelece um sistema integrado sobre a política da água e define um conjunto de normas e medidas com vista à proteção das águas, como forma de preservar a qualidade, proteger e melhorar os ecossistemas aquáticos e terrestres no que respeita as necessidades de água [1].

Nesse sentido, a legislação ambiental recomenda a determinação de parâmetros físico-químicos em águas superficiais e subterrâneas e em efluentes líquidos domésticos e industriais. Estes parâmetros são de extrema importância na caracterização da água, visto que fornecem os indicadores necessários para a avaliação da sua qualidade [2].

O presente trabalho consistiu na caracterização físico-química de amostras de águas superficiais, subterrâneas e residuais no âmbito da Diretiva Quadro de Água e envolveu a validação de métodos fotométricos de análise em cuvete *Hach Lange*, para a determinação da Carência Química de Oxigénio (CQO) e dos teores de Fluoretos e Sulfuretos. Os testes em cuvetes da *Hach Lange* permitem obter resultados fiáveis e precisos num curto espaço de tempo, usando equipamento de manuseamento simples, rápido e seguro. [3,4].

Na validação do método avaliou-se a linearidade da gama de trabalho para CQO, fluoreto e sulfureto através dos valores do coeficiente de correlação (r) os quais foram superiores a 0,995. Os limiares analíticos (limites de deteção e quantificação) foram determinados a partir dos parâmetros das curvas de calibração cujos valores foram para CQO 3,97mg/L O2 e 11,90mg/L O2 (com padrão da Hach) e 4,37mg/L O2 e 13,12mg/L O2 (com padrão preparado no laboratório) respetivamente. A precisão do método foi determinada através de ensaios de repetibilidade (CQO e sulfureto) e reprodutibilidade (CQO), que conduziram a valores dos coeficientes de variação inferiores à 5%. A exatidão do método de determinação de CQO foi avaliada com base nos resultados obtidos em ensaios interlaboratoriais cujos valores de z-score o (-1,7 com padrão da Hach e 1,8 com o padrão preparado no laboratório) cumpriram o critério de aceitação (-3 < Z-score < 3).

Em conclusão, os resultados alcançados nos procedimentos de validação do método de determinação de CQO em cuvetes de Hach Lange são comparáveis aos indicados nos documentos de referência usados no laboratório tendo sido possível reduzir, significativamente, a quantidade de reagentes utilizados, facilitando a reciclagem e tratamento dos resíduos, diminuindo os custos de análise e contribuindo para a redução dos impactes ambientais que estão associados ao método tradicional [4,5].

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Digestão anaeróbia de lamas de ETAR - Biogás e energia

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A concepção de sistemas de saneamento advém da crescente industrialização e urbanização observada durante o último século. Estes fenómenos traduzem-se num leque de actividades que produzem águas residuais com propriedades extremamente nocivas ao ambiente. Assim, é desejável que se concebam ETAR capazes de realizar uma gestão adequada das mesmas, minimizando os impactos ambientais e os bioresiduos produzidos. As biolamas podem ser reaproveitadas como um recurso renovável e valorizadas energicamente através da produção de biogás.

Em Portugal existiam cerca de 2.743 ETAR em 2016 [1], mas apenas as de média e grande capacidade têm estabilização de lamas, geralmente por digestão anaeróbica. Nos últimos anos, a quantidade de lamas não apresentou grande potencial de crescimento em volume (ou massa), uma vez que as infraestruturas do país já estão praticamente consolidadas. No entanto, existe a oportunidade de identificar potenciais para otimização e valorização do processo de digestão anaeróbica nas ETAR, quer seja por mudanças de processo ou pela incorporação de outros substratos. O presente trabalho tem como principal objectivo analisar a capacidade instalada e a eficiência do processo de digestão anaeróbia realizado nas ETAR e a possibilidade de realizar uma co-digestão anaeróbia com outros substratos, uma vez que este processo pode resultar numa melhor eficácia do sistema e optimização de produção de biogás e consequentemente a valorização energética [2].

Foi feito um levantamento das ETAR existentes, mas devido ao elevado número de ETAR, foi necessário seleccionar algumas regiões, nomeadamente centro e sul de Portugal (Tabela 1). Como resultado, verificou-se que o volume de biogás conseguido é consideravelmente elevado, porém a energia produzida a partir do mesmo não consegue suprir nem um quarto das necessidades energéticas das ETAR estudadas.

Tabela 1. Características do processo de digestão anaeróbia em 2 ETAR

Tabela 1. Características do processo de digestão anaeróbia em 2 ETAR

ETAR	Caudal de lamas (m^3/mês)	Nº de reatores	Biogás produzido (m^3/mês)	Metano (%)
Sul	2.691(±1592)	1	20.158.361 (±4.339.653)	63 (±2,2)
Centro	2.513(±514)	2	19.681 (±5.098)	67 (±1,3)

AGRADECIMENTOS: Os autores agradecem a todas as entidades gestoras de saneamento pelos dados fornecidos.

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Phenolic compounds concentration by membrane technology from autohydrolysis liquors of paulownia leaves

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Paulownia COT-2 belongs to the *Paulowniaceae* family and native to China, is known to be a fast-growing ornamental tree. For this reason, it is widely used for biomass and wood industry. In this work, the leaves of this tree considered as a waste in its final exploitation are used as raw material [1].
Leaves were subjected to extraction with pressurized hot water at different temperatures in order to select the liquor that contains a higher concentration of phenolic compounds. Once the optimum treatment temperature has been selected, the objective of this work is to concentrate and/or purify this extract by membranes of different pore sizes (1, 5 and 10 kDa).
As shown in Figure 1, the best results were obtained with the 1 kDa membrane. The total phenolic content of the retentate was 14.73 g eq GAE/100 g extract with an antioxidant capacity of 59.80 g eq Trolox/100 g extract.

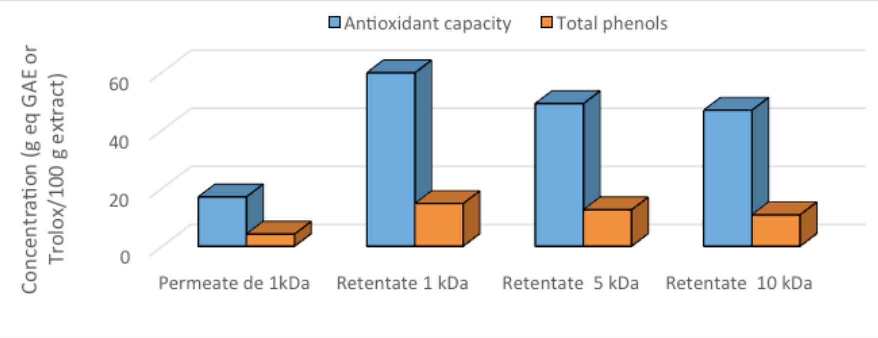

Figure 1: Total phenolic compounds content and antioxidant capacity of the retentates and permeates.

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lead elimination from aqueous solutions using entrapped grape marc in calcium alginate beads

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Lead is a non-essential and toxic heavy metal of extended presence in the environment. Industrial processes such as battery manufacturing, mining, smelting, metal finishing and other metal-based processes are the main sources of lead pollution because they generate a lot of contaminated effluents. The presence of high levels of lead in the environment may cause important health risks to humans and ecosystems, for this reason the Environmental Protection Agency (EPA) limited the maximum limit of lead in industrial wastewater in 0.05 mg/L [1]. For this reason, it is very important the treatment of industrial wastewaters in order to considerably reduce the lead content to be discharged into the aquatic and land systems. Different methods have been developed in this way such as chemical precipitation, adsorption, coagulation, ion exchange, etc [2]. Adsorption methods can be considered fast, simple and even more environmental friendly procedures. In the last years were proved new adsorbent material, including nano-adsorbents [3] as well as different bio-adsorbents, including agricultural residues such as banana peels [4], grape marc [5], etc. This kind of residues can be considered of great interest in order to be transformed in efficient and low cost adsorbents for water cleaning.

In this work was evaluated the bio-adsorption of lead (II) from aqueous solutions by entrapped grape marc in calcium alginate beads. The Box-Behnken Experimental Design was employed for establishing the optima experimental conditions to achieve the best sorption efficiency. Independent variables optimized were: pH (1.0-5.4), lead concentration (10-50 mg/L) and the ratio of bioadsorbent/volume of lead sample (0.2-1.0). Optima conditions provided by the factorial design, for lead concentrations between 30-50 mg/L, were pH= 3.2 and a ratio of 0.8, reaching estimated retention percentages around 100 % and retention capacities between 7.4 and 12.0 mg/g. In order to validate these theoretical values, different essays were carried out, using experimental conditions included in the range evaluated for each independent variable. No significant differences were found between the estimated values and the experimental results in both retention percentage (differences lower than 2.6 %) and retention capacity (differences lower than 1.3 mg/g). In all experiments were obtained quantitative retention percentages (97.7-98.4 %) and retention capacities ranged from 2.3 and 6.2 mg/g.

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Validation of a simple method for Sulphur determination in wastes

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European policies endorse a view of circular economy with the wastes recycling as the major issue for closing materials cycles, reducing the raw materials extractions and reduce the wastes landfilling . Some of the proposed technologies are related with the energy recovery of biowastes through combustion, pyrolysis or gasification, being the former the most common. Combustion obviously produces heating energy, which release carbon dioxide and water vapor, but also undesired products that must be controlled, otherwise may be a source of harmful emissions to the environment. This is the case of sulphur compounds. Simple analytical procedures must be used in a continuous and local controlling process and small laboratories, via common materials and equipments [1]. This work report the validation of a sulphur quantification methodology using an oxygen bomb combustion through the recovery of the produced gases trapped in absorbent solutions. The sulphur recovery was studied from the inner bomb solution and from the gases recovered under the bomb depressurization. The sulphur was quantified by the sulphate turbidimetric method using a spectrophotometer at 420 nm using a calibration curve (Method 4500-SO_4^{2-}E) [2]. The validation of an analytical procedure is the process of defining an analytical requirement, and confirming that the method under consideration has capabilities consistent with the application requirements. The validation parameters evaluated were the detection and quantification limits, LOD and LOQ, respectively, the repeatability and the recovery [3, 4]. It was also evaluated the results comparing the sulphur contents of solid wastes using this methodology and elemental analysis. These parameters were studied using pellets prepared with starch, as blanks, starch and sulfamic acid as spiked samples. The LOD and LOQ were 0.086% and 0.18%, respectively, assessed through the average of 10 determinations of sulphur in starch samples. Analytical precision is concerned with the variability between repeated measurements, irrespective of the presence or absence of bias. For the study of the repeatability of the method for validation purposes, ten independent tests were carried out on the same day with samples prepared with known amounts of sulfamic acid and starch . For the repeatability, the relative standard deviation was 11%, although slightly above the 10%, may be considered acceptable [4]. The recovery was 142.5% with a standard deviation of 14%. Interesting to notice is that the gases have in fact an amount of sulphur, representing about 4% of the evaluated in spiked samples. Comparing methodologies, the calorimetric methodology reveals higher values of sulphur content than elemental analysis.

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COMPARACIÓN DEL PODER COAGULANTE/FLOCULANTE DE LA SIMIENTE DE ACACIA, DEL QUITOSANO Y DEL SULFATO DE ALUMINIO PARA EL TRATAMIENTO DE PURINES PORCINOS

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La producción comercial de cerdos se ha intensificado de manera significativa en las últimas décadas; de forma que existe una mayor cantidad de cerdos, del mismo número reducido de razas y que se crían en cada vez menos granjas, lo que repercute en un incremento del rendimiento de los productos de origen animal [1], pero, también, con repercusión a nivel medioambiental.

Uno de los principales problemas de la actual ganadería es el tratamiento de los purines. Esta masa resultante de la mezcla de deposiciones, orín y aguas sanitarias presenta elevados contenidos en materia orgánica, metales pesados y otras sustancias tóxicas y contaminantes; por lo tanto es necesario garantizar que los efluentes y residuos generados sean tratados de forma efectiva, lo que supone desarrollar nuevas tecnologías o técnicas, o perfeccionar las ya existentes, que permitan un tratamiento eficiente de los mismos.

De las distintas alternativas existentes en el mercado para el purín porcino, en este estudio se optó por la vía química, mediante un tratamiento de coagulación-floculación, comparando la acción de un coagulante tradicional (sulfato de aluminio) y de dos biopolímeros naturales (quitosano y simiente de acacia). En la fracción líquida se analizaron los siguientes parámetros: pH, conductividad eléctrica, turbidez, color, nitrógeno Kjeldahl, sólidos volátiles, totales y en suspensión, y demandas química y biológica de oxígeno.

Los resultados obtenidos con este pre-tratamiento son positivos y, a pesar de que con el coagulante tradicional [2], en este caso, el sulfato de aluminio, se consiguieron los mejores resultados y que es la opción más económica, los biopolímeros también alcanzan buenos rendimientos, constituyendo, además, opciones más ecológicas [3,4].

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Development of a simple, cheap and eco-friendly strategy to reuse PVPP

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Polyvinylpolypyrrolidone (PVPP) is a synthetic water-insoluble polymer widely used in the food industries, as fining agent in the wine industry for removing low molecular weight phenolics. However, the use of PVPP creates large amounts of waste that nowadays ends up on the municipal wastewater treatment plants. In 2014, the use of PVPP was estimated in 1,034 tons, and after used, PVPP contains significant amounts of adsorbed phenolic compounds, having a significant and negative impact in the environment [1].

The main purpose of this work was to develop a simple, cheap and eco-friendly regeneration strategy for recycling used PVPP, using an ammoniacal solution of ethanol to desorb the phenolic compounds, after the fining experiments in white wine. The results showed that the performance of the recycled PVPP for white wine fining was not significantly different from the performance of the new one, and the PVPP can be recycled at least 4 times without loss of fining performance.

To conclude, applying a low cost and eco-friendly procedure it is possible to reuse PVPP at least 4 times, and the phenolic compounds recovered can be easily used by other industries.

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Caracterização de solos florestais queimados

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Em 2017, Portugal foi severamente afetado por incêndios florestais. A área ardida foi 4 vezes superior à média registada nos 10 anos anteriores, o que se traduz num aumento de 428% [1]. Dependendo da dimensão, da intensidade e do local de ocorrência, um incêndio pode constituir uma ameaça às propriedades do solo, na medida em que, pode contribuir para a sua contaminação, impermeabilização e erosão [2, 3]. Considerando escassa a informação disponível, este estudo tem por objetivo a avaliação preliminar dos possíveis efeitos de um incêndio na composição dos solos.

Selecionaram-se solos de uma zona florestal de Lever (Vila Nova de Gaia, Portugal) com predominância de pinheiros e eucaliptos. A amostragem foi feita um ano após o incêndio e em cada local foram recolhidas duas amostras a dois níveis, à superfície e a 30 cm de profundidade. Os solos ardidos foram recolhidos a cerca de 90 m e 900 m (distância linear) da parcela de amostra não ardida.

A análise de cada amostra incluiu estudos granulométricos, caracterização físico-química (densidade aparente, teor de humidade, pH, condutividade elétrica, matéria orgânica, carbono orgânico total e minerais), e análise de metais, hidrocarbonetos aromáticos policíclicos e retardadores de chama.

Este estudo evidenciou que as amostras, embora recolhidas em locais próximos, apresentaram diferenças nos parâmetros analisados.

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Resynthesis of $LiCoO_2$ from discarded lithium-ion cell phone batteries and its electrochemical performance

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Environmental issues, sustainability of primary resources as Co and Li as well as economic factors are driving forces to search for new, low-cost and environmentally regulated lithium-ion battery recycling processes, in special for the battery cathode material.

We describe a simple method to resynthesize the $LiCoO_2$ compound extracted from the cathode of discarded batteries aimed to recover the cathode' full charge capacity. The process starts by a thermal treatment of the spent cathode material at high temperatures to burn the conductor graphite and PVDF polymer present in the cathode material. Simultaneously, the treatment also decomposes the sub-stoichiometric as-extracted Li_xCoO_2 cathode in the stoichiometric $Li_{1.0}CoO_2$ and Co_3O_4 compounds. The resynthesis is carried out by a solid-state reaction between the thermally decomposed cathode material and lithium carbonate Li_2CO_3, at 750 °C in oxygen atmosphere.

To test the effect of the thermal decomposition temperature and the battery state of health (SOH) on the charge capacity of the resynthesized cathode, two batteries with SOH equals to 32 and 92% were selected and their cathode materials treated at 700, 800 and 900 °C decomposition temperatures.

X-ray diffraction patterns and Rietveld refinements show the highest lithium deficiency in the Li_xCoO_2 cathode material extracted from the battery with the lowest SOH (32%). The concentration of the thermal decomposition products, $Li_{1.0}CoO_2$ and Co_3O_4, were very dependent on the x stoichiometry and on the decomposition temperature: Co_3O_4 concentration increases with the decomposition temperature and decreases with the lithium concentration x, while the stoichiometric $Li_{1.0}CoO_2$ compound shows opposite behavior. The c/a lattice parameter ratio and the relative intensities $I_{(003)}/I_{(104)}$ of the (003) and (104) diffraction peaks indicted the highest disorder for the Li_xCoO_2 compound extracted from the low SOH battery. Well-ordered crystalline structures were observed for both $Li_{1.0}CoO_2$ resynthesized compounds [1].

Electrodes mounted from the resynthesized $Li_{1.0}CoO_2$ compound presented specific charge capacities around 130 mAh.g^{-1}, equal to that attained by $LiCoO_2$ commercial electrodes. The electrode charge capacity increases with the temperature employed to decompose the discarded cathode material. Stable charge capacities were obtained upon 20 charge-discharge cycles. Surprising, the charge capacity of the electrode assembled with the resynthesized cathode from the high SOH battery is slight lower than the electrode capacity coming from the low SOH battery.

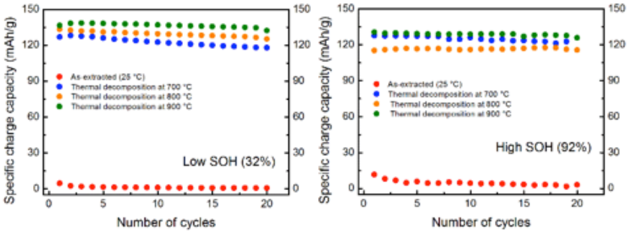

Fig. 1. Specific charge capacity for $Li_{1.0}CoO_2$ compounds resynthesized from cathode material of batteries with low and high SOH at different thermal decomposition temperatures.

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Children exposure to polycyclic aromatic hydrocarbons at school environments: Exposure levels and health risks

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Polycyclic aromatic hydrocarbons (PAHs) are a class of organic compounds widely known for their toxicity, mutagenicity, and carcinogenicity [1-2]. PAHs are emitted by pyrogenic and petrogenic sources, being some compounds included in the European and US Environmental Protection Agency (USEPA) priority pollutant list [3-4].

This work assesses children exposure to PAHs (indoors and outdoors) at school environments and estimates the potential risks.

PAHs in both particulate and gas phases were collected at the breathing air zone of children during four sampling campaigns performed at two pre-schools heavily exposed to traffic emissions. Concurrent sampling was realized inside classrooms and at schools' yard. Extraction of 18 PAHs (16 USEPA, benzo(j)fluoranthene, and dibenzo(a,l)pyrene) was performed by microwave-assisted extraction and analyzed by liquid chromatography with fluorescence and diode-array detection [5].

The concentrations of total PAHs (∑PAHs) in the total air (i.e., particulate and gas phase) varied between 26-151 ng/m^3 indoors and 2.8-47 ng/m^3 outdoors. Gaseous PAHs represented 93-95% of total air ∑PAHs and particulate-PAHs accounted with 5-7% [6]. Indoor-to-outdoor ratios revealed a predominant contribution of indoor sources to lighter PAHs while the penetration of outdoor air proved to be the major source of heavier compounds. Total levels of carcinogenic PAHs (possible/probable/known; [1-2]) in school's total air varied between 14.4-64.2 ng/m^3 at classrooms and from 0.73-23 ng/m^3 at schools' yard, being naphthalene, dibenz(a,h)anthracene, and benzo(b+j)fluoranthene the most predominant compounds [6]. Children were exposed to benzo(a)pyrene at concentrations ranging between 0.05-0.11 ng/m^3 indoors and 0.03-1.3 ng/m^3 outdoors, which exceeded in some days the European target of 1 ng/m^3 [3,6]. However, total carcinogenic risks calculated according to US EPA methodology [4] in schoolchildren were negligible [6-7].

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Determinación de elementos traza en MUESTRAS DE AGUA DE la Ría de VIgo (NO EspaÑa)

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Las Rías Gallegas están situadas al noroeste de la Península Ibérica y constituyen un lugar de referencia en el estudio de contaminación por metales pesados, dentro del enclave de la costa atlántica. En particular, la Ría de Vigo cuenta con un importante aporte antropogénico debido a la elevada actividad industrial situada en la zona (construcción naval, fabricación de automóviles, industrias conserveras, acuicultura, etc.). Esta casuística obliga a establecer un control de los vertidos industriales en base a lo dispuesto en la Ley 9/2010 de aguas de Galicia [1], que marca los límites máximos de emisión de diversos contaminantes, incluyendo metales pesados, para controlar la calidad de las aguas costeras gallegas.

En la ría de Vigo se ha observado, en los últimos años, un enriquecimiento de ciertos metales traza en sedimentos [2,3], pero la información sobre metales en disolución es mucho más escasa [4,5] probablemente debido a los bajos niveles de concentración que presentan; hecho se atribuye a que los elementos metálicos se fijan muy fácilmente sobre el material sólido en suspensión y terminan por incorporarse al sedimento [6].

En este trabajo se ha evaluado el contenido de diversos metales traza en disolución en 18 puntos de muestreo de la ría de Vigo (Figura 1), para poder conocer la existencia de posibles fuentes de contaminación. Se podrá también contrastar los resultados obtenidos con datos procedentes de estudios previos con el fin de evaluar el estado actual de contaminación de esta ría.

Figure 1: Puntos de muestreo (ría de Vigo)

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Monitoramento de grupos funcionais oxigenados na superfície de hydrochars por espectroscopia no infravermelho

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A produção de hydrochars tem se tornado um importante produto derivado de resíduos lignocelulósicos [1]. Suas aplicações diretas como combustível sólido, condicionante de solo e as aplicações indiretas como precursores para a síntese de matérias adsorventes e catalisadores, dependem principalmente dos grupos funcionais oxigenados (GFO) na superfície do hydrochar [2].

Por meio dessa pesquisa nos empenhamos em demonstrar as alterações ocorridas nos grupos funcionais oxigenados da biomassa lignocelulósica quando submetidas ao processo HTC.

Foi utilizado o defeito PVA do café como biomassa, e submetidas a um processo de carbonização hidrotérmica ocorrida nas temperaturas de 150 e 250ºC sob pressão autogênica. Os grupos funcionais da superfície do carvão foram analisados por espectroscopia de infravermelho.

Os resultados indicam que grupos hidroxilas (C-OH) e éteres (C-O-C) diminuem coma temperatura, devido a degradação de celulose e hemicelulose. Em contrapartida houve um aumento na formação de grupos carbonílicos (C=O), em virtude da formação do char. Os GFO podem inferir em retenção de cátions no solo, hidrofobicidade em combustíveis sólidos e facilitador de ativação química.

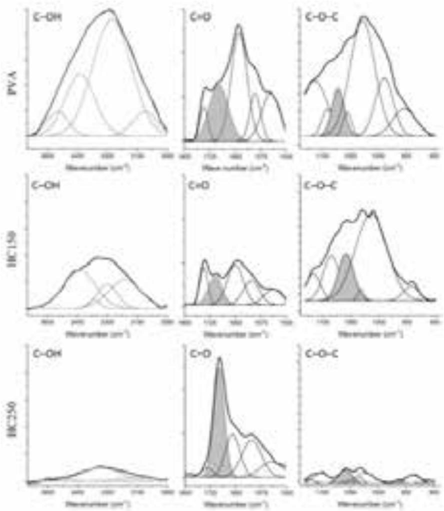

Fig. 1. Deconvolução de bandas FT-IR referente a grupos oxigenados.

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Fotocatálise heterogénea usando UV-LEDs e TiO_2 imobilizado aplicada ao tratamento de efluentes agro-industriais

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No tratamento de efluentes vinícolas, devido ao seu elevado conteúdo orgânico, o tratamento biológico é amplamente usado. No entanto, existem compostos que não são facilmente biodegradáveis, diminuindo a eficácia deste tipo de tratamento.

Os processos de fotocatálise são uma solução promissora para a degradação de efluentes recalcitrantes, já que oxidam e mineralizam moléculas orgânicas, através de reações de oxidação, convertendo-as em H_2O, CO_2 e moléculas inorgânicas. Podem ser combinadas com processos de tratamento biológicos, por exemplo como um pós-tratamento, com o objetivo de aumentar a eficiência global [1].

Fotocatálise usando sistemas UV-LEDs tem sido usada como uma alternativa de baixo custo e baixo impacto ambiental no tratamento de efluentes vinícolas [2].

Entre os fotocatalisadores semicondutores, o dióxido de titânio (TiO_2) é o mais usado em processos fotocatalíticos. Em processos conventuais, o TiO_2 é usado sob a forma de pó, que é disperso no efluente, tornando difícil a separação do catalisador no final do processo de tratamento. A imobilização em suportes sólidos como o vidro é uma alternativa. [3,4].

Neste trabalho, foi desenvolvido um processo de imobilização de TiO_2 em cilindros de vidro (anéis de Raschig), usando uma suspensão de TiO_2-P25/etanol. Este catalisador suportado foi testado usando sistemas de LEDs (365 nm), na remoção do carbono orgânico total de um efluente vinícola sujeito a um tratamento biológico prévio. Obteve-se uma massa imobilizada de cerca de 0,6 mg TiO_2/cilindro de TiO_2. No final de cada ensaio e após a lavagem dos suportes de vidro, verificou-se uma perda de catalisador de 3 – 4%.

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Degradação do ácido oxâmico por ozonização fotocatalítica na presença de nitreto de carbono

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A ozonização fotocatalítica é uma tecnologia emergente para a eliminação de compostos orgânicos persistentes em águas e águas residuais [1]. A presença de efeitos sinérgicos quando radiação, ozono e um catalisador adequado são combinados no meio reacional conduz a uma degradação eficaz dos poluentes, bem como a elevados níveis de mineralização. Com este trabalho pretendeu-se avaliar a atividade catalítica do nitreto de carbono (C_3N_4), um nanomaterial com propriedades semicondutoras recentemente classificado como um dos polímeros mais inovadores para aplicações em catálise, na ozonização fotocatalítica do ácido oxâmico (OMA). O OMA foi selecionado como composto modelo uma vez que é um produto final da degradação de inúmeros compostos com grupos funcionais azotados e por apresentar um caracter refratário à oxidação. Além disso, encontra-se pouca informação na literatura sobre a degradação deste poluente. Realizaram-se ensaios não catalíticos e com os métodos individuais com o objetivo de compreender o mecanismo reacional. Nas reações foto-assistidas utilizaram-se LEDs como fonte de radiação na gama do visível (l_{exc} = 417 nm; I = 450 W m^{-2}) e como catalisadores, o nitreto de carbono (CN) e um material exfoliado por pós-tratamento térmico do CN designado por CN-500 [2]. Foi ainda utilizado TiO_2 (Evonik P25), como fotocatalisador de referência. A ozonização simples (O_3) e a fotólise (LED) revelaram não serem capazes de remover o OMA e que quando combinados estes dois processos (O_3 + LED) apenas 30% do OMA é removido após 120 min de reação (Fig. 1). A presença dos catalisadores produz um efeito positivo na degradação do OMA quando combinados com o O_3 e luz. O nitreto de carbono exfoliado termicamente (CN-500) apresenta uma atividade catalítica bastante superior à do CN e do TiO_2, promovendo a remoção completa do OMA ao fim de 120 min de reação. Os resultados obtidos serão discutidos tendo em conta as propriedades óticas, eletrónicas e texturais dos diferentes catalisadores.

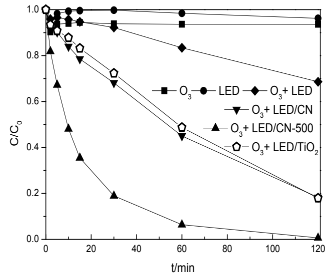

Fig.1. Degradação do OMA por ozonização fotocatalítica (C0 = 1 mM; Ccat = 0.5 g L-1).

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Recovery of Co and Li compounds and resynthesis of $LiCoO_2$ from discarded cell phone batteries

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Recycling of discarded Li-ion batteries is a strategy to ensure the sustainability of scarce materials employed in their manufacture as Co and Li. Environmentally compatible, industrially scalable and cost-effective recycling processes should be formulated in complying with these goals. We describe a close-loop process with these characteristics from which Co_3O_4 and Li_2CO_3 compounds were recovered from the cathode material of spent cell phone batteries and from them, stoichiometric and high ordered $LiCoO_2$ compound was resynthesized.

$LiCoO_2$ cathode material ($LiCoO_2$+polyvinylidene fluoride binder (PVDF)+carbon) detached from the cathode strip was submitted to a thermal treatment at 700 °C, in an O_2 atmosphere, burning the PVDF and the conductive carbon. Li_1CoO_2 and Co_3O_4 were identified as the thermal decomposition products in mass concentrations of 86.7% and 13.3%, respectively, under Rietveld refinement on the X-ray pattern of the calcined cathode powder.

The thermal-treated powder was leached in citric acid solution and the Co_3O_4 was retained on filtration. Upon oxalic acid, $CoC_2O_4.2H_2O$ was precipitate from the solution, filtered and further calcined to Co_3O_4. The remaining Li solution was evaporated and its product calcined at 600 °C, by 6 hours in air, resulting in the Li_2CO_3 compound, stoichiometric $LiCoO_2$ (in a very low concentration) and ashes. Water dissolution of these calcination products and filtration resulted in a solution containing only lithium that further evaporated resulted in the Li_2CO_3 compound. Co_3O_4 and Li_2CO_3 were recovered at efficiencies of 98% and 75%, respectively.

From the recovered Co_3O_4 and Li_2CO_3 compounds, stoichiometric and structurally ordered $LiCoO_2$ cathode material was resynthesized by a solid-state reaction at 750 °C. Charge capacity of 120 mAh g^{-1} was measured after 20 consecutive charge-discharge cycles on electrodes manufactured with the resynthesized $LiCoO_2$.

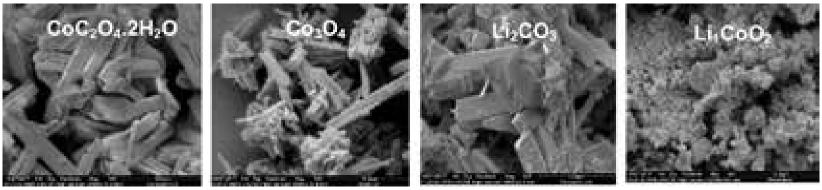

Fig. 1. Compounds recovered from the cathode of spent cell phone batteries by applying the proposed close-loop recycling process.

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Effects of artificial weathering on microplastics of packaging materials

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Microplastics (MPs) can be present in the environment as manufactured microplastics (known as primary microplastics) or as a result of the continuous weathering of plastic litter, which yields progressively smaller plastic fragments (known as secondary microplastics) [1]. The assessment of the changes and processes that MPs suffer during weathering is essential to understand their effects in the environment.

In the framework of the BASEMAN project (EU-funded JPI Oceans Program) microplastics of nine different polymers, in two size presentations (100-500 µm and pellets ≤1 mm) were weathered artificially under controlled conditions. A pilot-scale device for weathering (simulating shoreline dry conditions and seawater marine conditions), using UV/Vis metal halide lamps, filtered seawater, sand and water agitation, was deployed.

In this report we focus on characterizing the changes that accelerated artificial weathering produced in MPs of the most common polymers used to packaging: HDPE, LDPE, PS, PP and PET. This could be useful to reliably identify plastics and microplastics found in samples withdrawn from the marine environment, and understand how aging affects the surface and chemical structure of those materials. In addition, note that these five polymers are the most commonly used and abundant ones worldwide [2].

The FT-IR spectral analysis of degraded MPs (Perkin Elmer Spectrum 400, with a Spotlight 200 microscope) revealed changes in the spectral bands (and, so, in their major structures). Differences between polymers are observed as well. SEM microscopy (Scanning electron microscopy, JEOL JSM 6400) was capable of identifying morphological changes and degradation in the surface of polymers.

The overall results reveal that an adequate knowledge of the weathering process is needed for the adequate monitoring of microplastics in the environment. Further, the introduction of spectra from weathered MPs in the infrared databases is mandatory to correctly identify some particles found in the samples.

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PLS-DA model for biomonitoring of *Coffea arabica* leaves exposed to increased atmospheric CO_2

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Biomonitoring consists of the use of responses of individual plants to detect changes in the environment. These changes are predicted by the accumulation, loss or biosynthesis of chemical compounds present after exposures to environmental changes [1]. An analytical strategy for this monitoring is the use of direct measurement tools associated with chemometric classifications. This work reports the use of Near Infrared Spectroscopy (NIR) combined with multivariate analysis as a rapid tool for discriminating *Coffea arabica* leaves grown in current atmospheric levels of carbon dioxide and under higher atmospheric CO_2 conditions.

The coffee trees were cultivated under the Free Air Carbon Dioxide Enrichment (FACE) experiment (590µL CO_2 L^{-1}) for five years. Lateral leaves were collected at different positions during flowering in the fourth year of the experiment and seven months after CO_2 enrichment was suspended. Six spectral measurements of reflectance were made on the adaxial surface of the leaves avoiding the central vein. Partial Least Squares for Discriminant Analysis (PLS-DA) was used to evaluate leaves from two air CO_2 concentrations plots. The spectra were preprocessed applying the Multiplicative Scatter Correction (MSC), taking the second derivative and mean centering. The Variable Importance in Projection (VIP) values greater than 1 inform the relevant spectral regions for good PLS-DA model performance. The 1572, 1610, 1664, 1684 and 1698 nm bands were important discriminators. Bands at 1610, 1664, 1684 and 1698 nm may be attributed to the C-H stretch [2]; to which 1664 and 1684 nm are characteristics of the first harmonic stretch of the C-H bond related to the methylxanthine molecules. Band at 1572 nm may be attributed to the N-H stretch, also present in the methylxanthines already found in the coffee leaves. According to the PLS-DA scores, the leaf samples with high CO_2 concentration presented more negative values on the second Latent Variable (LV) and the respective negative loading values for LV2 were the bands indicated by VIP scores. Thus, we may conclude that the methylxanthines appear to discriminate these coffee leaves.

The use of NIR spectroscopy associated with PLS-DA discriminated coffee leaf samples cultivated under current and enriched CO_2 levels. After 7 months of suspension of CO_2 emission, the PLS-DA model was applied to the new leaves, which were classified as leaves grown in the current CO_2 levels, confirming the model robustness and the use of leaf methylxanthines in *Coffea arabica* as bioindicator of atmospheric CO_2 changes.

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Valorisation of wastes as biosorbents for the simultaneous removal of pharmaceuticals and personal care products

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Pharmaceutical and personal care products are widely used nowadays including a wide variety of products (parabens, medicaments…). These products are potentially dangerous when they are released into the environment, causing serious problems due to their persistence and low degradability. These compounds, considered emerging pollutants, are found in wastewater in different concentrations, being highly present in some areas, such as urban or hospital areas.

The current wastewater treatment plants are not design to treat and eliminate these contaminants, so it is necessary to look for alternatives to solve this environmental problem such as adsorption. Adsorption is a treatment technique with low energy and maintenance costs and operational simplicity, however, nowadays, new low-cost adsorbents, widely available in the environment are required.

This work proposes the elimination of two pollutants such as sulfamethoxazole (SMX) and methyl paraben (MePa), through the adsorption process. Initially, different wastes were selected from an industrial company as potential biosorbents. Those wastes were characterized and the main properties: structure, composition, point of zero charge and functional groups were determined by different techniques including Scanning Electron Microscopy. Then, the feasibility of these wastes in the removal of the selected pollutants was evaluated. Once the best option among the potential biosorbents was selected the adsorption process was studied and the determination of a series of parameters, such as operative and kinetic parameters, was performed. These were evaluated considering pseudo-first and pseudo-second order models, the latter being those that give higher correlation coefficients. The adsorption isotherms were also evaluated and two different models (Langmuir and Freundlich) were considered. For the experimental models the Freundlich isotherm adjusted to the results and a heterogeneous adsorption was suggested, which could be explained because the strongest binding sites were initially occupied and when the degree of site increases, the binding strength is decreasing.

The results obtained in this study showed that the selected raw materials could be used effectively in the elimination of SMX and MePa. In addition, the adsorption kinetics studies revealed that the pseudo-second order model proved the best fit to the experimental data and the adsorption isotherms showed the best adjustment model for the description of the adsorption equilibrium by Freundlich model.

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Combinação de agentes físico-químicos na degradação de geotêxteis – o projeto geosinergismo

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Os geotêxteis, materiais poliméricos usados na construção de várias estruturas de Engenharia Civil, podem estar expostos a vários agentes de degradação, tais como: espécies químicas presentes nos solos e/ou em fluidos (ácidos, bases, lixiviados de aterros de resíduos), temperaturas elevadas, oxigénio ou radiação ultravioleta (UV). O contacto prolongado com estes agentes pode causar alterações indesejáveis nas propriedades dos geotêxteis, afetando o seu desempenho e reduzindo o seu tempo de vida útil.

A durabilidade dos geotêxteis é normalmente considerada tendo apenas em conta a ação isolada dos agentes de degradação. Contudo, a ação simultânea de vários agentes de degradação (que ocorre em situações reais) pode ser muito diferente do somatório dos efeitos isolados desses agentes [1]. Assim, a avaliação do efeito combinado de vários agentes de degradação permite obter uma melhor previsão do comportamento a longo prazo dos geotêxteis.

O projeto GeoSinergismo [2], associando a Química à Engenharia Civil, pretende contribuir para uma melhor compreensão e previsão da durabilidade dos geotêxteis, tendo em consideração a combinação de vários agentes de degradação. Este trabalho, incluído no projeto GeoSinergismo, estuda algumas combinações de agentes físico-químicos na degradação de geotêxteis: ação de líquidos, termo-oxidação e ação da radiação UV. Numa primeira fase, os geotêxteis foram expostos de forma isolada aos agentes de degradação (exposição única). Em seguida, os materiais foram expostos sucessivamente a dois, ou mais, agentes de degradação (exposição múltipla). Os danos ocorridos nos geotêxteis foram avaliados pela monitorização de alterações no seu comportamento à tração. Tendo em conta as alterações ocorridas, o efeito combinado dos agentes de degradação foi comparado com o somatório dos seus efeitos isolados e avaliou-se a existência de interações entre os vários agentes de degradação.

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Methyl deoxycholate monosulfate, a new antifouling compound with low bioaccumulative potential

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Fouling on ships represents serious economic and environmental problems due to accelerated fuel consumption, increased costs and time for cleaning and maintenance, emission of harmful gases, and transport of non-native species, causing a major human health and environmental impacts. The search for new antifouling products has become a fast-growing research field since the ban of the main antifouling paints in use, due to toxicological issues. Among the search for solutions for these issues, nearly fourteen sulfated steroids (thirteen of which were monosulfated), isolated from different marine species, were found to display antifouling activity [1]. Sulfation is used by Nature to avoid toxicity; therefore, the synthesis of sulfated derivatives could be an opportunity to develop new non-toxic antifouling compounds.

In this work, the synthesis of methyl deoxycholate 3-sulfate was achieved in two steps: Fischer esterification of the commercial deoxycholic acid under acidic conditions (HCl conc.), in methanol in excess at reflux (40% yield), followed by sulfation using triethylamine-sulfur trioxide adduct (3 equiv/OH) in dimethylacetamide at 100ºC (3% yield). Structure elucidation of this new compound was established by infrared (IR) and nuclear magnetic resonance (NMR). The sulfated derivative as well as the non-sulfated parent compound, methyl deoxycholate, were tested against the adhesive larvae of *Mytillus galloprovinciallis*. Following, KOWWIN™ v1.68 program developed by Syracuse Research Cooperation jointly with the Environmental Protection Agency (EPA) was used for *in silico* calculation of log Kow (octanol-water partition coefficient) in order to evaluate the bioaccumulation potential of both compounds and their predicted biomagnification through the food chain.

Both compounds were able to inhibit the settlement of mussels larvae with EC_{50} values around 8 μM but while sulfated derivative revealed a log Kow value of 1.49, the non-sulfated parent compound exhibited a log Kow value of 5.34. These results show the potential of sulfation to obtain new antifouling derivatives with low bioaccumulative potential (log Kow <3).

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Remoção do ibuprofeno através da ozonização catalítica

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A ozonização catalítica resulta da combinação do ozono (O_3) com um catalisador e é um processo frequentemente utilizado para combater a formação de intermediários que apresentam elevado grau de resistência à degradação através da ozonização simples. Assim, surge a necessidade de desenvolver catalisadores ativos que permitam obter uma mineralização completa das soluções [1]. O fármaco ibuprofeno (IBP) foi selecionado como composto modelo, pois é um dos anti-inflamatórios mais vendidos em todo mundo, para além de já ter sido detetado em recursos hídricos [2]. O IBP leva à formação de vários intermediários que não são facilmente removidos atrav**és dos** métodos tradicionais. Com este trabalho pretendeu-se avaliar a remoção do IBP através da ozonização catalítica. Para tal, foram selecionados catalisadores à base materiais de carbono, nanotubos de carbono, amostra CNT, e ferro suportado em nanotubos de carbono, amostra Fe/CNT [3]. A atividade catalítica foi avaliada em termos de concentração de IBP, mineralização, formação de intermediários e toxicidade das soluções tratadas. Na Fig. 1 estão apresentados os resultados da degradação de IBP e remoção de carga orgânica (TOC) através da ozonização catalítica. Tal como era de esperar, a ozonização simples é suficiente para remover eficazmente o IBF da solução, verificando-se uma degradação completa do composto após 15 min de reação, devido à alta reatividade do O_3 com a molécula de IBF. Contudo, a presença de catalisador é necessária para obter rapidamente uma mineralização elevada. A ozonização catalítica na presença dos catalisadores testados conduz a uma remoção de TOC de mais de 40% em apenas 30 min de reação. Verificou-se que a toxicidade das soluções tratados por ozonização catalítica é inferior **à** observada na ozonização simples, sugerindo que o mecanismo reacional **é diferente** quando o O_3 é combinado com CNT e Fe/CNT de quando este se encontra sozinho, levando à formação de compostos intermediários menos tóxicos.

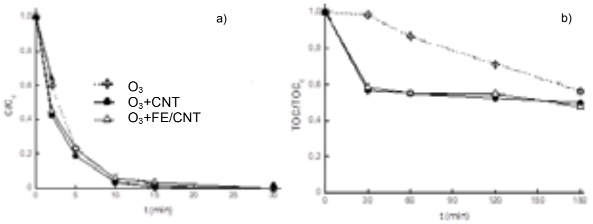

Fig.1. Evolução da concentração adimensional de IBP (a) e TOC (b) na ozonização catalítica.

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Caracterização do ruído em vias de grande tráfego de Lisboa

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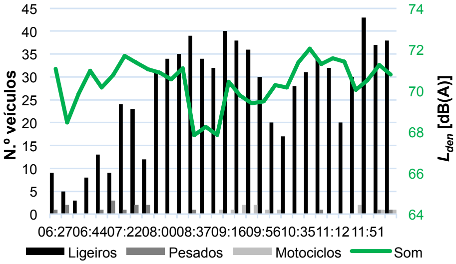
O ruído proveniente de tráfego rodoviário constitui a maior fonte de poluição sonora na Europa. Estima-se que cerca de 100 milhões de pessoas são afetadas por níveis prejudiciais de ruído proveniente de tráfego rodoviário [1] e das emissões de poluentes por eles gerados. As medições de ruído são realizadas com sonómetros devidamente calibrados. No entanto, diversos estudos apontam para a utilização de *smartphones*, como dispositivo de medição de som, com a utilização de aplicações como NoiseTube, SoundPrint e iHEARu. Os utilizadores podem partilhar os níveis de ruído e a geolocalização utilizando o áudio e GPS dos dispositivos para mapear níveis de ruído em cidades [2].

Para todos os tipos de veículos, o nível de pressão sonora aumenta com a velocidade nas estradas de asfalto seco e molhado e, além disso, o ruído do pneu / estrada domina o ruído do motor em qualquer velocidade. Assim, o ruído do pneu / estrada é cada vez mais provável de dominar o ruído do veículo à medida que a velocidade aumenta [3].

O objetivo do presente estudo é caracterizar uma das vias mais movimentadas de Portugal, a segunda circular, mais especificamente no Nó Azinhaga das Galhardas/Campo Grande (Figura 1) com a utilização destes mesmos dispositivos. Posteriormente, pretende-se desenvolver um modelo matemático que relacionará o número, o tipo de veículos e a velocidade média a que se deslocam, com o ruído e com a emissão de gases poluentes. O modelo e resultados obtidos poderão suportar futuras decisões de construção nas proximidades bem como fornecer orientações nas medidas de mitigação do ruído em instalações já existentes como escolas, hospitais, grandes edifícios, entre outras.

Numa primeira instância, os resultados obtidos permitem relacionar os dados de som obtidos com o número de veículos. Nas horas de maior tráfego rodoviário observa-se um maior número de veículos a circular, logo uma menor velocidade, devido ao congestionamento. Regista-se assim um menor valor de ruído como se mostra na Figura 2.



Os dados de ruído permitirão, assim estimar o número de veículos e a sua obtenção é bastante mais simples que a contagem dos mesmos. A partir do número de veículos poderá ser estimada a qualidade do ar a partir de uma medida simples de ruído.

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Concentraciones de actividad de ^{137}cs, ^{40}k, ^{214}bi, ^{214}pb, ^{212}pb, ^{210}pb, ^{208}tl, ^{228}ac, ^{7}be y ^{212}bi en muestras de vegetación asociadas al suelo de la costa norte de galicia (nw españa)

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El estudio de la presencia y dispersión de radionucleidos naturales y artificiales en el suelo cobra cada día más importancia debido a accidentes como los de Chernobyl (1986) y Fukushima (2011), que han abierto los ojos a la sociedad acerca de la importancia del estudio y control de la radiactividad.

La radiación natural presente en nuestro planeta procede de diversas fuentes y genera la mayor parte de la radiactividad que nos rodea. La radiactividad antropogénica se debe a dos causas fundamentales: la radiactividad procedente de materiales relacionados con actividades realizadas por el hombre, y la radiactividad artificial, debida a las pruebas nucleares.

El suelo está constituido por una gran cantidad de minerales que contienen elementos radiactivos naturales, emitiendo así radiación que afecta al medio ambiente. La caracterización del suelo se realiza con el objetivo de establecer niveles de referencia para futuras investigaciones

En este trabajo se han recogido 33 muestras de suelo de la costa norte de Galicia que se han dividido en dos porciones diferentes: una correspondiente al suelo propiamente dicho y otra a la vegetación asociada a dicho suelo. Para ello se ha cortado la hierba superficial existente y se ha almacenado en un recipiente hermético para su posterior análisis individual mediante espectrometría gamma [1, 2, 3]. El motivo de esta división es el estudio de la transferencia de radionucleidos entre la muestra de suelo y la de vegetación asociada, así como la posible detección de isótopos volátiles que puedan depositarse en la superficie de dicha vegetación.

Las actividades medias obtenidas para 137Cs, 40K, 214Bi, 214Pb, 212Pb, 210Pb, 208Tl, 228Ac, 7Be, y 212Bi fueron: 9,1± 1,1, 397 ±38, 20,1±2,4, 17,8±1,8, 14,2±1,6, 120,5,1±2,3, 13,4±1,6, 18,4±2,0, 497±43, 14,2±2,9 Bq.kg-1, respectivamente.

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Synthetic improvements of a new antifouling agent and its application in marine coatings

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Gallic acid persulfate (AGS) was discovery as a promising antifouling compound, with an effective anti-settlement activity against *Mytilus galloprovinciallis* larvae without toxicity (LC_{50}/ EC_{50} = 26.61) [1]. This sulfated compound also did not show ecotoxicity against the marine bacterium *Vibrio fisheri*, other fouling organism, as well as against the non-target organism *Artemia salina*, and presented a low bioaccumulation potential (calculated log Kow < 3) [1].

Following these previous ecological results, AGS was selected for compatibility studies in marine coatings. To overcome the need for larger amounts of supply, a more reproducible and feasible synthesis of AGS, with better yields, was achieved. The synthesis of gallic acid persulfate was accomplished by sulfation of gallic acid with triethylamine sulfur trioxide adduct (6 equiv/OH), in dimethylformamide. The use of MW irradiation decreased the reaction time (from 24 h to only 1 hour) and significantly increased the yield (from 36% to 96%) when compared to the previous described procedure in which conventional heating was used [2].

Moreover, the compatibility of this sulfated compound with two polymeric-based marine paints (silicone and polyurethane) was tested through conventional incorporation methods. Stirring tests (adapted from ISO15181) were performed and the leaching of AGS from the polymeric coatings to artificial seawater was measured by HPLC-DAD. After a period of 45 days, the leaching percentage of AGS was around 20 %(w/v) in both coatings showing the potential of AGS as a future eco-friendly additive for coatings formulations.

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Los oxihidroxidos de Fe y su papel en la geoquímica del Cr, Ni, Zn, Cu en sedimentos de la Ria de Ortigueira (NW Iberian Peninsula)

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Los óxidos de hierro desempeñan un papel muy importante en los suelos, por la facilidad con que cambian valencia y pueden formar complejos con numerosos productos orgánicos y minerales. Los óxidos de hierro son anfóteros, a valores de pH ácidos los protones son retenidos por la superficie de los grupos funcionales Fe-OH, incrementando la carga positiva: $Fe\text{-}OH + H+ = Fe\text{-}OH_2^+$, mientras que en pH alcalinos, el ión H^+ puede ser liberado y crear una carga negativa: $Fe\text{-}OH = Fe\text{-}O^- + H^+$ [1]. Los oxihidr**ó**xidos de hierro se forman dentro de los sedimentos en las capas superficiales **ó**xicas-subóxicas, pudiendo desempeñar un papel importante en la regulación de las concentraciones de elementos traza, por mecanismos de coprecipitación-adsorción acumulándose en los sedimento [2]. Al encontrarse inundado el Fe y los metales se reducen, incrementando su solubilidad, excepto en ambientes con sulfuros donde la coprecipitación con la pirita los estabiliza.

En la Ria de Ortigueira se analizó 115 sedimentos superficiales, utilizó una extracción secuencial propuesta por Ferreira, 2006 [3], consta de 6 etapas capaces de separar los metales asociados a seis formas definidas del Fe: F1 intercambiable; F2 a carbonatos; F3 a la ferrihidrita; F4 lepidocrosita; F5 goetita-hematita y F6 pirita. Encontrando (Fig.1), que el Cu se encuentro asociado a las formas de goetita y pirita por su afinidad a los sulfuros. El Cr se encuentra asociado a las formas menos cristalinas del Fe y presenta un bajo grado de piritización, por sus tendencia a formas óxidos que son insolubles en condiciones suboxicas. El Zn y Mn tienden a asociarse a las formas pobremente cristalinas del Fe y a los carbonatos, esto le facilita su salida del sedimento al medio acuso. El Ni se encuentra asociado a las formas pobremente cristalinas del Fe que le hace muy móvil en la solución suelos agua. En general los sedimentos presentan un alto grado de piritización 24% DOP que mantiene estables los metales.

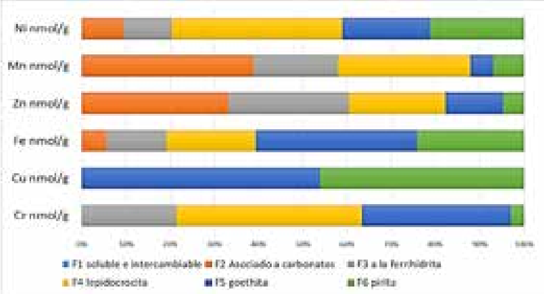

Fig.1. Contenido de Ni, Mn, Zn, Fe, Cu y Cr asociado a las formas de Fe de la extracción secuencial.

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QAMB49

Use of recycled tires in synthetic football pitches

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A large volume of used tires enters the waste stream in the world each year and recycled rubber from ELT is used as filling in synthetic turf fields and playgrounds [1]. After research published in the past 10 years, concerns exist regarding the safety of synthetic turf fields and the governmental agencies US-EPA, in April 2016 [2] and European Chemicals Agency (ECHA), in Feb 2017 [3] found the need to obtain further information.

Rubber crumb is any material derived by reducing scrap tires or other rubber into uniform granules, with the inherent fabric materials (steel, fibres) and contaminants (dust) removed. There are essentially two tire recycling processes for rubber crumb - ambient grinding and cryogenic [4]. Tire rubber is composed of 40-60% rubber polymer, reinforcing agents such as carbon black or silica (20-35%), extender oils (up to 28%), vulcanisation additives, antioxidants, antiozonants, and processing aids (plasticizers and softeners). The tires may contain or acquire during their use several chemicals of potential concern, including heavy metals, volatile organic compounds or polycyclic aromatic hydrocarbons (PAHs).

This study intends to provide a comprehensive review regarding the use of rubber crumb in synthetic football pitches. The levels of potentially harmful contaminants found in pitches worldwide, the potential health risks and the actions under consideration to mitigate the presence of those chemicals in rubber crumb are the main objectives under aim.

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Multimilligram enantioresolution of norketamine on polysaccharide phase using microporous silica as support

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The current and growing evolution of the chemical industry has contributed to an urgent environmental problem, since numerous substances, including drugs and illicit drugs, have been detected in the environment, behaving as environmental contaminants [1,2]. Excessive consumption and continuous disposal of these substances may present potential short-term or long-term risks for humans and other exposed organisms [1,3]. Ketamine (K) is used in pediatric and veterinary medicine as an anesthetic, however, its abusively used by adolescents and young adults in recreational environments due to its hallucinogenic and sedative effects has been increased [2]. After consumption, K and its main metabolite, norketamine (NK), are excreted into the sewage networks and have been detected in effluents from wastewater treatment plants (WWTP) and in aquatic environments [1-3]. Thus, it is urgent to evaluate the ecotoxicity of K and NK, either as racemate or in the enantiomeric pure forms, for a correct risk assessment. In ours previous studies, the acute and chronic toxicity of K and NK in aquatic organisms (both in their racemic form) was evaluated. In acute toxicological assays, NK presents a higher mortality for crustacean *Daphnia magna* compared to K. For chronic toxicological assays, K demonstrated greater growth inhibition for *Tetrahymena thermophila* compared to NK. However the ecotoxicity of the enantiomers of K and NK have never been evaluated (either acute or chronic toxicity). This work presents the preparative enantioseparation of NK in order to obtain the enantiomers for further enantioselective ecotoxicity studies. Preparative chromatography was performed using the Merck Hitachi LaChrom HPLC with DAD detector at 220 nm using the semi-preparative amylose 3,5dimethylphenylcarbamate column coated on to APS-Nucleosil (500 A, 7µm, 20%, w/w) and packed into a stainless-steel 20 x 0.7 cm I.D. size column at an isocratic mobile phase consisting of n-hexane (0.1% DEA (diethylamine)) and ethanol (0.1% DEA) (65:35) and flow-rate of 1.5 mL/min. The chromatographic separation was performed with a concentrated solution of 10 mg/mL NK in ethanol and injection volume of 50 µL. In this chromatographic separation three fractions were collected: fraction 1 - corresponding to the first enantiomer eluted from NK (NK1), intermediate fraction - containing mostly NK1 and some residues of the second enantiomer eluted (NK2) and fraction 2 - corresponding to NK2. The enantiomeric purity was evaluated using analytical lux® 3 µm cellulose 4 column (150 × 4.6 mm column size) for each enantiomer and injection volume of 10 µL, fraction 1 and 2 showed enantiomeric ratio higher than 99% for NK1 and NK2. Acute and chronic enantioselective toxicity tests of NK in Daphnia magna organisms and the protozoan Tetrahymena thermophila will be carried out in accordance with national and international standards (ISO and OECD).

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Evaluation of the adsorption potential of biochars prepared from agro-food wastes for the removal of fluoxetine

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Fluoxetine is a pharmaceutical widely used to treat depression. Although, as only a part its metabolized by human body, much of it (and its metabolites) may end up in domestic wastewaters. As conventional wastewaters were not designed specifically for removal of pharmaceuticals, they will be discharged in the aquatic environment being able to negatively affect aquatic organisms [1]. Due to the increasing levels of such contaminants, it is crucial to develop remediation strategies in order to remove these pollutants. An effective methodology for wastewater purification is adsorption. In particular, biochar materials have been shown to be a promising solution, with high adsorption efficiency [2].

Many industrial activities generate large quantities of biomass wastes, and biochar production from these wastes is currently one of the more innovative and unexplored field of research [2, 3]. Thus, the present work aims to evaluate the possibility of using different agro-food wastes to produce biochars, which will be tested for the removal of fluoxetine. For that, thirteen wastes from different sources (*Quercus ilex, Eucalyptus, Pinus, Quercus sube, Malus pumila, Prunus, Cydonia oblonga, Eriobotrya japonica, Juglandaceae, Actinidia, Citrus sinensis* and *Vitaceae* pruning residues) were pyrolyzed. All the produced biochars were milled and the moisture and ash content, as well as the volatile matter were determined. The results showed very similar characteristics, with some differences in the ash and volatile matter contents. Concerning the results obtained in the preliminary assays performed to evaluate the capacity of biochars for fluoxetine removal, an adsorption percentage ranging from 36 to 100% for pine and eucalyptus residues, respectively, was reached. These preliminary data enable us to pre-select the produced biochars with the highest adsorption capacity, namely *Quercus ilex*, *Cydonia oblonga, Eucalyptus*, *Juglandaceae* and *Vitaceae* pruning residues, in order to be subsequently fully characterized. Kinetics and equilibrium assays are being carried out to determine the effectiveness of the selected biochars on fluoxetine adsorption. Overall, these first results have been demonstrating that residues from agro-food industries can be converted into efficient materials for environmental remediation.

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Simultaneous Removal of cyanide and heavy metals from aN electroplating wastewater USIGN calcium alginate beads

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Cyanide is a highly toxic chemical compound for animals and humans [1] and it is widely used in metal finishing industries in order to assure the high quality of electroplated products. It is usually found as contaminant in different industrial effluents including electroplating, metal processing, mining, etc. [2] and generally co-exists with different heavy metals. Cyanide can be found in different chemical forms: free cyanide or coordinated with metallic elements. Free cyanide (CN_f) includes the most toxic forms: cyanide anion and hydrogen cyanide. However cyanide-complexes are classified according to the stability of the metal cyanide bond. Weak and moderately strong cyanide-complexes refer to complexes such as Cd, Cu, Ni, Zn and strong cyanide-complexes include complexes such as Co, Au and Fe [3]. Total cyanide (CN_t) includes the summary of all available chemical forms of cyanide.

Industrial effluents generally contain values lower than 10 mg/L of total cyanide, however some effluents from electroplating plants and other metal finishing processes may contain considerably higher values (10.000-30.000 mg/L) and even can reach 100.000 mg/L [4]. These highly contaminated effluents must be adequately treated before to be discharged into the environment. Several physical, chemical and biological treatments have been developed for cyanide removal from industrial wastewaters [5], including adsorption methods based on active carbon and ion exchange resins. These same adsorbents in addition to zeolites and diverse bio-adsorbents had been effectively applied for removal of metal ions [6]. In fact, the biopolymer calcium alginate (free or impregnated with different materials) can be considered an efficient and low cost adsorbent for remediation of diverse contaminants [7], and it could be an interesting proposal for cyanide sorption.

In this work were used calcium alginate beads for simultaneous removal of free cyanide (CN_f) and heavy metals (Cu, Ni and Zn) from an industrial wastewater collected in a nickel electroplating factory located next to the Vigo town. The use of this biopolymer in two successive contact steps allowed to reduce about 85 % the cyanide levels and between 93-98 % the contents of heavy metals. The use of other sorbents such as active carbon or entrapped grape marc in calcium alginate beads did not significantly increase the retention capacity of any of the pollutants studied.

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Reutilização de Águas Residuais e de Lamas da ETAR de Santa Cruz (Cabo Verde)

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A escassez de água sente-se em todos os setores da sociedade, desde águas para consumo humano como para usos industrial, agrícola e pecuário. Essa escassez incentiva não só a sua conservação, mas também o seu uso cada vez mais eficiente e sobretudo a sua reutilização [1].

Em Cabo Verde, tal como no resto de África, a agricultura é o sector que apresenta o maior consumo da água. Face a essa alta procura, a reutilização da água residual tratada (ART) na agricultura é uma alternativa que merece a melhor atenção. A aplicação da ART na agricultura diminui a pressão sobre a água potável, aumenta a produção agrícola em regiões com escassez de água, contribuindo assim para irradicação da escassez de alimentos. Essa prática pode ainda contribuir para a diminuição do uso de fertilizantes, visto que a ART é rica quer em macronutrientes (N, K e P) quer em micronutrientes tais como Ca, Mg, B, Mg, Fe, Mn e Zn [2].

O tratamento da água residual tem com subproduto lamas, que recebendo o tratamento adequado, poderão ser aplicadas nos solos favorecendo a produção agrícola. A aplicação de lama proveniente das Estações de Tratamento de Águas Residuais (ETAR) atua como fonte de nutrientes essenciais para as plantas, estimula a atividade microbiana, melhora a estrutura do solo e minimiza a erosão [3].

A ETAR de Santa Cruz (Cabo Verde) foi dimensionada para um caudal máximo de 111 m^3/h. A instalação de 6 050 m^2, contempla de um desarenador/flotador, dois decantadores/digestores, duas bacias de infiltração, um filtro mecânico e um tanque de armazenamento. O tratamento das lamas processa-se em leitos de secagem [4].

Com este estudo, pretende-se encontrar uma solução economicamente viável a qual garanta os requisitos da reutilização da água residual tratada. Um tratamento inadequado, exporia tanto as pessoas como o ambiente a organismos potencialmente patogénicos. Adicionalmente, poderá ainda haver a acumulação no solo e nas águas de substâncias nocivas que poderão conduzir à degradação ambiental [3].

Tabela 1. Características típicas dos afluente e efluente da ETAR de Santa Cruz [4]

	SST [mg/L]	CQO [mgO_2/L]	CBO [mgO_2/L]	Azoto Amoniacal [mgN/L]	Azoto Orgânico [mgN/L]	Nitratos [mgN/L]	Fósforo [mgP/L]
Afluente	771	1340	817	187	33	3	27
Efluente	6	21	1	-	-	1 256	7

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Heterogeneous photocatalysis using TiO_2 and wireless UV-A LEDs

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The use of ultraviolet (UV) radiation sources such as low and high pressure mercury vapour lamps is not only beneficial as its use shows some important drawbacks. Among these the power instability during long operation time, the low photonic efficiency, the high voltage at initial stage, the need for cooling and vapour pressure, the low lifetime and use of hazardous metals (e.g. mercury) are the main ones. In order to overcome these limitations, the UV light emitting diodes (LEDs) are emerging as a valuable alternative, being safer, having long lifetime and high energy efficiency [1].

Among the Advanced Oxidation Processes, heterogeneous photocatalysis using semiconductor materials rises as an alternative technology for water purification. TiO_2 is a well-known nanomaterial with high photocatalytic activity, chemical and biological stability, relatively low-cost and non-toxic [2].

In this work, a lab-scale bubble column reactor with a Reactive Black 5 solution (330 mL), a bottom air injection through an aquarium air pump, TiO_2 and 15 wireless UV-A LEDs (7 InGaN Roithner RLS-UV355E and 8 InGaN Roithner RLS-UV365E) were used to assess the degradation of the textile dye. Each LED has a radiant flux of 1 mW and a viewing angle of 30°. The LED emitters are placed inside the reactor and the electrical power to each one is provided by wireless power transfer using a resonant inductive coupling system. This system has four emission coils wrapped around the tubular reactor and each LED has a RLC receiver tuned to maximize the power coupling by having the same resonance frequency of the emission system.

The proof of concept was investigated in the photocatalytic degradation of Reactive Black 5 dye with different concentrations of TiO_2 and H_2O_2 (Fig. 1).

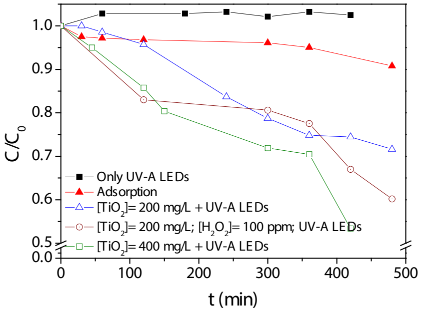

Fig.1. Photocatalytic degradation of the azo dye Reactive Black 5 ([RB5] = 10 mg/L; pH = 6.5 ± 0.5; T = 25° C).

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Development of a methodology for quantification of pharmaceuticals and personal care products in hydric media

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Emerging micropollutants are substances found in the environment in very low concentrations, as micrograms or nanograms per liter, but that can cause harmful effects even in these low quantities [1]. Since this is a recent issue, these pollutants are not legislated yet, but depending on the results of toxicity, bioaccumulation and other studies, they can be regulated in the future [2].

The Pharmaceuticals and Personal Care Products (PPCP's) are a subclass of emerging micropollutants. Although they are very relevant to society, these compounds are eliminated in high quantities by the human body and are not efficiently removed from water in sewage treatment plants [2]. Since they are present in very low concentrations, the analysis and study of PPCP's is a tough task, demanding sophisticated instrumental methods of analysis [1].

Therefore, the aim of this study is to develop a method of analysis to quantify and to monitor the concentration of some PPCP´s, such as, ibuprofen, diclofenac, naproxen, sulfamethoxazole, azithromycin and carbamazepine in aqueous media from Bragança region. These were the pharmaceutical drugs chosen since they are compounds most likely to be found in the aqueous matrices of the area. Table 1 gathers data from some studies that quantified these substances in different hydric media.

Table 1. Pharmaceutical drugs quantified in selected published studies.

Compound	Limit of Quantification (ppm)	Hydric Media	Method of analysis	Reference
Ibuprofen	0.17	Effluent	SPE/HPLC-DAD	[3]
Diclofenac	22.9	Raw sewage	SPE/HPLC-MS	[2]
Naproxen	120	Wastewater	SPE/HPLC-DAD	[4]
Azithromycin	13	Wastewater	SPE/HPLC-MS-MS	[5]
Sulfamethoxazole	6.25	Raw sewage	SPE/HPLC-MS	[2]
Carbamazepine	0.71	Pool water	SPE/GC-MS	[6]

In addition, to allow understanding which compounds would be indicated for the study, this data collection of already published works, allows the initial perception of which instrumental techniques can be employed for extraction and quantification. The possibilities that are considered for extraction methods are Solid Phase Extraction (SPE) and Solid Phase Micro-Extraction (SPME). The instrumental methods of analysis could be High Performance Liquid Chromatography coupled with mass spectrometry (HPLC-MS) and Gas Chromatography coupled with mass spectrometry (GC-MS).

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content and distribution evaluation of metals in sediments from the manhuaçu river basin, brazil

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Brazil is a unique country regarding the amount of water, as it has the largest reserve of fresh water available on the planet, reaching 14% of the world total [1]. The present work covers the Manhuaçu river basin, located in the southeast region of Brazil, where coffee cultivation plays an important role in the economy, in addition to mining. A sub-basin of the Doce river basin, The Manhuaçu river basin receives the acronym DO6 by UPGRH (Unit of Planning and Management of Water Resources) and contains 9,186.06 m^2 of drainage area [2]. The basin has 26 municipalities, totaling approximately 300 thousand inhabitants. About 39% of the total population of the Manhuaçu river basin is rural [3]. The most frequent water and environmental problems in the Manhuaçu river basin are the lack of sewage treatment, urban pollution, erosion, silting and lack of protection to riparian forests.

The aim of this work was to quantify the metal content in sediments from the Manhuaçu river, including Fe, Cr, Co, Ni, Mg, V, Na, K, Sr, Zn, Ca and Cu. The environmental diagnosis was performed through the demarcation of 30 sampling points throughout the Manhuaçu river and its main tributaries. Two sediment sampling campaigns were conducted, the first during the dry season (March 2016) and the second during the rainy season (November 2016).

This study revealed that the content of metals along the basin is in accordance with the standards established by CONAMA (National Environment Council). The metals found in the Manhuaçu river basin did not show any anthropic environmental impact, since when correlating the chalcophile, siderophile and lithophile elements of natural joint occurrence, they present the same tendency, indicating a possible occurrence or lithological derivation when compared to the DO6. By contrast, the sample from Doce river presented high levels of metals, due to the high industrialization throughout the basin, in addition to the recent collapse of a mining dam that lead to an increase in metal content in Doce river. As a result, the DO6 is in some way contributing to dilute the stronger impacts from the environmental tragedy in Doce river.

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Remoción de metales pesados con zeolitas magnéticas

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Hoy en día, la contaminación del agua por metales pesados es uno de los problemas más graves en el mundo. El aumento de la producción industrial y de las aguas residuales mineras son unas de los orígenes importantes de contaminación por metales pesados, siendo considerados nocivos para todas las formas de vida [1].

Por lo tanto, se están tomando medidas de adsorción económicas usando materias primas de bajo costo tales como minerales de arcilla, carbón activo y silicatos de aluminio (zeolitas) para obtener alta efectividad, menor consumo de energía y reproducibilidad. Las zeolitas naturales se han utilizado como materiales de intercambio catiónico para el tratamiento de metales pesados y otros contaminantes debido a sus excelentes propiedades como adsorbentes [2]. También tienen la ventaja de ser muy abundantes en la naturaleza y poseen una alta estabilidad química.

En este estudio, se sintetizó Zeolita A usando el método alcalino y el tratamiento de fusión alcalina, que forman Zeolita A por 8 cubo-octaedros unidos a través de 12 cuboides que tienen poros con diámetros en torno de unos 0,42 nm permitiendo que diferentes iones se difundan fácilmente [3] . Atavrés del anclaje de nanoaprticulas de magnetita (Fe3O4) a la superdificie de las zeolitas A, se añade funcionalidad magnética a las mismas, permitiendo la extraccion de las mismas del medio a tratar mediante la aplicación de un campo magnético externo. Se sintetizaron ademas compuestos magnéticos zeolíticos A-quitosano [4], aprovechando que el quitosano posee un gran numero de grupos amina ($-NH_2$) e hidroxilo (-OH) y actúan como puntos de coordinación para formar complejos con diversos iones de metales pesados, dotanco al conjunto de una gran capacidad de bioadsorcion.

Además, se realizaron experimentos de absorción de diversos metales para valorar la capacidad de remediacion de estos materiales.

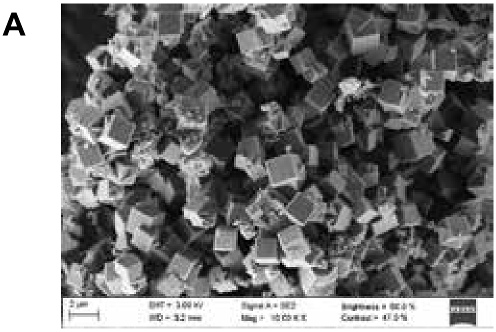

Fig.1. Micrografías SEM de la zeolita A sintética por fusión alcalina (A) y zeolita A dopadas con nanopartículas de magnetita

AGRADECIMIENTOS: Este trabajo fue financiado en parte por EP-INTERREG V A (POCTEP) (proyecto NANOEATERS / 1378), y por los fondos FEDER (proyecto MYCONTROL / ITC-20161072-2)

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chalcones as α-amylase and α-glucosidase inhibitors for the management of diabetes *mellitus*

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Diabetes *mellitus* (DM), one of major health challenges of the twenty-first century, is a chronic, developing and incompletely understood metabolic condition, mainly characterized by hyperglycemia [1]. The inhibition of the carbohydrate-hydrolyzing enzymes, α-amylase and α-glucosidase, is one of the major therapeutic strategies for the treatment of type 2 DM. The inhibition of these enzymes delays the absorption of monosaccharides on the gastrointestinal tract, preventing the occurrence of postprandial hyperglycemia. However, current therapeutic inhibitors have gastrointestinal adverse side effects. Low to moderate α-amylase inhibition with potent α-glucosidase inhibition might overcome the troublesome adverse effects [2]. Chalcones, secondary metabolites of terrestrial plants and precursors of the flavonoids biosynthesis, have been recognized for its multiple biological activities, including the anti-diabetic properties [3]. A panel of chalcones with hydroxyl, methoxy, methyl, nitro, chlorine, fluorine and bromine groups were evaluated, most of which for the first time, against α-amylase and α-glucosidase activities. An *in vitro* microanalysis method was performed to measure the substrate breakdown by these enzymes in the absence and presence of increasing concentrations of chalcones. The results showed that the substitution pattern influences the inhibitory activity of the compounds, the presence of hydroxyl groups being favorable for the intended effect at 2' and 4' positions of the A ring and at 4 and 5 positions of the B ring. Also, the presence of a hydroxyl group at 2' position of the A ring, together with a nitro group at 4 position of the B ring seems to be essential for the inhibitory activity of the chalcones. This study provided potential anti-diabetic compounds that should serve to the basis for the design and synthesis of more structures, in order to obtain the most potent chalcone' scaffold for the intended activity.

ACKNOWLEDGEMENTS: This work received financial support from the European Union (FEDER funds POCI/01/0145/FEDER/007265) and National Funds (FCT/MEC, Fundação para a Ciência e Tecnologia and Ministério da Educação e Ciência) under the Partnership Agreement PT2020 UID/QUI/50006/2013, and "Programa Operacional Competitividade e Internacionalização" (COMPETE) (POCI-01-0145-FEDER-029241), and under the framework of QREN (NORTE-01-0145-FEDER-000024).

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Characterization of the phenolic profile of *Caryota urens* L. – preliminary evidence on its antidiabetic properties

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Commonly known as kitul, *Caryota urens* L. is an indigenous plant from tropical Asia mainly reputed due to its utilization on the production of sweet sap (extracted from the inflorescences), as well as on the preparation of toddy and jaggery [1]. Despite its economic value, studies on its chemical composition are scarce. Thus, we attempted the HPLC-DAD-ESI-MS^n characterization of the phenolic profile of the methanolic extracts obtained from the inflorescences and fruits, nine caffeic acid derivatives being identified. Relevantly, several kitul products obtained from the sap of inflorescences are claimed not only to be suitable for diabetic patients, but also reported to exhibit potential antidiabetic properties [2,3]. Nevertheless, evidence of these alleged properties remains unclear. Hence, we additionally assessed the ability of both extracts to interfere with α-glucosidase and α-amylase, a potent inhibitory effect towards α-glucosidase being observed upon exposure to the inflorescences' extract (IC_{50} = 1.44 μg/mL) (**Fig. 1.**). Kinetic studies (**Fig. 1**) pointed to a model of mixed inhibition. Furthermore, given the strong evidence between oxidative stress and diabetes, we evaluated the scavenging properties of both extracts, significant scavenging effects being noted, particularly upon superoxide radical. *C. urens* inflorescences and fruits phenolic profile is here undisclosed for the first time, which might be related, at least partially, with the observed antidiabetic and scavenging effects.

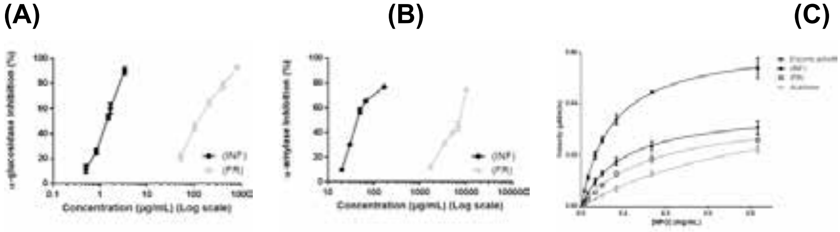

Fig. 1. α-Glucosidase (A) and α-amylase (B) inhibition upon exposure to the methanol extracts obtained from C. urens inflorescences (INF) and fruits (FR), and Michaelis-Menten plot of kinetics inhibition of α-glucosidase inhibitory effect (C). Data represent the mean ± SEM of three independent experiments, in triplicate.

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Development and application of a synaptosomal model for the study of peroxynitrite - induced lipid peroxidation

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Reactive pro-oxidant species are generated as a consequence of the normal functioning of the human organism. However, when produced in excess or when there is a deficit in the antioxidant defenses, oxidative stress may occur. Lipid membranes are particularly susceptible to oxidative stress as they suffer a chain reaction designated as lipid peroxidation (LP). Since the brain is mainly constituted by lipids (60%), brain tissue can be considered a good model basis for the evaluation of the deleterious effects of pro-oxidant species and the antioxidant effect of lipophilic compounds, in conditions close to a real scenario environment. Therefore, the main aim of this work was to develop a synaptosomal model to evaluate peroxynitrite (ONOO-)-induced LP and evaluate of the pro- / antioxidant activities of quercetin and b-carotene. Synaptosomes, isolated from rat brain tissue as previously described [1], were used to optimize the method for the ONOO--induced LP evaluation. To establish this method, various parameters were optimized: synaptosomes protein concentration, ONOO- concentration for LP induction and the incubation time of synaptosomes with ONOO-. The optimized method was defined: synaptosomes (with a protein concentration of 0.1 mg.mL-1) were incubated with ONOO- (10 mM), for 15 min, at 37 °C. Following this optimization process, the LP extent was evaluated through the thiobarbituric acid reactive substances (TBARS) method. Quercetin and b-carotene were added during the synaptosomes preparation step, aiming their incorporation into synaptosomes. Both quercetin and b-carotene showed protective behavior towards LP and none of the compounds induced LP, under the tested conditions. This work allowed the development and application of an experimental procedure for the ONOO--induced LP evaluation in rat brain synaptosomes, reporting, for the first time, the antioxidant protective behavior of quercetin and b-carotene towards LP in a synaptosomal model.

AKNOWLEDGEMENTS: This work received financial support from the European Union (FEDER funds POCI/01/0145/FEDER/007265) and National Funds (FCT/MEC, Fundação para a Ciência e Tecnologia and Ministério da Educação e Ciência) under the Partnership Agreement PT2020 UID/QUI/50006/2013, and "Programa Operacional Competitividade e Internacionalização" (COMPETE) (PTDC/QEQ-QAN/1742/2014 – POCI-01-0145-FEDER-016530), and under the framework of QREN (NORTE-01-0145-FEDER-000024).

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Synthesis and evaluation of self-illuminating photosensitizers for Photodynamic Therapy of Cancer

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Photodynamic therapy (PDT) is a minimally-invasive approach for cancer treatment, PDT requires only a non-toxic photosensitizer (PS), presence of $^3O_2$ and light. Namely, light irradiates the target site and photoexcites the PS. Upon in a singlet excited state, the PS crosses to relatively long-lived triplet states and induces the generation of reactive oxygen species (ROS), by energy transfer to $^3O_2$. As only tissue containing the PS and irradiated by light undergoes PDT, this is considered a selective therapy with limited side-effects, thereby possessing potential for superseding conventional therapies (such as chemo- and radiotherapy). However, due to problems regarding the depth of light penetration into biologic tissue, PDT can only be used on tumors located on the lining of internal organs/cavities and under the skin [1]inducing transfer of energy to a cytoplasmic acceptor molecule and the generation of reactive oxygen species that initiate damage to cellular membrane components and cytolysis. The expanded use of PDT in the clinic is hindered by the lack of Ps target-cell specificity and the limited tissue penetration by external light radiation. This study demonstrates that bioconjugates composed of transferrin and haematoporphyrin (Tf-Hp.

Herein, we have developed new PSs for PDT that can be self-activated inside tumor cells without the need for an external light source. More specifically, these PSs are capable of self-activation in the absence of light by undergoing a chemiluminescent reaction. Furthermore, they are chemiexcited directly into a triplet state, which allows them to interact with $^3O_2$ to generate ROS, without previous energy transfer steps [2]. Proof-of-concept was provided by fluorescence monitoring of ROS-probes and *in vitro* toxicity assays. This opens the door for using PDT for treating tumors irrespective of their size and localization in the body.

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Photodynamic inactivation of antibiotic resistant bacteria using cationic chlorin dyes

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The attempt to design new photosensitizers (PS) has been a scientific challenge for synthetic researchers to study their applicability in many scientific areas, especially in photodynamic inactivation (PDI) of resistant microorganisms (e.g. bacteria) [1,2]. This process uses three different elements: light, oxygen and a PS which lead to the formation of cytotoxic reactive oxygen species that cause lethal oxidative damage in microbial targets [2,3]. In this communication it will be reported and discussed the synthesis and characterization of cationic free-base and zinc(II) chlorin derivatives **1a**-**2a** and **1b**-**2b**, respectively (Figure 1). The photodynamic efficiencies of these dyes against the Gram-negative bioluminescent *E. coli* bacteria will be also analysed.

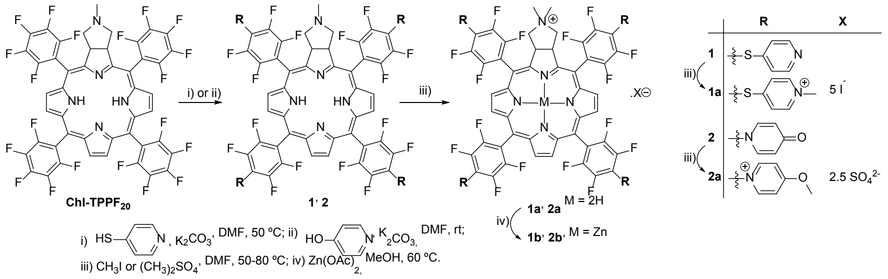

Figure 1: Chlorin derivatives 1a, 2a, 1b and 2b.

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Amphiphilic porphyrins and phthalocyanine as potential antimicrobial agents

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Nowadays, microorganisms have become more resistant to current antibiotics. Photodynamic inactivation of microorganisms, using photosensitizers (PSs), such as porphyrin (Por) and phthalocyanine (Pc) derivatives, can be an important alternative to conventional therapeutics. Pors and Pcs are photoactive molecules that in combination with appropriate visible light and oxygen produce reactive oxygen species that are cytotoxic against a wide range of pathogenic microbial agents, such as: bacteria, viruses, fungi and protozoa [1-3].

In this communication, we will report and discuss the synthesis, structural, and photophysical characterization of novel cationic Pors (**1**, **2**) and Pcs (**3**, **4**) decorated with trimethylammonium units. The results of the photoinactivation assays towards a Gram-negative bioluminescent bacteria *E. coli* will be also examined.

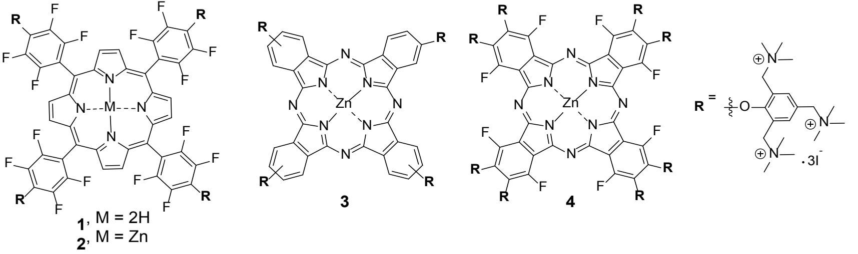

Figure 1: Structures of cationic porphyrins (1, 2) and phthalocyanines (3, 4) bearing trimethylammonium units.

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Microfluidic paper-based analytical devices for the determination of salivary NO_x

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Salivary content of nitrite and nitrate (NOx) has been primarily believed to be correlated with oral cancer and other disfunctions and infections in the mouth. However, recently some studies reported newly found benefits to the presence of nitrite and nitrate in the oral cavity.

In any case, it has become more and more relevant to carry out its assessment. In this context, the objective of this work was to develop a microfluidic paper-based analytical device (μPAD) for nitrite/nitrate determination in saliva samples. The choice of the μPAD approach intended to explore the advantages of these devices, which make them ideally suited to conduct on-hand analyte determinations. While many of the current monitoring techniques require specialized skills, laborious laboratory processes, or/and expensive equipment, μPADs provide a way to very quickly and cheaply attain an analytical result. The minimal use of reagent and sample, coupled to the portability has enabled the developed devices ideally suited for unskilled operators and regular monitoring.

The determination was based upon the conversion of nitrate to nitrite using zinc powder followed by the colorimetric determination of nitrite with the Griess reaction.

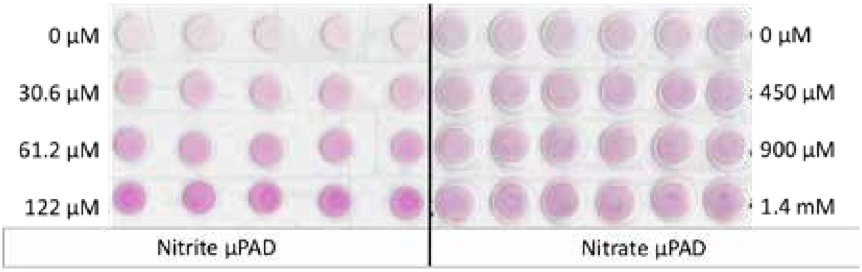

Fig.1. Photograph of nitrite and nitrate mPAD’s.

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Absorption of mycotoxins using *in vitro* models of human gastric and intestinal epithelium

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Mycotoxins, namely aflatoxin B1 (AFB1), deoxynivalenol (DON), fumonisin B1 (FB1), and ochratoxin A (OTA) are highly prevalent mycotoxins co-occurring in food, thus the ingestion of contaminated foodstuffs might contribute to their absorption through gastrointestinal epithelium. The intestinal absorption of mycotoxins has been studied, however only considering their isolated exposure; whereas their gastric absorption in humans has not been explored yet.

In this sense, the main goal of this work was to evaluate the *in vitro* transepithelial transport of those mycotoxins across human differentiated gastric NCI-N87 and intestinal Caco-2 cells, in both transport directions (apical to basolateral and basolateral to apical), when exposed isolated or in mixture. Further, a QuEChERs-based extraction followed by LC-MS/MS detection was developed to analyse the samples.

A bidirectional transport across both epithelial cells was observed for AFB1 and DON, more rapidly for AFB1; while OTA and FB1 were only transported in the apical to basolateral direction, the first in both gastric and intestinal epithelium, and the second only in gastric epithelium. Also, different cell uptake/excretion ratios were observed when mycotoxins were exposed in mixture. AFB1 exhibited the highest fraction absorbed (FA) - >96% - either isolated or in mixture, followed by DON with FA of 72.8 and 82.9%; and finally OTA with 11 and 66% when transported isolated and in mixture, respectively.

Data concerning DON, FB1, and OTA for *in vivo* absorption in humans is not available, being only described for AFB1 as mentioned in IARC reports. However, *in vitro* studies show different absorption patterns for single compound or mixture of mycotoxins, pointing that both gastric and intestinal absorption are of major relevance and should be considered for the proper evaluation of human absorption and toxicity

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New fluorophores for protein aggregates detection

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Luminogenic materials with aggregation-induced emission (AIE) properties have attracted much interest recently [1]. These materials were first discovered in 2001 when a series of silole derivatives were described as non-emissive in dilute solutions but highly luminescent when aggregated in concentrated solutions or casted into solid films [2].

Cells express several distinct proteins to convey a diversity of functions. However, under several stress conditions protein misfolding can occur. Misfolded proteins can acquire different forms such as soluble oligomers, amyloid fibrils and amorphous aggregates [3]. Protein aggregation is well documented and is related with aging and age-related diseases, such as neurodegenerative (Alzheimer, Huntington, Parkinson or prion disease), cancer and cardiovascular (atherosclerosis, heart failure and ischemic heart disease) [3]. Fluorescence-based techniques have been a reliable tool on the study of such protein aggregates, especially fluorophores with AIE properties [4].

Herein we report our recent work on the synthesis and characterization of new fluorophores, as well as the study of their AIE properties. Their application as protein aggregates fluorosensors will also be addressed.

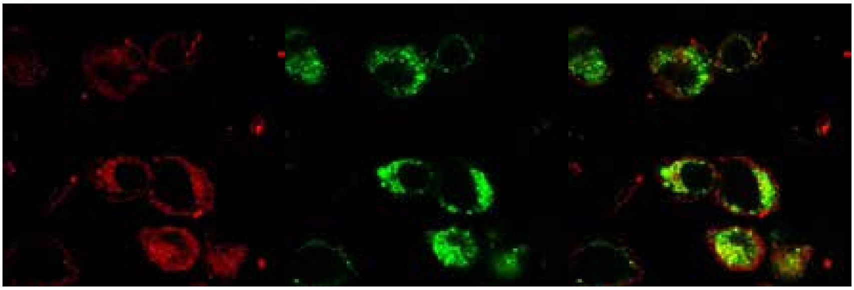

Fig.1. Confocal microscopy imaging of HeLa cells incubated with a inhibitor of the proteasome 5uM MG132 and a. new AIE fluorogen developed by us, b. commercial protein aggregates sensor and c. merged (AIE fluorogen + commercial protein aggregates sensor).

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Sequential flow injection analysis with potentiometric detection for the determination of ammonium and urea in human saliva

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In this work, a sequential injection (SI) system for the simultaneous determination of ammonium and urea is described. An ammonia ion selective electrode (ISE) was used for potentiometric detection of ammonium. The determination of urea was based on enzymatic hydrolysis using urease to convert urea to ammonium. The urease enzyme was immobilized and packed in a mini-column (E) connected to the selection valve, as shown in Fig.1. After conversion, the stream of the ammonium plug merged with a sodium hydroxide solution to form molecular ammonia and to act as ionic strength adjuster (ISA). The produced ammonia was propelled to the ammonia ISE enabling to determine urea concentration. For ammonium determination, standard solutions were aspirated and propelled to the confluence point to merge with ISA hydroxide solution before reaching the ammonia ISE. This SI method could be useful for fast and sensitive detection to quantify salivary ammonium and urea in patients with some oral or chronic kidney disease.

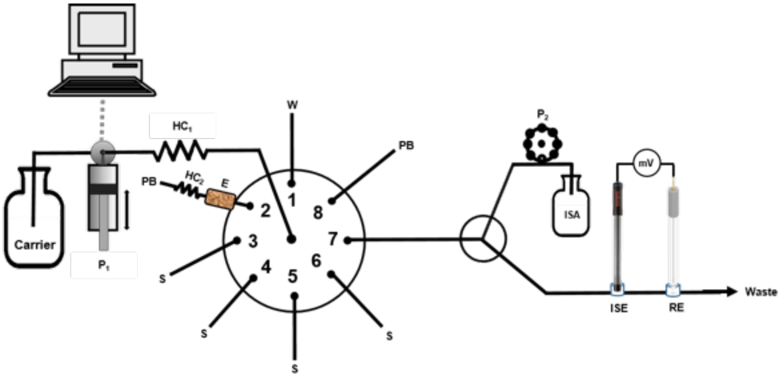

Fig. 1 SI manifold for the determination of urea in human saliva. P_1, syringe pump; P_2, peristaltic pump; HC_1 and HC_2, holding coil; E, urease enzymatic reactor; Carrier, deionized water; ISA, 0.2 M NaOH; PB, phosphate buffer (pH 7); S, standard solution or sample; ISE, ammonia ion selective electrode; RE, reference electrode; mV, potentiometer; W, waste.

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Uso da espectroscopia de infravermelho médio na análise do fluido crevicular gengival

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O fluido crevicular gengival (FCG) está localizado na cavidade oral entre o dente e a gengiva. Este fluido é excretado pelas células epiteliais da gengiva e a sua composição é semelhante ao soro [1]. Nas últimas décadas tem sido utilizado como um meio de diagnóstico de diferentes doenças orais devido a uma elevada presença de biomarcadores na sua composição [2]. É possível recolher uma amostra do FCG de uma forma simples e não invasiva através da colocação de uma fita de papel absorvente no sulco gengival embora o volume recolhido seja muito reduzido. Isto dificulta a análise do FCG pelos métodos bioquímicos tradicionais. Assim sendo, é necessário o desenvolvimento de uma ferramenta analítica capaz de analisar o FCG de uma forma rápida, não invasiva, de baixo custo e que não necessite de um elevado volume de amostra.

A espectroscopia de infravermelho médio apresenta todas as características necessárias referidas anteriormente. Esta técnica analítica é capaz de detectar as seguintes ligações químicas, C-H, N-H, O-H, S-H, logo em amostras de natureza biológica é capaz de fornecer uma "impressão digital" da amostra. Assim pequenas alterações na composição química entre amostras podem ser detectadas.

Neste sentido, este trabalho teve como objectivo testar a aplicação desta técnica na análise do FCG para verificar se é possível discriminar diferentes pacientes, diferentes locais de recolha e a presença de distúrbios alimentares. Foram recolhidos amostras do FCG de diversos pacientes (com e sem distúrbios alimentares) e em diferentes locais da cavidade oral através da colocação de uma fita de papel absorvente no sulco gengival. Seguidamente foram retirados espectros de infravermelho médio das mesmas tiras. A análise dos espectros foi realizada através da utilização de diferentes ferramentas quimiométricas, nomeadamente: análise de componentes principais (PCA) e análise discriminante pelo método dos mínimos quadrados parciais (PLSDA).

Os resultados preliminares obtidos são bastante promissores e revelam que esta técnica pode efectivamente ser utilizada na análise do FCG.

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Benzodiazepines: An Integrated Approach Based On Consumption, Risk Assessment And Monitoring Results

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In 2004, Portugal was the second country in Europe with the highest consumption of benzodiazepines (anxiolytics, sedatives and hypnotics), exceeded only by Ireland [1]. In the report of the International Narcotics Control Board for 2005, diazepam, alprazolam and oxazepam were the most consumed benzodiazepines. When the crude consumption was investigated for our country (2015) [2], diazepam was the most used substance, representing around 21.1%, followed by oxazepam (13.4%). However, the consumption of alprazolam was overtaken by several other substances. Around 2.33 tons of anxiolytics, sedatives and hypnotics was used by the portuguese population.

In the present work, a prospective/retrospective surface water (SW) exposure of benzodiazepines was compared. Prospective exposure assessment: the compounds with crude PEC (predicted environmental concentrations) in surface water greater than 0.01μg/L were selected. [2] This calculation was based on the amount of each substance consumed in Portugal in 2015 and refined ($rPEC_{sw}$) with the excretion rate of unchanged/glucuronide forms, as well as the pharmacological active metabolites excreted in urine and feces of humans. Retrospective exposure assessment: based on occurrence literature studies, the maximal occurrence for each substance in wastewater treatment plants effluents was selected; these concentrations enable MEC (measured environmental concentrations) in surface water by the application of dilution factor of 10 (MEC_{10}). The $rPEC/MEC_{10}$ racio between 0.5 and 1.4 was considered reliable. The chemical properties (e.g. pKa, log Kow, log Koc) were also considered.

Ten molecules from this subgroup showed a rPEC threshold above 0.01μg/L, what means they pose a possible risk to the environment. Six of them were found in the occurrence literature studies. The calculated ratio $rPEC/MEC_{10}$ lead to the conclusion that for diazepam, lorazepam and oxazepam existed a reliability between the prespective and the retrospective approach (see figure 1). However, for zolpidem and the metabolite nordiazepam a overestimated predictive value was observed. The metabolite nordiazepam occurs in the environment from diazepam and dipotassium chlorazepate metabolism. The intergrated approach showed that none of these molecules seems to be degraded in waste water treatment plants and oxazepam and nordiazepam had a persistent profile.

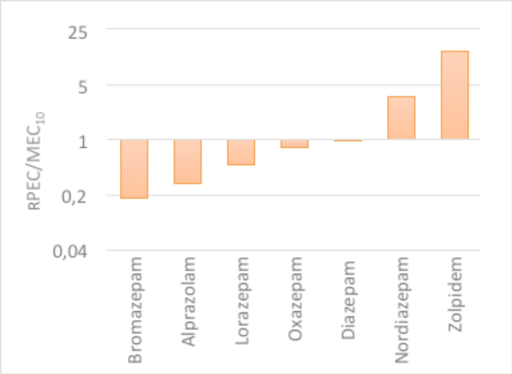

Fig 1. Racio rPEC/MEC10

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Risk assessment of nickel in baby food

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The main sources of exposure of metallic elements, namely nickel, to the general non-smoking population are found in food and water. Once absorbed by the body, nickel can promote toxic effects and is classified by the International Agency of the World Health Organization for Cancer Research (IARC) as carcinogenic to humans (Group 1) [1]. Children, especially newborns, compared to the rest of the population have higher susceptibility to food contaminants, mainly due to the higher food intake per Kg of body weight (b.w.). Furthermore, the mechanisms that could minimize the toxicity of these compounds are not yet fully developed in children. However, although the IARC classification, there are no maximum residue limits for nickel in food, including baby foods. Nonetheless, the European Food Safety Authority (EFSA) suggested a tolerable daily intake (TDI) of 2.8 **μg** Kg^{-1} b.w. [2]. Therefore, the aim of the present work was to evaluate the occurrence of nickel in premade baby food and access the risk promoted by this exposure in children up to 2 years old.

The analytical methodology used for the determination of nickel was dry ashing followed by graphite furnace atomic absorption spectrometry, which presented the limit of detection of 12.5 **μg** Kg^{-1}. This methodology was applied in 85 samples of premade baby foods: 26 ready meals (jars), 31 fruits (jars), 8 deserts (jars) and 20 flours. The results showed that 76 samples were contaminated with values up to 225.7 **μg** Kg^{-1}. The group with the highest average contamination levels was the fruits (50.2 **μg** Kg^{-1}) followed by the ready meals (40.4 **μg** Kg^{-1}). Biological samples presented higher detection frequency and average concentration than the non-biological ones. When analysing the daily intake, it was observed, for all the studied age groups (6 months, 1 year and 2 years), that the TDI proposed by EFSA for nickel was surpassed. This was perceived not only when using the worst case scenario approach, but also when using the average values of nickel contamination. The most exposed age group was the 2 years old children, with an average daily ingestion of 5.8 **μg** Kg^{-1} b.w., twice the TDI. This is mainly explained by the higher amount of ready meals ingested by this age group, since these are the major contributors for nickel ingestion in the studied premade baby foods.

The exposure to nickel through these baby foods should be thoroughly monitored since the suggested TDI was surpassed in all age groups and legislation should be implemented regarding maximum residue levels of nickel in baby foods.

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New symmetrical indolenine squaraine dyes: synthesis and studies of their photostability, ability of singlet oxygen formation and *in vitro* phototherapeutic potential

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Photodynamic therapy (PDT) is a minimally invasive therapeutic procedure which, in the case of cancer treatment, consists in the administration of a photosensitizer (PS), its selective accumulation in the target tissue and subsequent activation by light. PSs used in this therapy should have several properties, such as: innocuity in the absence of light and high cytotoxicity in its presence, high photostability and high singlet oxygen formation ability.

In this work several symmetrical indolenine squaraine cyanine dyes were synthesized by procedures adapted from the literature [1,2] and their structures fully characterized by NMR, HRMS, Vis, IR and m.p.. To evaluate its singlet oxygen formation ability, 1,3-diphenylisobenzofuran (DPBF) assay was used, in which its decay was evaluated over 40 minutes. The decay of the compounds when exposed to a light was also analysed, in order to evaluate its photostability. Their in *vitro* potential as PSs for PDT was evaluated by the MTT assay after incubation of several tumoral (MCF-7 and PC-3) and normal (NHDF) cell lines with several concentrations (0, 0.01, 0.1, 1.0, 2.5, 5.0 and 10.0 μM) of the compounds followed by irradiation with several energies by LED systems emitting at the wavelength of maximum absorption of the squaraine dyes (Fig. 1).

The results evidenced that the indolenine squaraine cyanine dyes showed a high production of singlet oxygen but poor photostability. Analyzing the cytotoxicity evaluation results, it can be concluded that the introduction of amines into the squaric ring of these compounds results in a marked increase in cytotoxicity.

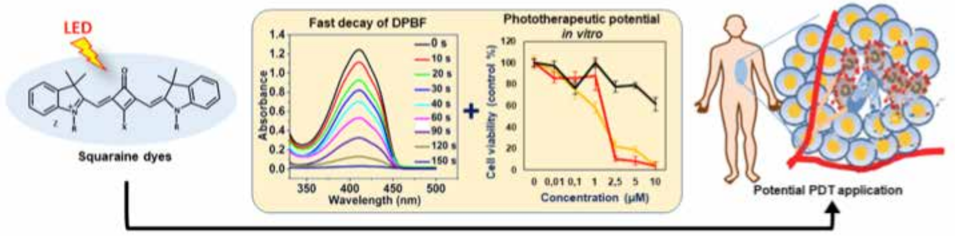

Fig.1. General structure of evaluated squaraine dyes (X = O–, NH2; R = C2H5, C6H13; Z = CF3SO3–) and general outline of the purpose of the work of this communication.

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Uhplc-ms a tool to disclose phenolic profiles and/or to validate species medicinal significance

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Plants that grow wild in several countries are used in traditional medicine. Among those we have in Portugal the cases of *Calendula officinalis* L. and *Pterospartum tridentatum* (Spach) K. Koch.

Flavonoids and chlorogenic acids are amongst the secondary metabolites, the ones that are associated with health effects such as antioxidant, anti-inflammatory and antitumor activities. UHPLC-MS profiles can reveal the presence of these bioactive metabolites and guide future phytochemical studies.

Following our interest in the isolation and full characterization of secondary metabolites, polar extracts of the above mentioned species were analyzed and interesting metabolites were found (Figure 1). Our findings will be presented and discussed.

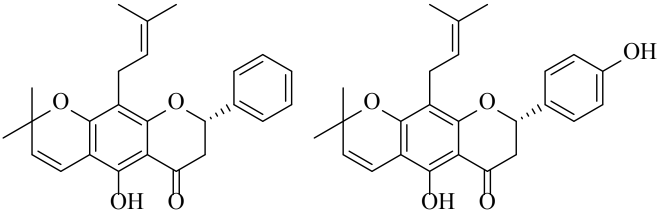

Figure 1: Examples of secondary metabolites

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Antioxidant activity of (styryl)pyrazoles and preliminary structure-activity relationship studies

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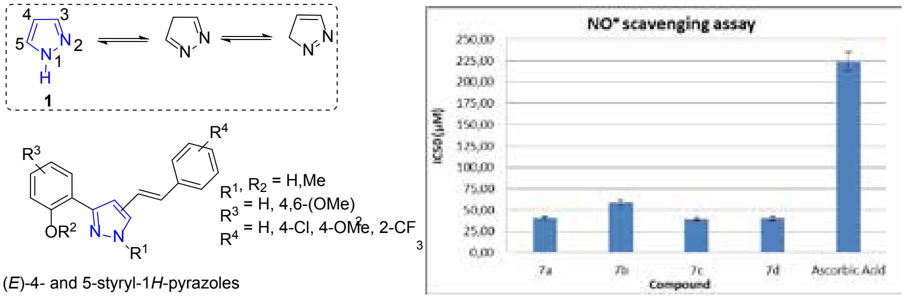
The search of new antioxidants, as drugs candidates, is an active field of medicinal chemistry since these molecules play a vital role in the body defence mechanism, against oxidative stress, e.g. by scavenging or regulating the generation and elimination of oxygen and nitrogen reactive species (ROS and RNS).

Pyrazole scaffold occupies a prime place in medicinal chemistry because it is present in many drugs with real medicinal application and in several remarkable compounds with a wide range of pharmacological activities, namely analgesic, anti-inflammatory, antidepressant, anticancer and cannabinoid activities, among others [1]. The antioxidant activity of the pyrazole (1,2-diazole) **1** (Fig. 1) was revealed when it was used to treat nephrotoxicity caused by Cisplatin, an antineoplastic drug used in the treatment of various cancers [2]. Until 2008, only a few numbers of papers were published concerning the study of pyrazole as a pharmacophore with interest in the development of potential antioxidant compounds. However, since 2009, several compounds incorporating the pyrazole core or its reduced forms in their structures have been described as potential antioxidants [3].

In this communication, we present our recent results on the screening of the antioxidant activity of a series of (styryl)pyrazole derivatives, which have been synthesised by our group (Fig.1) [4-6]. The antioxidant activity was examined using *in vitro* assays to evaluate the ability of these pyrazoles to scavenge $ABTS^{\cdot+}$, $NO^{\cdot}$ and $O2^{\cdot-}$ free radicals. Based on the experimental results, some preliminary structure-activity relationship (SAR) studies were developed. These SAR studies will allow the design of novel and more potent pyrazole-type compounds in the near future.



(*E*)-4- and 5-styryl-1*H*-pyrazoles

Fig.1. Structures of pyrazole 1, (E)-4-/5-styryl-1H-pyrazoles and NO· radical scavenging activity of 4-styryl-1H-pyrazoles (7a-d) in comparison with ascorbic acid.

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Copper(I)-phosphane complexes as promising anticancer agents

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Cancer is still a leading cause of death and disability nowadays, despite the intensive efforts continuously taken during the past decades by researchers worldwide. To date, cisplatin and its analogues (oxaliplatin and carboplatin) are the sole metallodrugs with approved use in cancer therapy. Even though the clinical relevance of the platinum-based medicines in the treatment of several types of tumours (e.g. ovarian, testicular, breast, head and neck, lung, among others), their use is keenly limited due to the severe side effects observed and to the increasing reports of drug resistance cases. As a possible alternative, the study of novel chemotherapeutics based on copper complexes has attracted increasing interest within the scientific community, not only because they can be less toxic and overcome platinum resistance by acting through different mechanisms, but also because they are relatively inexpensive to synthesise [1]. In this frame, very recently, our group has been developing new copper(I)-phosphane derived complexes, showing most of them higher cytotoxicity than cisplatin against ovarian and breast cancer cell lines [2,3].

In this communication, we report the synthesis of a family of copper(I) complexes of general formula $[Cu(PP)(LL)][BF_4]$, in which PP represents different bi- or monodentate phosphanes and LL corresponds to several N,O-heteroaromatic ligands (Fig. 1). All the compounds were fully characterised by elemental analysis and by FT-IR, UV-Visible, and 1D/2D multinuclear NMR spectroscopic techniques. X-ray diffraction studies were done for the compounds presenting single crystals. The stability of the complexes over time in organic and aqueous solutions was studied by UV-Visible spectrophotometry. The anticancer activity was determined by the MTT assay in different human cell lines with low, medium and high resistance to conventional metallodrugs.

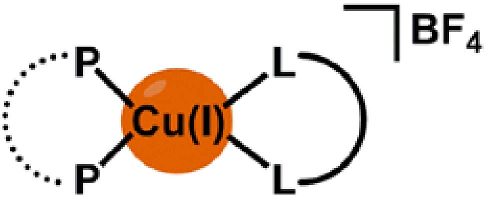

Fig.1. General structure of the copper(I) complexes where PP = bi/monodentate phosphanes and LL = N,O-heteroaromatic ligands.

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Characterization of nanoformulations produced with the aqueous extract from *Annona muricata* L.

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Annona muricata L. (Annonaceae Family) is a tropical plant species extensively used in traditional medicine against an array of human diseases such as fever, pain, respiratory and skin illness, bacterial infections, hypertension, inflammation, diabetes, cancer, anxiety and depression. More than 200 compounds were already identified from different parts of this plant, including phenolic compounds, alkaloids and acetogenins [1].

The objective of this study was to evaluate the neuroprotective effect of the decoction prepared from the leaves of *A. muricata*, and to assess the safety of the decoction, due to recent studies reporting the neurotoxic effect of acetogenins. First, we demonstrated the neuroprotective effect of the decoction prepared from the leaves of *A. muricata* through enzyme inhibition (against monoamine oxidase A, IC_{50} = 185.8 ± 46.9 μg/mL) and reactive oxygen species scavenging activity (against hydrogen peroxide, IC_{50} = 48.9 ± 2.5 μg/mL). Then, with the purpose of increasing the permeability of this extract across the blood-brain barrier (BBB), phosphatidylcholine-based nanoformulations functionalized with mApoE were also produced. Cytotoxicity and permeability studies were carried out using an *in vitro* transwell model of the BBB, composed of immortalized human microvascular endothelial cells (hCMEC/D3). In general, phytosomes were less toxic than liposomes in hCMEC/D3 cells and, when present, cholesterol improved the permeability across the cell monolayer. The extract and the nanoformulations were also characterized by chromatographic, spectrophotometric, fluorescence and dynamic light scattering methods. Phytosomes had mean particle sizes of 106 ± 9 nm (with cholesterol) and 161 ± 12 nm (without cholesterol) and PDI values of 0.245 and 0.275, respectively. The phosphatidylcholine-extract binding efficiency was 49 ± 3%. Regarding liposomes, mean particle sizes of 138 ± 29 nm (with cholesterol) and 195 ± 33 nm (without cholesterol), with a PDI of 0.193 and 0.261 were obtained, but the entrapment efficiency was lower than for phytosomes (26 - 27%). Based on UV-vis and MS spectra, phenolic compounds were identified, including caffeoylquinic acids, procyanidin derivatives, quercetin and kaempferol derivatives; two alkaloids were found in trace amounts, namely coclaurine and reticuline; and acetogenins were not detected.
These results contributed to the valorization of this species, reinforcing its traditional use throughout the world.

ACKNOWLEDGMENTS: This work was financed through project UID/QUI/50006/2013, receiving financial support from FCT/MEC through national funds, and co-financed by FEDER, under the Partnership Agreement PT2020. Clara Grosso thanks FCT for the FCT Investigator(IF/01332/2014/CP1255/CT0001). The authors would also like to acknowledge Sílvia Maia from CEMUP for her technical assistance with LTQ Orbitrap XL analyses.

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Computational studies with oxindole frameworks

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The design, synthesis, structure-activity relationship studies, inhibition and toxicity assays, as well as docking studies were conducted with analogues of deoxinojirimicin (DNJ), 1,4-dideoxy-1,4-imino-D-arabitol (DAB-1) [1,2] and isatin derivatives in the crystallographic structures of human AChE (PDB 4EY7), human BuChE (PDB 4TPK) and human MAO-B (PDB 1OJA) as well as in our previously developed Alpha-Glucosidase homology models (3AJ7 [1] and 3L4U [2] Chimeras), rendering sensitive information about the broad biological activity of oxindole frameworks [3,4].
Robust computational indication of Cholinesterases and Alpha-Glucosidases Dual Inhibition and insights into structural and mechanistic features of MAO-B inhibition will be presented.

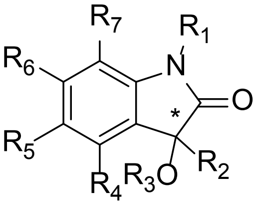

Fig.1. Oxindole framework

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Evaluation of in vitro anti-diabetic potential of 2,3-diarylxanthones through the inhibition of α-glucosidase

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Type 2 diabetes mellitus is a chronic metabolic disorder caused by abnormal carbohydrate metabolism with a consequent hyperglycemia status, resulting from inadequate insulin secretion, action, or both. One possible therapeutic approach to decrease postprandial hyperglycemia is to retard the absorption of glucose via inhibition of carbohydrate hydrolyzing enzymes, such as **α**-glucosidase [1]. This enzyme catalyzes the final step of the digestive process of starch and break down oligosaccharides to monosaccharides. The currently marketed **α**-glucosidase inhibitors are confined to glycosidic compounds, such as acarbose, miglitol and voglibose, with moderate affinity for the enzyme and with disturbing side effects. Thus, in the last two decades, considerable interest has been given to the pursuit of novel drugs, structurally diverse, in which several xanthone derivatives are included [1,2].

Our goal was to study the inhibitory activity of a panel of hydroxylated 2,3-diarylxanthones **XH1-XH9**, against of **α**-glucosidase activity. The *in vitro* assay was performed by monitoring the hydrolysis of the substrate *p*-nitrophenyl glucopyranoside into the product *p*-nitrophenol at 405 nm. In addition, the study of the inhibition type was carried out through nonlinear regression Michaelis-Menton enzymatic kinetics and the corresponding Lineweaver-Burk plot [3].

The IC_{50} values obtained ranged from 9 to 27 **μ**M, considerably lower than the positive control acarbose (IC_{50} = 515 ± 19 **μ**M). For the active compounds, a noncompetitive type inhibition was recorded. More details concerning the structure-activity relationship will be presented and discussed in this communication.

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The influence of age on the toxicity induced by mitoxantrone: *in vivo* studies with mice

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Mitoxantrone (MTX) is a chemotherapeutic drug commonly used for the treatment of several types of cancer, such as breast cancer and multiple sclerosis [1]. However, it causes several side effects, namely cardiotoxicity [2]. At this point, MTX mechanisms of cardiotoxicity are still not properly clarified and its metabolites may be, in part, related with cardiotoxicity. Additionally, several risk factors could aggravate or induce the incidence of MTX-related toxicity, such as age at diagnosis.

This work aimed to study the toxicity induced by MTX in different aged CD-1 mice and the possible age-related differences on the metabolic profile of this chemotherapeutic drug. Twelve infants (4 weeks), twenty-four adults (3.5 months; two assays) and ten elderly (1.5 years) mice were used. The MTX-treated animals received 6 intraperitoneal injections, twice a week (cumulative dose of 6 mg/kg), while the controls where injected with saline, in the same administration schedule. General welfare, animal weight and food and water consumptions were recorded through the all experiment. The sacrifice occurred 17 or 7 days after the last administration for infants and adults/ elderly, respectively. The organs (brain, heart, kidneys, spleen, liver) and blood of the animals were collected. The heart tissues were analyzed through light microscopy. Plasma was used to biochemical determinations and to inject in a high-performance liquid chromatography with a diode array detector (HPLC-DAD) system in order to detected MTX and one of its metabolites (naphtoquinoxaline, NAPHT).

MTX caused a significant weight loss in the adult mice, and significant reductions in food and water consumptions in the adult and infant mice treated with MTX, when compared with the respective controls. All the organ weight/ brain weight ratios in the adult mice treated with MTX and the spleen weight/ brain weight in the MTX-treated elderly were significantly decreased, in comparison with the respective controls. MTX caused morphologic and structural changes in the heart tissue, specially in adults. Moreover, MTX and NAPHT could not be detected in any of the mice plasma samples analyzed by HPLC-DAD, at the conditions set by us.

Summing up, the adult mice seemed to be more susceptible to MTX-induced cardiotoxicity. Moreover, the pharmacokinetic features of the chemotherapeutic drug and its metabolite in plasma may have influence their detection through HPLC-DAD, namely the elapse time between sacrifice and the last administration. On the other hand, the concentrations of MTX and/ or NAPHT in plasma could be under the limit of detection of the method used and other matrixes must be investigated to validate our method.

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Síntese de 2,1-benzisoxazoles e espiroindolin-3-onas derivados de ácidos (tio)barbitúricos potencialmente bioativos

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Os ácidos (tio)barbitúricos e seus derivados, geralmente conhecidos como barbituratos, são principalmente conhecidos como depressores do sistema nervoso central, sendo atualmente muito utilizados no desenvolvimento de potenciais novos fármacos. Importante neste contexto é o facto do seu anel pirimidínico permitir várias substituições em N1, N3, C2 e, especialmente, em C5, a posição mais explorada [1]. No decorrer dos nossos estudos com o objetivo de desenvolver novos barbituratos potencialmente bioativos com um segundo anel fundido nas posições 5 e 6 do anel pirimidínico, observou-se a formação inesperada de 2,1-benzisoxazoles. De facto, este sistema formou-se após a condensação do 2-nitrobenzaldeído em C5 dos (tio) barbituratos seguida de redução do grupo nitro, sendo esta uma nova abordagem para a sua obtenção [2]. Além disso, e por tratamento térmico ocorreu a formação de novos produtos, mais tarde caracterizados como sendo espiroindolin-3-onas (Fig.1). Dada a novidade destas vias sintéticas e o seu potencial em química medicinal, estas transformações foram posteriormente exploradas no sentido de otimização da obtenção das mesmas, designadamente mediante utilização de micro-ondas, e do alargamento da sua aplicabilidade para permitir diversificação estrutural. A citotoxicidade, bem como a capacidade de inibição da xantina oxidase (XO) de vários destes compostos foram também avaliadas sendo que alguns deles, principalmente as espiroindolin-3-onas, apresentam significativa ação inibitória da XO. Nesta comunicação serão apresentados os nossos principais resultados destes estudos.

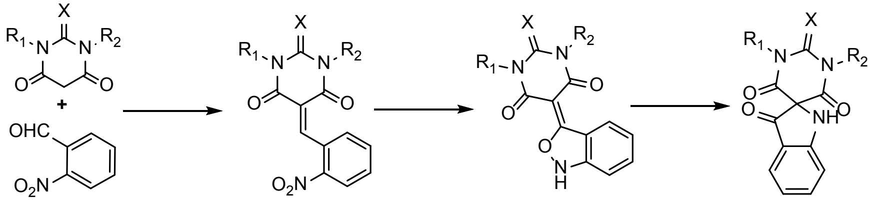

Fig.1. Nova via sintética para 2,1-benzisoxazoles e espiroindolin-3-onas derivados de ácidos (tio)barbitúricos

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In vitro evaluation of the photoreactivity of natural phenolic antioxidants

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Polyphenols (PPs) are a large family of natural compounds widely used in cosmetic products due to their antioxidant and anti-inflammatory beneficial properties. Although it is believed that these compounds can protect human skin against deleterious effects of solar irradiation or ozone, preventing premature skin ageing and environment associated skin defects, current knowledge recognizes PPs and their metabolites as substances causing a majority of phytodermatoses. The physical-chemical properties of PPs and their resemblance to some biologically active substances in humans determine their high reactivity towards a number of organic molecules, free radicals, and ions. Moreover, due to their chemical structures, PPs may act as exogenous chromophores photosensitizers.

Given the existing gap of scientific information on the photoreactive potential of PPs and since, in some cases, they are applied directly on the skin, the aim of this study was to evaluate the photoreactivity of four natural phenolic antioxidants with documented use in cosmetic products. The UV/VIS spectra in the range of 290-700 nm were analyzed and afterwards their photoreactivity was assessed based on a reactive oxygen species (ROS) assay. The results obtained will be presented in this communication.

KEY WORDS: Photochemistry, Photosafety, Photoreactivity, Natural phenolic antioxidants, Reactive Oxygen Species;

Synthesis of barbiturate substituted squaraine dyes and evaluation of their interaction with bovine serum albumin

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In the last few years the interest in squaraine dyes is increasing, especially because of their biological and biomedical applications[1]. Some reports showed that this class of compounds have ability to be used as fluorescent probe for detection of BSA protein[2,3]. Considering the wide applications of the fluorescence molecules, we have synthesized new squaraine cyanines dyes derived from indolenine, which contain in the four-membered central ring a barbituric (**1**), a thiobarbituric (**2**) or a dimethylbarbituric (**3**) acid moiety. The structural elucidation of dyes, as well as of its precursors, was performed using ^{1}H-NMR, ^{13}C-NMR, IR, Vis, m.p. and HRMS techniques and based on their properties we evaluated their Interaction with bovine serum albumin (BSA). For this study was applied a similar procedure recently reported by some of us[1] that allows to increase the concentration of BSA and maintain the concentration of each dye.

The results (**Fig.1**) showed an increase in fluorescence intensity with increasing of protein concentration, so that we can conclude that there is a strong interaction between all dyes studied and the BSA. Compound **1** demonstrated a greater increase in fluorescence intensity in the presence of BSA than the other compounds.

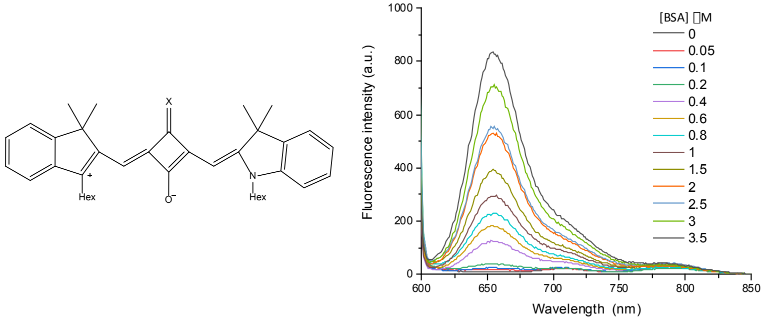

Fig.1. General structure of synthetized compounds and fluorescence spectra of compound 1 with different concentrations of BSA.

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Ionic Systems Approaches for Pharmaceuticals

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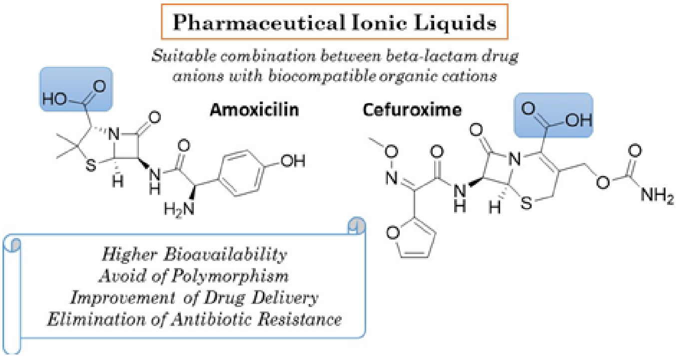
The discovery of alternative solutions related with costly problems from pharmaceutical industry such as polymorphism, drug diversification and as modulators of Biopharmaceutical Drug Classification System (BCS) is mandatory. The possibility to use Ionic Systems based on Biocompatible Ionic Liquids in combination with different pharmaceutical drugs seems a very attractive research topic to explore [1]. Our team already reported examples of API-ILs based on anti-inflammatory (e.g. ibuprofen); antibiotics (beta-lactams and fluoroquinolones); anti-tumoral (bisphosphonates) and anti-viral drugs with significant advantages comparing with original systems [2-4]. It is important to focus that some ampicillin-based API-ILs. possess a very high anti-bacterial activity especially against resistant Gram-negative bacteria (RDIC values >100 and 1000) which agrees with theoretical prediction of drug improvement [3]. Although these recent developments, API-ILs seem to be an ideal drug delivery system for APIs by improving solubility, permeability and eliminate polymorphism.



Herein, we present our latest developments in the field of API-ILs using antibiotics from several therapeutic groups as anions, namely the β-lactam antibiotics (Ampicillin and Amoxicillin), cephalosporin (Cefuroxime) and carbapenem (Meropenem). These APIs can be combined with appropriate biocompatible organic cations (e.g. choline, cetylpyridinium, alkylimidazolium). The prepared API-ILs are characterized by standard spectroscopic techniques as well as thermal properties. Additionally, the solubility in water and biological fluids as well as the toxicological profile of new API-ILs will be evaluated.

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Bacterial sensitivity metal ion in aqueous solution by microcalorimetric techniques

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In this paper, the effect of aqueous solutions of metal ions on bacterial growth using microcalorimetric techniques is analyzed. Metal ions solutions with concentrations of 0 to 250 mM were used. A suspension of 10^6 CFU mL^{-1} of different bacteria was used and as a culture medium, a liquid liquid digested with soybean-casein. The measurements were carried out in a Calvet microcalorimeter at a constant temperature of 309.65 K. The reference cell was filled with 6 ml of culture medium, 1 ml of metal solution and 1 ml of medicinal mineral water. In the experimental cell, the latter was replaced by the bacterial suspension. The data was collected by a data acquisition and processing system, at intervals of 22 s by 48 h. Representing the difference in the heat yield generated between the experimental and control cells versus time, the bacterial growth curves were obtained and the thermograms were compared using different concentrations of the metal solution. This thermodynamic technique demonstrates the potential use of metallic dissolution in the medical industry, among others, to take advantage of its bactericidal property.

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Chemical and microbiological characterization of Serra da Estrela cheese: A traditional Portuguese dairy product

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Milk and dairy products are an excellent source of well-balanced nutrients [1] with multiple uses as a snack, dessert or food ingredient. Cheese, namely Serra Estrela (SE) cheese, a traditional variety manufactured in the center region of Portugal, is part of the mankind´s ancient cultural heritage, made from raw sheep milk it is assumed as an iconic gourmet cheese, when compared with other Portuguese cheeses.

This work intended to monitor the manufacturing process along the period of production, to evaluate the factors that are decisive for the reproducibility of SE cheese in geographical and temporal terms, as well as to achieve the knowledge of the SE cheese lipid nutritional characteristics. With the approach undertaken, we are also promoting future work with a broader evaluation of the multifactorial causes that contribute to the diversity of organoleptic and yield characteristics of SE cheese [2], as well as to the chemical analysis of this cheese. Cheeses originating from representative dairy farm producers, were analyzed for their nutritional characteristics, such as moisture, fat, protein and salt, using the FTNIR technique as an expeditious method. In all the cheeses studied, the moisture varied from 42% to 53%, the butyric content between 19.6 and 33.3%, the protein content between 18.6 and 26.7% and the salt between 0.7 and 2.2%.

Considering that the microbiological evaluation is one of the mandatory parameters for the certification of cheese made from raw milk, *Escherichia coli* and coagulase-positive *Staphylococcus* determinations were carried out. *Listeria monocytogenes* and *Salmonella* spp determinations were also performed. It was found that some cheeses exceeded the maximum allowed values of microorganisms (fig.1).

The evolution of the lipid fraction, namely unsaturated fatty acids such as monounsaturated and polyunsaturated (omega 3 fatty acids and omega 6 fatty acids), was evaluated for a period of 9 months. Chemically it was possible to verify differences in terms of lipids constitution between the analyzed samples. SE cheese was characterized by a relatively high content of monounsaturated fatty acid (MUFA) and the evaluation of the lipid profile of SE cheese allowed possible future work in determining bioactive lipid compounds with possible health promoting functions.

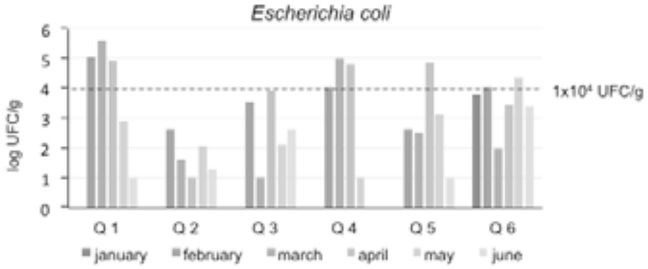

Fig.1. *Escherichia coli* determinations in SE cheese samples.
CFU/g: colony forming units/gram of cheese; Q1-Q6: dairy farm producers; dashed line: maximum limit allowed.

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Quantification of Bisphenol A in human saliva by HPLC-FD.

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Derivatives of bisphenol A (BPA), such as BPA-diglycidyl methacrylate (bis-GMA), BPA- dimethacrylate (bisDMA), ethoxylated BPA-glycol dimethacrylate (bis-EMA), polycarbonate-modified bis-GMA (PC bis-GMA), or 2,2-bis[(4-methacryloxy polyethoxy)phenyl]propane (bis-MPEPP) are commonly used in dental composites. Pure BPA is not a component of these resins; however BPA can occur as an impurity or as a degradation product in some resins, depending on their dimethacrylate monomer based [1].

BPA is an endocrine disruptor with estrogenic properties, which also exhibits inflammatory, oxidative and antiandrogenic properties. Consequently, exposure to BPA could severely affect bone health in humans. Furthermore, BPA can also induce structural changes in unborn children mammary glands, which may promote subsequent tumor growth, and has been shown to exert effects on the brain and induce behavior modifications. Additionally, it may affect the female reproductive system, metabolism and obesity [2].

Nonetheless, the exact composition of dental resins currently available in the market is not well defined and most contain BPA derivatives. As such, it is necessary to determine whether BPA can leach from these dental composites. Hence, in the present work, we set out to develop and to validate a method by high performance liquid chromatography equipped with a fluorescence detector (HPLC-FD) for the quantification of BPA in salivary samples from individuals subjected to orthodontic treatments comprising the use of different dental resins.

ACKNOWLEDGEMENTS: This work was partially supported by CESPU, through the project MLIA-CESPU-2018.

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Síntese e avaliação do potencial de uma cianina esquarílica derivada da indolenina como sonda para deteção da BSA

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As cianinas esquarílicas são compostos que apresentam estruturas polimetínicas 1,3-zwiteriónicas, com um anel central de quatro membros, o qual possui dois átomos de O e, anéis heteroaromáticos nos extremos da cadeia polimetínica. Nas últimas décadas, tem-se observado um elevado interesse no desenvolvimento de novos métodos para a deteção de biomoléculas, que envolve entre outras áreas científicas, a síntese de novos fluoróforos. As cianinas esquarilicas são uma classe de fluoróforos referidos na literatura que apresentam propriedades inerentes a uma boa sonda fluorescente para a deteção de proteínas[1].

Após caracterização pelas técnicas de EMAR-ESI-TOF, RMN de ^{1}H e de ^{13}C, IV, UV/Vis e p.f. foi realizado o estudo das intensidades de fluorescência da cianina esquarílica (Fig 1) em estudo na ausência e na presença de albumina sérica bovina (BSA) a diferentes concentrações (0,6; 1,0; 1,5; 2,0; 2,5; 3,0 μM) de acordo com a metodologia descrita recentemente[2].

Os resultados obtidos (Fig.1) permitem-nos concluir que existe uma linearidade desejada entre a intensidade de fluorescência e o aumento da concentração de BSA, no entanto, o valor de I_{BSA} (3,0 μM) é de apenas cerca de 4 vezes superior ao obtido na ausência de proteína (I_0).

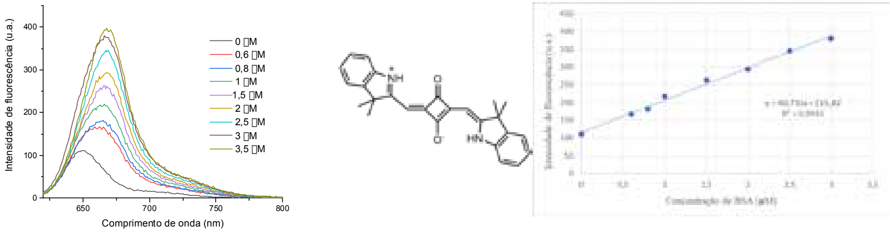

Fig.1. Espetros de fluorescência da cianina esquarílica sintetizada, na ausência e na presença de BSA (0,5-3,5 mM) e respetiva correlação linear entre a concentração de BSA e a intensidade de fluorescência.

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Thermal properties of peloids using mineral water from galicia

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In Galicia, there are numerous thermal spas in its four provinces. The waters of the spas can be of low mineralization, medium mineralization and strong mineralization. In this work, the thermal properties of bentonite mixtures are presented with the mineral waters of some Galician Spas, such as Laias, Lobios, Mondariz and La Toja. The properties studied are thermal conductivity, specific heat and thermal diffusivity.
The mixtures of clays and mineral waters are a type of thermal peloid [1] used for therapeutic purposes in thermal spas. The thermal properties of this type of mixtures define their thermo-therapeutic applications [2, 3].
The thermal conductivity has been determined using a Decagon KD2 Pro conductivitymeter (Decagon Devices Inc., Pullman, WA, USA) [4, 5]. The specific heat has been determined using a CALVET microcalorimeter [6, 8]. While thermal diffusivity has been calculated from density, specific heat and thermal conductivity [9].

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Bisphosphonate-Based Materials: Development of a 3-in-1 Multidelivery System for Osteoporosis Treatment

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Bisphosphonates (BPOs) are largely prescribed for osteoporosis prevention in aged population. This class of drugs induces the apoptosis of osteoclasts, allowing a reduction on the extensive bone resorption characteristic of osteoporotic patients. Besides BPOs it is also recommended the administration of calcium and magnesium ions. These are important oligo-elements for bone health, whose administration has been proven to be beneficial on the management of osteoporosis. In this way, the development of BPO-based materials composed simultaneously by BPOs, calcium and magnesium ions could ensure a better treatment for this disease.

Three anti-osteoporotic components (BPOs, Ca^{2+} and Mg^{2+}) were combined in a network-based system, into the final form of BPO-based materials. In this work, two distinct materials are described: (i) a coordination polymer $[Ca_4(Halen)_2(H_2O)_x]\times yH_2O$ (x+y = 3) and (ii) a dimer $[Ca_{0.7}Mg_{1.3}(H_4alen)_4(H_2O)]\times H_2O$. Both contain the well-known BPO alendronate (H_5alen) as the organic linker, which is coordinated to either (i) Ca^{2+} or both (ii) Ca^{2+} and Mg^{2+}. Upon preparation, the materials were extensively characterized by X-ray diffraction, NMR, FT-IR, electron microscopy (SEM and EDS), thermogravimetric and elemental analyses. These techniques allow a clear and complete study of the chemical composition and structure features of the materials, which is a vital first step to better understand their possible therapeutic potential.

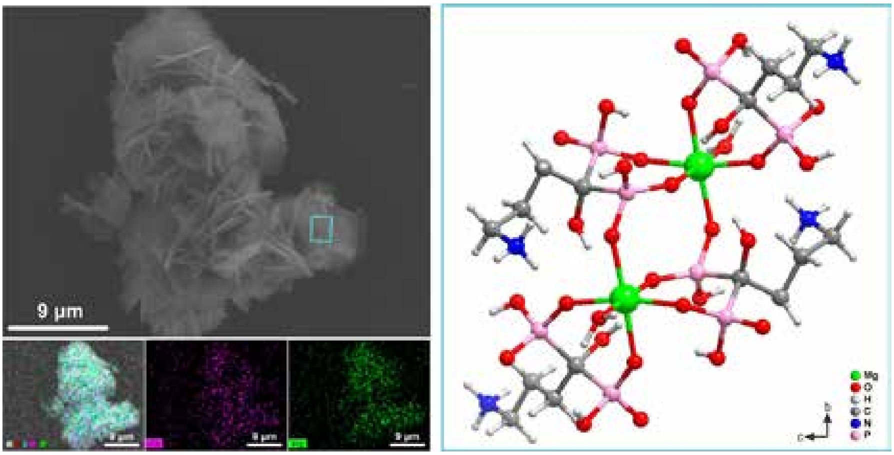

Fig. 1. SEM images of [Ca0.7Mg1.3(H4alen)4(H2O)]×H2O. (Left) EDS mapping showing the uniform distribution of Ca and Mg throughout the material. (Right) Structural representation of the dimeric unit.

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breast cancer and prostate cancer cell lines as target of benzophenones: *in vitro* assays

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Cancer is the second leading cause of death, globally, it is estimated to have risen to 18.1 million new cases and 9.6 million deaths in 2018, and deaths are projected to reach over13 million in 2030 [1]. Breast cancer and prostate cancer appear as the two most common invasive cancers in woman and men, respectively [1].

Although significant advances are being made in their treatment, the cancer heterogeneity [2], and the development of resistance to anticancer drugs [3] constitute some of the major problems to be overcome. Thus, development of drugs for specific cancer-related targets, are the key in the effort to cure cancer.

Natural and synthetic benzophenones are reported to have potential anticancer activity [4], [5].

We have designed and synthesized substituted benzophenones **1**, prepared for anticancer screening in breast (MDA-MB-231, T47-D) and prostate (PC3) cancer cell lines. Here, we will focus on their cytotoxicity evaluation, cell cycle effect and structure-activity relationship (SAR).

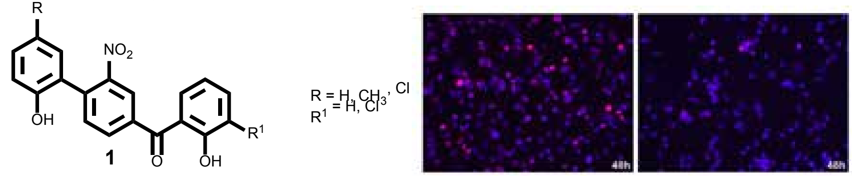

Figure 1

ACKNOWLEDGEMENTS: Thanks are due to University of Aveiro and FCT/MEC for the financial support of QOPNA (FCT UID/QUI/00062/2013) and iBiMED (UID/BIM/04501/2013) research units through national founds and, where applicable, co-financed by the FEDER, within the PT2020 Partnership Agreement, and to the Portuguese NMR Network. Djenisa Rocha is grateful for financial support from the project PT-DZ/0005/2015.

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D-Pinitol [(1S,2S,4S,5R)-6-metoxiciclohexano-1,2,3,4,5-pentol] de *Mimosa caesalpiniifolia* para tratamento preventivo de diabetes mellitus

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Mimosa é um dos maiores gêneros da família Fabaceae e da subfamília Mimosaceae e é fonte de alcalóides, ácidos fenólicos, terpenóides, carotenoides e principalmente, flavonóides [1]. *Mimosa caesalpiniifolia,* possuiu uma diversidade de espécies com ação hipoglicemiante, sendo capazes de minimizar os efeitos colaterais da doença e melhorar a qualidade de vida dos pacientes. Este trabalho teve por objetivo obter a partir do extrato hidroalcoólico 70%, a fração acetato de etila (Fr-AcOEt) e avaliar a atividade hipoglicemiante em camundongos diabéticos induzidos por estreptozotocina. A Fr-AcOEt mostrou resultados promissores para a atividade hipoglicemiante. T**écnicas cromatográficas** foram utilizadas (HPLC, preparativa) e isolou-se um dos composto majorit**ário** (D-Pinitol [(1S,2S,4S,5R)-6-metoxiciclohexano-1,2,3,4,5-pentol]). As doses de 62,5 mg/kg e 125 mg/kg durante 14 dias foram eficientes para diminuir a glicemia dos camundongos diabéticos tratados, em cerca de 50% no final do tratamento quando comparamos ao primeiro dia. Os resultados são de extrema importância, visto a necessidade de estudos que incorporem novos agentes hipoglicemiantes e mais eficazes ao mercado farmacêutico.

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Valorisation of *scabiosa stellata* L.: a medicinal plant that grows wild in algeria

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Scabiosa stellata L. is an accepted species belonging to the genus *Scabiosa* and also the less studied one. In the present study GC-MS and UHPLC-DAD-ESI/MS^n were used to establish the chemical composition of *S. stellata* extracts. Simultaneously the phytochemical study allowed the isolation of interesting natural products (Fig. 1 shows one example), some found for the first time in *Scabiosa* genus.
The *S. stellata* phenolic composition seems to be correlated with the extracts *in vitro* antioxidant activities and the lipophilic profile allowed to conclude that fatty acids and their derivatives (87%) are the major chemical families (Fig. 1). Moreover, the obtained results, together with the index of atherogenicity (AI = 0.55), index of thrombogenicity (TI = 0.23) and the fatty acids ratio (w-6/w-3 = 0.55) point out the nutritional value of *S. stellata*.
In the present communication, the chemical profile will be presented and discussed. Additionally their relevance to the species valorization will also be addressed.

Figure 1: Relative abundance of the compounds groups detected in S. stellata lipophilic extract and the structure of tamarixetin {3-b-L-rhamnosyl-(1→2)[b-L-rhamnosyl-(1→6)]β-D-glucoside]}.

ACKNOWLEDGEMENTS: Thanks are due to the University of Aveiro, to the FCT/MEC and POPH/FSE for the financial support of the QOPNA research Unit (FCT UID/QUI/00062/2013) through national founds and, where applicable, co-financed by the FEDER, within the PT2020 Partnership Agreement and to the Portuguese NMR Network. Thanks are also due to the Algerian MESRS (Ministère de l'Enseignement Supérieure et la Recherche Scientifique) via PNE (Programme National Exceptionnel) for financial support, namely the NR displacement.

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Estudio de la actividad antitumoral de complejos de vanadio con ligandos hidrazona derivados de pyridoxal

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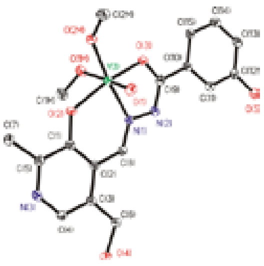
Existe un gran interés en la búsqueda de compuestos metálicos que puedan ser efectivos y presenten menos efectos adversos, ya que los fármacos empleados en quimioterapia, como por ejemplo el cis-platino, dan lugar a efectos secundarios graves y resistencia al tratamiento [1].

Por esta razón, se han diseñado, sintetizado y caracterizado, nuevos compuestos de vanadio, con el propósito de estudiar la potencialidad de este centro metálico en el tratamiento del cáncer. Todos los compuestos que han sido sintetizados siguiendo la misma ruta de reacción [2].

El cáncer de pulmón es responsable de un elevado número de muertes a nivel mundial. Por ello, la actividad anticancerígena fue estudiada sobre la línea de cáncer de pulmón A549, obteniendo como resultado que, para el caso de algunos complejos el porcentaje de supervivencia se redujo en un 10-25% después de 24h de tratamiento.



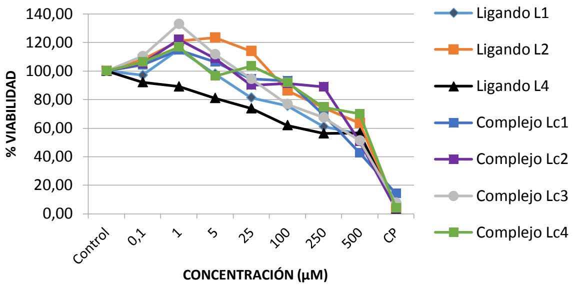


Figura 1:Compuesto Lc2 estudiado por difracción de Rx de monocristal.
Figura 2: Resultados del estudio de MTT.

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Figura 1:Compuesto Lc2 estudiado por difracción de Rx de monocristal.

QS36

Prostate cancer: antitumor effect of chalcones on androgen-dependent and androgen-independent prostate cancer cell lines

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Chalcones have a plethora of properties, including antitumor effects. Because they share a simple chemical structure and can be easily modified or synthesized, several new chalcones have been synthetized to potentiate their biological properties [1].
The aim of this work was to evaluate the cytotoxic effect of eighteen structure related chalcone derivatives against two prostate cancer cell lines, namely the androgen dependent LNCaP and androgen independent PC-3.
The cytotoxic activity of chalcone derivatives was evaluated by the MTT-viability assay after 48 h exposure to the compounds [2].
All chalcone derivatives displayed cellular toxicity in both cell lines. MB4 demonstrated one of the highest activities in the screening, showing 76.93 ± 4.56% and 87.60 ± 3.69% of cytotoxicity for LNCaP and PC3, respectively, at 20 μM. Besides that, for MB4 it was possible to obtain inhibitions around 50%, for both cell lines at 10 μM, and around 30 – 40% at 5 μM. Most of the compounds seem to inhibit PC-3 and LNCaP cell lines without significantly differences of sensitivity between them. However, DT, TB4 and T5 were significantly more active ($p<0.05$) against PC-3 than LNCaP. Our results showed that chalcones are potent antitumor compounds against prostate cancer cell lines, with significant sensitivities between cell lines that might be related with different hormone requirements.

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A new strategy against malaria – antimalarial ionic liquids derived from aminoquinolines and fatty acids

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Based on the recent promising results obtained by us, where ionic liquids (ILs) derived from primaquine were found as triple-stage antimalarial hits [1], we have now produced, by simple, quantitative, and low-cost methods, new ILs *via* simple acid-base titration of antimalarial aminoquinolines (primaquine and chloroquine) with natural fatty acids (Figure 1) [1]. We have also synthesized, in good to high yields, the covalent amide analogues of these ILs (Figure 1), in order to establish how the nature of the chemical bond (ionic ammonium carboxylate *versus* covalent amide) between both building blocks influences the physico-chemical and biological properties of the final compounds [2]. Results obtained thus far allow us to conclude that both ionic and covalent compounds (i) have higher thermostability than the parent drugs, and (ii) display remarkable *in vitro* activity against liver-stage malaria parasites.

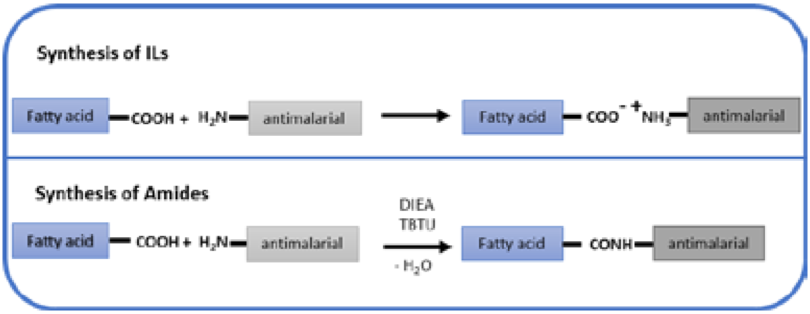

Figure 1. Schematic view of antimalarial-derived ILs and their covalent amide analogues.

Ongoing studies will hopefully allow to confirm the therapeutic potential of these new compounds, and allow us to build structure-activity relationships that will guide future efforts towards potent, safe and low-cost antimalarial drugs.

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Envisioning bladder cancer in liquid biopsies by high resolution mass spectrometry

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Developing a non-invasive method for bladder cancer detection would have a profound effect on patients' quality of life and on the economy of health systems [1], as bladder cancer is the most expensive neoplasia on cost per patient [2]. Cystoscopy is still the most used method to diagnose bladder cancer, and in addition to being invasive and not cost effective, lacks sensibility [3]. As an early detection would benefit treatment success, in this study we look for biomarkers that could serve as potential targets for the early stages of Ta, T1, T2+ bladder cancer stages. Urine samples were collected from volunteers of the following groups: i) individuals with bladder cancer (stages Ta, T1 or T2+), ii) individuals with genitourinary disorders and iii) individuals without any urinary pathology. The urinary proteome was purified and digested, through filter aided sample preparation and quantified by liquid chromatography coupled to mass spectrometry. Statistical analysis and Cytoscape were used for data integration. A biomarker panel was developed based on proteins that discriminate between bladder cancer' stages and other urinary pathologies. Our results suggest that the urinary proteome can be used as a tool to diagnose Ta, T1 and T2+ bladder cancer stages.

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Phytochemical analysis and anti-aging activities of compounds from *juniperus brevifolia* bark

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Juniperus brevifolia (Seub.) Antoine (Fig. 1a) is an endemic Azorean taxon which is present in all islands of the Azores archipelago with the exception for Graciosa [1]. Although Juniperus brevifolia is not used in Azorean folk medicine, its interest comes from the wide range of biological activities reported for other Juniperus species and for their secondary metabolites [2]. In continuation of our study on the valorization of endemic plants of the Azores archipelago, we have examined this species.

Several secondary metabolites were isolated from hexane bark extract by chromatographic techniques and their structures were elucidated by spectroscopic methods. The anti-aging effects of some secondary metabolites identified in this extract were evaluated based on their elastase and tyrosinase inhibition ability, two enzymes whose activity causes loss of elasticity and skin hyperpigmentation, respectively. The compounds β-sitosterol (1), totarol (2), 12-methyl-sugiol ether (3), stigmast-4-en-3-one (4), abiet-8,11,13-trien-7-one (5), 5,6-dehydro-12-methyl-sugiol ether (6), 6α-hydroxy sugiol (7) were identified. Compounds 5 and 6 were here identified for the first time in J. brevifolia species while compound 7 has never been identified before in a Juniperus species. Furthermore, compound 7 (Fig. 1b) is the only one exhibiting anti-elastase activity whereas the communic acid (8), previously identified in this extract [3], was the only compound exhibiting anti-tyrosinase activity.

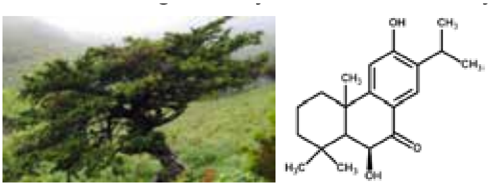

Figure 1. a) Juniperus.brevifolia; b)Compound 7.

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Especiación de complejos de vanadio(v) con ligandos hidrazona derivados de 2,6-diformil-4-metilfenol y estudio de su interacción con el adn

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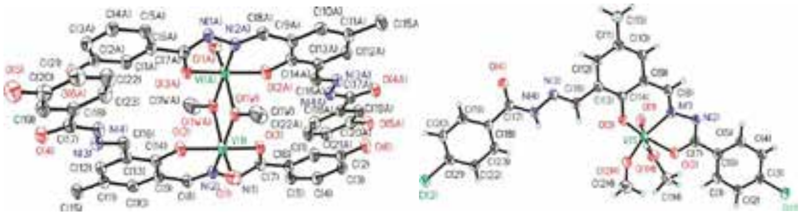
QUÍMICA E SAÚDE

POSTER

Los complejos de vanadio(V) con ligandos hidrazonas derivados de 2,6-diformil-4-metilfenol fueron sintetizados de acuerdo con las rutas sintéticas encontradas en la bibliografía [1].

Una vez aislados y caracterizados por las técnicas de análisis elemental, espectrometría de masas, espectroscopia IR y difracción de Rayos-X de monocristal se observó que en disolución podían estar presentes tanto especies mononucleares como dinucleares en equilibrio.



Compuesto 1

Compuesto 2

Figura 1: Especies dinuclear y monuclear de vanadio(V) aisladas y estudiadas por difracción de Rayos-X de monocristal.

Los datos de Rayos-X obtenidos se utilizaron para evaluar su posible interacción con el ADN a través de la técnica molecular docking, en busca de estudiar su potencial aplicación como agentes antitumorales, de acuerdo con la línea de investigación que se siguió para estudiar al cis-platino.

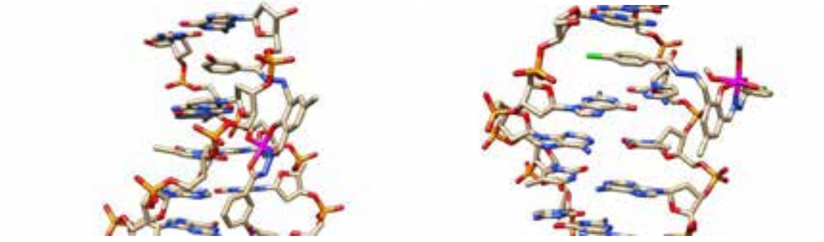


Figura 2: Interacción de compuesto 1(izda) y del compuesto 2(dcha) con el ADN.

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Pinpointing protein differences between chromophobe renal cell carcinoma and renal oncocytoma

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Chromophobe renal cell carcinoma (chRCC: malignant) and renal oncocytoma (RO: benign) are tumors with markedly different outcomes but similar histological phenotypes that confound diagnosis [1]. In proteomics, the quantitative analysis of tissue proteins enables the detection of a larger panel of proteins which can be useful in the characterization and differentiation of normal and disease stages. However, the methodology applied to preserve the samples collected for clinical researching, sometimes, is unsuited for mass spectrometry (MS) analysis. For instance, the use of Optimal Cutting Temperature (OCT) compound, to embed and preserve tissues, hampers the MS analysis by suppressing the peptide signals [2,3]. Herein, we present an effective workflow to overcome the drawbacks of OTC-embedded samples and interrogate the proteome of chRCC and RO neoplasms.
Methods: Ultrasonic energy were assessed to clean OCT from OCT-embedded samples. Biopsies tissues from human kidneys diagnosed with chRCC (n=5) and RO (n=3) were treated and compared. Non-tumoral kidney specimens (n=5) were used as control. Protein identification and quantitative proteomics (label free) was carried out by nanoLC-MS/MS, and RNA expression profiles were also interrogated and compared with proteomic signature.
Results: OCT compound was successfully removed with the aid of ultrasonication. Proteomes of the human kidney samples were compared by LC-MS/MS, and a panel of proteins specific to each tumor vs NAT was identified. An unsupervised clustering analysis of the spectra precisely validated the presence of the 3 phenotypic classes.
Conclusions: The development of a new methodology which enables OCT-embedded tissues samples for MS was achieved. The proteomic profiles of chRCC, RO, and NAT specimens were successfully assessed providing new insights into the different mechanisms underlying formation of these tumors.

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Antioxidant activity of chalcones related to the scavenging of hypochlorous acid

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Chalcones are heterocyclic compounds of natural origin, considered as a class of open chain flavonoids with the 1,3-diaryl-2-propen-1-one molecular pattern (Fig.1). The chalcone family has an extensive structural diversity and their chemistry continues to be of interest within the scientific community due to its recognized biological activities, from which the antioxidant property stands out [1].

Hypochlorous acid (HOCl) is a powerful bactericidal oxidant generated by activated neutrophils, during the respective oxidative burst. However, when overproduced, HOCl can induce oxidative damage in the surrounding tissues, playing an important role in the pathogenesis of chronic inflammatory diseases [2]. Therefore, HOCl scavenging compounds may be considered as therapeutic agents through the prevention and resolution of the oxidative burst.

The aim of the present study was to evaluate the ability of structurally related methoxylated and hydroxylated chalcones to scavenge HOCl. To accomplish this aim, an *in vitro* microanalysis methodology with fluorimetric detection was used where the ability of HOCl to oxidize the non-fluorescent probe dihydrorhodamine (DHR) to the fluorescent rhodamine 123 was measured [3]. The preliminary results obtained for the studied structurally related chalcones indicate that the hydroxylated ones display better scavenging activity against HOCl. This appear to indicate that hydroxyl groups are important substituents to determine the antioxidant activity of chalcones.

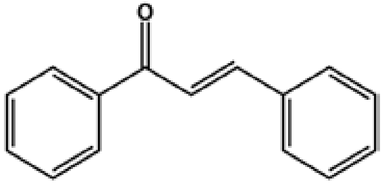

Fig.1. Chalcones' basic chemical structure

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Disposable electrochemical biosensors for early diagnosis of chronic kidney disease

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Chronic kidney disease (CKD) is a health problem with increasing prevalence worldwide. CKD patients usually suffer from a gradual loss of kidney function until its permanent damage [1]. The traditional biomarkers to evaluate kidney injury are not well suited for the identification of the asymptomatic early stages of CKD [1]. In recent years, cystatin C (CysC) and neutrophil gelatinase-associated lipocalin (NGAL) have emerged as new powerful biomarkers for the early diagnosis of CKD. CysC is established as a valuable biomarker for the calculation of glomerular filtration rate and evaluation of kidney function [2], and NGAL has been indicated as a promising biomarker for the diagnosis and prognosis of the disease [3].

The development of non-invasive diagnostic methods that ensure real-time results at a point-of-care level is a constant concern of modern healthcare. Furthermore, the development of new technologies to improve the diagnosis, prognosis and even self-management of CKD is highly demanded. Therefore, in this work electrochemical immunosensors for the detection of CysC and NGAL were developed.

The experimental parameters were carefully optimized and characteristics such as sensitivity, selectivity and precision were studied. The proposed sensors were used for the analysis of CysC and NGAL in CKD patients' samples (serum and urine), providing accurate results.

Because of their miniaturized size, the need of low reagents/sample volumes, the fast analysis time, and high sensitivity and portability, the developed biosensors can certainly contribute as new approaches for CKD front-line diagnosis.

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QS44

Structure-based virtual screening approach to identify alpha-glucosidase inhibitors

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The prevalence of diabetes mellitus is increasing at an alarming rate and it is already considered as one of the biggest health problems in the world, with significant health and economic burdens on patients and communities. Although insulin results efficient in most cases, unfortunately, its continued administration means also a number of side effects and complications. For those reasons, the search for oral active drugs with antidiabetic activity without side effects remains crucial.

Alpha-glucosidase (EC 3.2.1.20) has been regarded as an important therapeutic target in the fight against diabetes because it was shown that the inhibition of its catalytic activity resulted in the retardation of glucose absorption and the decrease in postprandial blood glucose level.

In the present study, a structure-based virtual screening targeting the active site of the enzyme was performed in order to develop a dataset of potential new alpha-glucosidase inhibitors. 53 compounds identified from the precedent virtual screening were further assayed for IC50, using absorbance-based assay method to evaluate the activity of alpha-glucosidase from Saccharomyces cerevisiae.

The results revealed the potential of 11 compounds with higher activity (IC50 <100 μM) than that of acarbose (commercial inhibitor; IC50 = 390 μM). Moreover, the mode of inhibition by these compounds against alpha-glucosidase was also rationalized through enzyme kinetic analysis.

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Design and development of a µPAD device for magnesium determination in saliva

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Magnesium is the second most important intracellular cation and the fourth most prevalent. Disorders involving magnesium are categorized into two groups: hypomagnesemia (magnesium deficiency) and hypermagnesemia. Therefore, the determination of magnesium can be of great interest, because it helps in the clinical context and epidemiological research.

In this context, the objective of propose work was to develop a microfluidic paper-based analytical device (µPAD) for magnesium quantification in saliva. There are two main advantages on using saliva as an alternative biological sample namely being easy to collect and non-invasive. The µPADs have several characteristics which make them ideally suited to conduct on-location analyte determinations: there is no need for specialized skills or expensive equipment; all materials are cheap and easily obtained; the overall size is ideally for on-hand determination; and they can be discarded after use in a disposable approach. Another advantage of these devices is that they use small amounts of sample and reagent, still providing both immediate and accurate results.

The developed µPAD was based on the color reaction between magnesium and eriochrome cyanine dye. The µPAD was assembled with the reagent, and then the sample was added, followed by the sealing of the device. After 5 min (for the reaction to occur) a scanner was used to obtain a high resolution image of the detection zone and then the colour intensity was measured (Image J software) to established calibration curves.

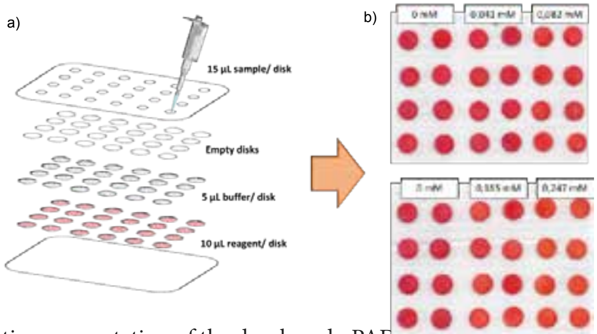

Fig.1. Schematic representation of the developed µPAD (a) and photo of the two µPADs representing a calibration curve (b)

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Novel 16*E*-arylidene-5α,6α-epoxydehydroepiandrosterone derivatives: synthesis and cytotoxicity evaluation

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Steroids represent a pharmacologically active class of molecules associated with a variety of physiological functions. Therefore, natural, semi-synthetic and synthetic steroidal derivatives constitute a rich source of drug candidates [1-3]. 16*E*-Arylideneandrostane derivatives have been considered potent anti-cancer agents for the treatment of leukemia, breast cancer, prostate cancer and brain tumours [4]. In addition, 5a,6a-epoxycholesterol is an oxysterol known for several biological activities, including regulation of cell proliferation and cholesterol homeostasis [2]. Moreover, several pregnenolone derivatives combining these two modifications with potential neuroprotective activity were already described [5]. In the present study, a new serial of 16*E*-arylidene-5a,6a-epoxydehydroepiandrosterone derivatives were successfully synthesized (Fig.1) and their cytotoxicity was evaluated on tumoral and non-tumoral cell lines. These 16*E*-arylidene-5a,6a-epoxyandrostanesteroids were obtained from dehydroepiandrosterone by aldol condensation with different aldehydes followed by a diastereoselective 5a,6a-epoxidation. The cytotoxicity of these compounds in normal human dermal fibroblasts and several tumoral cell lines was evaluated by the 3-(4,5-dimethylthiazol-2-yl)-2,5-diphenyltetrazolium bromide assay.

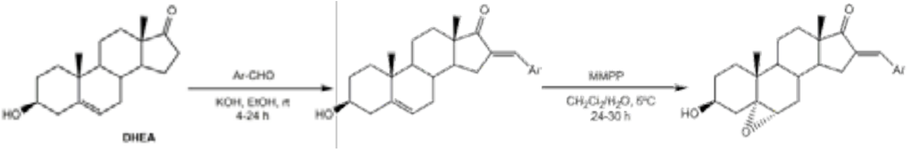

Fig.1. Synthesis of 16E-arylidene-5a,6a-epoxydehydroepiandrosterone derivatives, reagents and reaction conditions.

AGRADECIMENTOS: This work is supported by FEDER funds through the POCI - COMPETE 2020 – Operational Programme Competitiveness and Internationalization in Axis I – Strengthening research, technological development and innovation (Project No. 007491) and National Funds by FCT - Foundation for Science and Technology (Project UID/Multi /00709). VB also acknowledges the grant SFRH/BD/131059/2017.

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Unraveling the splicing events underlaying nasopharyngeal carcinoma progression by label free quantitative mass spectrometry analysis

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Nasopharyngeal carcinoma (NPC) is a rare type of cancer that has one of the worst prognoses among head tumors. It is characterized by his misleading diagnosis [1]. Alteration of alternative splicing mechanism is a ubiquitous process that is often observed in cancer and has a direct connection with the process of tumorigenesis [2]. NPC tissue samples are normally preserved for long-term storage in formalin-fixed, paraffin-embedded (FFPE) form. This type of samples represents an easy storage method and are a valuable source of biological information to identify new biomarkers with potential prognostic value. However, RNA is usually degraded in FFPE samples limiting its use to investigate alternative splicing events [3]. We proposed to investigate the alternative splicing at the protein level in FFPE tissues of NPC. FFPE samples were deparaffinize and protein extraction was performed by the synergetic combination of temperature and ultrasound energy. The digestion of the extracted proteins was done using the filter aided sample preparation (FASP) method. Finally, samples were interrogated by mass spectrometry using the label-free protein quantification methodology. Cytoscape was used for proteogenomic analysis. Our results showed a regulation of mRNA metabolic processes through alternative mRNA splicing in non-metastatic nasopharyngeal stage associated with Epstein-Barr virus infection.

ACKNOWLEDGEMENTS: Authors acknowledge the funding provided by the PROTEOMASS Scientific Society to the Laboratory for Biological Mass Spectrometry - Isabel Moura; the Associated Laboratory for Green Chemistry LAQV which is financed by national funds from FCT/MEC (UID/QUI/50006/2013) and co-financed by the ERDF under the PT2020 Partnership Agreement (POCI-01-0145-FEDER-007265). H.M.S. acknowledges the Portuguese Foundation for Science and Technology for his Investigator Program (IF/00007/2015).

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Tomato glycoalkaloids as new drug candidates: an overview of mechanisms of action and clinical applications

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Glycoalkaloids are characteristic secondary metabolites in plants of the Solanaceae family. Although perceived as potentially toxic, these compounds display different bioactivities and pharmacological effects. The glycoalkaloid tomatine can be found in green tomatoes and comprises a junction of α-tomatine (A) and dehydrotomatine (B). As shown in Figure 1, dehydrotomatine differs from α-tomatine by having a double bond in the steroidal B ring of the aglycone; but both glycoalkaloids have the same tetrasaccharide (lycotetraose) side chain. Therefore, while α-tomatine has lycotetraose bonded to the aglycone tomatidine, dehydrotomatine has the side chain attached to the aglycone tomatidenol. Up to 500 mg/kg of tomatine can be found in unripe (green) tomatoes, levels that decrease with ripening (approximately 5 mg/kg in ripe red tomatoes) [1].

We revised the mechanisms of action of tomatine and their involvement in human health [1]. Its bioactivity derives mainly from the capacity to inhibit acetylcholinesterase (AChE) and butyrylcholinesterase (BuChE) and to complex with membrane 3**β**-hydroxy sterols. In inflammatory processes, the aglycone tomatidine is able to reduce inducible nitric oxide synthase (iNOS) and cyclooxygenase-2 (COX-2) expression through blocking nuclear factor kappa B (NF-κB) and c-Jun N-terminal kinase (JNK) signalling in lipopolysaccharide-stimulated macrophages. In turn, α-tomatine has the ability to decrease the cholesterol and triglyceride levels, enhance the immune system, and inhibit the growth of different type of cancer cells. Several *in vitro* and *in vivo* studies have been highlighting the pharmacological potential of these compounds, which have high potential to be used in the development of new anticancer drugs, among others.

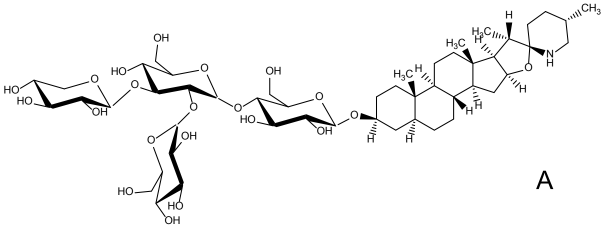

Fig.1. Chemical structures of (A) α-tomatine and (B) dehydrotomatine.

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Enantioseparation of xanthone derivatives of proteinogenic amino acids on cellulose tris(3-chloro-4-methylphenylcarbamate) stationary phase

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Xanthones are a class of compounds with great interest in drug discovery and development [1]. A variety of natural and synthetic bioactive derivatives are described, but their stereochemistry are often neglected. Our group synthesized a large library of enantiomerically pure bioactive chiral derivatives of xanthones (CDXs) with examples of enantioselectivity being observed for some biological activities [2,3].

Recently a library of CDXs were obtained using the chiral pool strategy, by coupling a suitable funtionalized xanthone derivative with pure enantiomers of different proteinogenic amino esters and amino acids, for further biological activity screening. Consequently, searching for new chromatographic methods to evaluate the enantiomeric purity of CDXs is one important task to determine the enantiomeric ratio (e.r). Herein, we describe the enantioseparation and determination of the enantiomeric purity by liquid chromatography (LC) of a library of proteinogenic amino acids and amino esters of CDXs. Their enantiomeric separation was optimized on cellulose tris(3-chloro-4-methylphenylcarbamate) CSP- Lux^{TM} 3 µm cellulose-2 column, under normal elution mode at room temperature. Very high enantioselectivity and resolution were obtained, using hexane/ethanol (50:50 v/v) as mobile phase, with **α** and Rs ranging from 1.13 to 1.92 and from 1.57 to 9.74, respectively. The enantiomeric ratio (e.r.) for all synthesized CDXs was measured achieving values higher than 90%, except for CDXs of phenylglicine, where racemization was observed.

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Development of *in vitro* and *ex vivo* methods for the evaluation of dipeptidyl peptidase-4 activity

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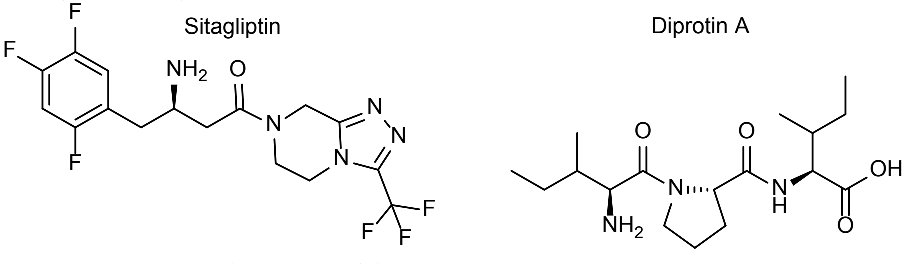
Among the different classes of antidiabetic agents, dipeptidyl peptidase-4 (DPP-4) inhibitors are one of the most recent class of drugs used in the treatment of type 2 diabetes *mellitus* (DM). The proteolytic enzyme DPP-4 rapidly inactivates the incretin hormones glucagon like peptide-1 (GLP-1) and glucose-dependent insulinotropic polypeptide (GIP). Thus, inhibition of DPP-4 increases the half-life of incretins, contributing to the stimulation of insulin secretion in a concentration-dependent manner.

In that sense, the use of DPP-4 inhibitors, which targets fast and postprandial hyperglycemia and reduces hypoglycemia risk, represents a unique approach for the management of type 2 DM.

In the present study, *in vitro* colorimetric and fluorometric methods, using isolated human recombinant DPP-4, and an *ex vivo* methods, in human whole blood and plasma, were developed for the evaluation of DPP-4 activity. The *in vitro* assays were performed in order to compare their sensitivity, while the two *ex vivo* models were selected to compare the obtained results for the soluble DPP-4 enzyme in plasma, and blood, a more complex and physiological matrix. Sitagliptin and diprotin A (Figure 1) were used as positive controls.

Concerning the *in vitro* methods, the fluorometric assay proved to be the most sensitive one. As such, the *ex vivo* methods applied were based on the fluorometric assay. The IC_{50} values found for the positive controls in human whole blood and plasma were similar, but higher than the ones found for the colorimetric and fluorometric assays, with the human isolated enzyme. This is possibly due to the binding of these compounds to blood plasma proteins, in particular human serum albumin. In conclusion, the developed methods for the evaluation of DPP-4 activity, are of utmost importance for the discovery of new and safer DPP-4 inhibitors, as promising agents for the management of type 2 DM.



Sitagliptin

Diprotin A

Fig.1. Chemical structures of the positive controls, sitagliptin and diprotin A.

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Avaliação *in vitro* das atividades antioxidante e de inibição da acetilcolinesterase de extratos de *Hibiscus sabdariffa*

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Hibiscus sabdariffa é uma espécie vegetal que possui grande importância medicinal principalmente devido a sua capacidade antioxidante [1]. Na literatura já foi demonstrada uma correlação positiva entre compostos fenólicos e flavonoides e capacidade antioxidante e neuroprotetora [2], [3]. Visto que a abordagem terapêutica mais apropriada para as doenças neurodegenerativas, tal como a doença de Alzheimer, seria restabelecer o número de sinapses colinérgicas inibindo a enzima acetilcolinesterase (AChE) [4], há um crescente interesse na busca de inibidores de AChE em extratos com atividade antioxidante, ricos em polifenóis.

O objetivo do presente estudo foi determinar os teores de compostos fenólicos totais e flavonoides, avaliar a atividade antioxidante e, de maneira inédita, avaliar a atividade de inibição da enzima AChE de extratos etanólicos de cálices (EEHSC) e folhas (EEHSF) de *Hibiscus sabdariffa*.

Os valores de compostos fenólicos totais e flavonoides das amostras foram determinados por meio de ensaios colorimétricos. A capacidade antioxidante foi avaliada pelos métodos de sequestro dos radicais livres DPPH e $ABTS^{\bullet+}$ e de redução férrica (FRAP). A atividade de inibição da enzima acetilcolinesterase foi determinada por método espectrofotométrico.

O EEHSC apresentou um maior teor de compostos fenólicos, enquanto que o EEHSF exibiu maior teor de flavonoides. O EEHSF demonstrou uma maior atividade antioxidante que EEHSC em todos os métodos utilizados. Apenas o EEHSC demonstrou uma atividade de inibição da acetilcolinesterase maior que 50% e, portanto, somente foi possível calcular o valor de IC_{50} para o mesmo, 2,80 mg/mL.

Verificou-se a existência de uma correlação tanto entre os teores de flavonoides e a capacidade antioxidante como também entre a quantidade de compostos fenólicos totais e a ação de inibição da AChE como já evidenciado em outros estudos [5-7].

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LOOKING FOR MORE ACTIVE, LESS TOXIC ANTIMICROBIALS

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A number of complexes with camphor derived ligands ($L{=}OC_{10}H_{14}NR$) were synthesized and their antimicrobial and/or cytotoxic properties evaluated. Promising results were obtained from silver camphorimine complexes $[Ag(NO_3)(L)]$, $[Ag(NO_3)(L)_2]$ or $[Ag_2(L^A)(L^B)_2]$ [1,2] that in some cases are even better than the active principles actually in use, although the toxicity is higher.

New complexes were designed and their synthesis is under progress aiming at optimizing the antibacterial effectiveness and decrease the toxicity towards applications other than topic. The cores of the new sets of camphorimine complexes are silver acetate, silver chloride and copper dichloride.

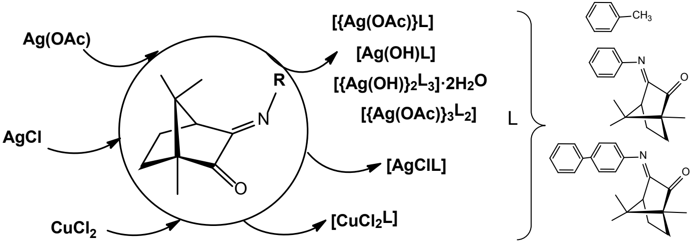

Figure 1: Scheme of the types of the new complexes whose antimicrobial properties assessment is under progress

Preliminary results on [Ag(OH)L] (R= $(C_6H_4)_2NC_{10}H_{14}O$) showed that the antibacterial activity towards *E. coli*, *S. aureus, B. contaminans*, and *P. aeruginosa* strains (respectively 62.5, 125, 125, 62.5 μg/ml) are similar to those of the moderate active silver nitrate complexes [1] while the toxicity (assessment under progress) is expected to be lower since no nitrate is in the complex.

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4-Azasteroid derivatives as inhibitors of prostate cells proliferation: study of three-dimensional quantitative structure–activity relationship (3D-QSAR)

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Azasteroids have been reported as inhibitors of human 5a-reductase, which interfere in the androgen biosynthesis, converting testosterone into 5a-dihydrotestosterone. These molecules were design by substitution of one carbon atom of steroidal A ring by heteroatom nitrogen [1,2]. In the other hand, steroids with modifications on D ring have been reported as anticancer agents, as abiraterone acetate, used in prostate cancer treatment, acting as a CYP17A1 inhibitor, interfering as well as in the androgen synthesis [3]. Thus, it was pertinent synthesize several compounds with both structural properties to better understand the effects on prostate cells proliferation.

In a previous study, it was synthesized several novel 4-azasteroids and its effects on cell proliferation were tested [4]. At the present work, in order to clarify the relationship between the structure of 4-azasteroid derivatives and precursors and its effects on proliferation of LNCaP cells, prostate cell line androgen-dependent, ligand based approach was used to build a three-dimensional quantitative structure–activity relationship (3D-QSAR) model applying the software Open3DQSAR [5]. Moreover, understanding the quantitative structure-activity relationships of the synthesized compounds and its precursors help to facilitate the process of drug discovery.

The data set for the 3D-QSAR analysis contained 23 4-azasteroid derivatives and respective precursors. The main calculations were performed in the Open3DALIGN software based on *in vitro* results of cell proliferation percentage in the initial screening at 30 **μM** in the LNCaP cells.

Regarding the results, at a future development of new azasteroids with potential prostate anticancer properties, its 3D structures must be taken in consideration.

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Enhanced extraction of chlorophylls from *Spartina patens* and *Puccinellia maritima* and their potential as photosensitizers

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Chlorophylls are essential compounds not only in plant physiology but also in food, cosmetic and pharmaceutical industries [1]. These molecules have gain interest due to their ability to generate reactive oxygen species, namely single oxygen ($^1O_2$), which could be translated on its use as photosensitizer agent in photodynamic therapy [2]. Current methods for extraction of these compounds are mainly solid liquid extraction from fresh or freeze-dried biomass [1]. The aim of this work is to optimize a suitable extraction of chlorophylls from *Spartina patens* and *Puccinellia maritima*, two halophytes from Poaceae, with potential use in the pharmaceutical and agricultural fields. Furthermore, we also aim to test the potential of the extracts to act as photosensitizers.

To accomplish this, fresh samples of each *taxon* were subjected to extraction with ethanol using microwave, ultra sound and room temperature stirring techniques. To evaluate the potential ability of the extracts to act as photosensitizers, the photophysical properties as singlet oxygen production and photostability were analyzed.

Through the accomplished data it was evident that the microwave extraction could be a reliable alternative to room temperature stirring technique. Photophysical parameters revealed that both extracts have noteworthy photostability and are able to produce singlet oxygen. Nonetheless, more studies need to be conducted to fully enhance the extraction of these molecules as well as to understand their potential as photosensitizers' agents.

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Effect of heptaphylline and two related secondary metabolites on cervical (HeLa) and prostate (LNCaP and PC-3) cancer cell lines

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Heptaphylline is a carbazole alkaloid, isolated from *Clausena heptaphylla*, with promising antitumor effects [1]. Herein, heptaphylline (M1) and two related secondary metabolites (M2 and M3) were evaluated for their the cytotoxic effect against cell lines of cervical cancer (HeLa), androgen-dependent (LNCaP) and androgen-independent (PC-3) prostate cancer, and their interference with nitric oxide (NO) production by RAW 264.7 macrophages cell line. Cervical and prostate cancers are two of most prevalent cancers [2]. Tumor associated macrophages are described as influencing the tumor development [3]. The cytotoxic activity of compounds was assayed by the MTT-viability assay. The effect on macrophages' NO was assessed by Griess reaction [4].
All derivatives displayed cellular toxicity for all cell lines. Significant differences were observed for some compounds, concerning the selectivity for different cancer type. The most active compound against HeLa, M1, resulted in 70.46 ± 0.75 % of cytotoxicity. M3 was more active on PC-3 than LNCaP (66,39 ± 6,97 % vs 39,85 ± 2,96 %; $p<0.05$), that might indicate different mechanisms of action and be related with different hormone requirements. In a preliminary experiment, M1 seemed to interfere with nitric oxide produced by LPS-stimulated macrophages. These results demonstrate the antitumor activity of the compounds and, based on preliminary results, a possible effect on macrophages.

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In the trail of Topotecan-lipid membrane interactions

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Topotecan is a Camptothecin derivative constituted by a planar aromatic five-ring system with a lactone ring that is responsible for its anticancer activity. In neutral or basic aqueous solutions, the ring opens leading to the carboxylate form of Topotecan. This carboxylate form is biologically inactive and uncapable of passively cross membranes. However, despite this inability to passively cross membranes, Topotecan may still be capable to interact and disturb phospholipid bilayers.

In this context, phospholipid models, mimicking normal and cancer cell lipid membranes, were used to assess the interactions that may occur between Topotecan and these membranes. Langmuir isotherms of monolayers coupled with Brewster angle microscopy, differential scanning calorimetry of liposomes and X-ray scattering of small and wide angle of stacked multilayers were used as complementary techniques. The results demonstrated that the composition of the lipid membranes conditions the interactions and that Topotecans seems to preferably interact with the glycerol backbone of phosphatidylcholine phospholipids.

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Estudo dos compostos fenólicos presentes em tintas ferrogálhicas medievais obtidas através do uso de reconstruções históricas

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A degradação de manuscritos (medievais) é uma preocupante questão de conservação e uma séria ameaça ao património mundial escrito. As tintas ferrogálhicas, utilizadas desde a Idade Clássica, eram o material de escrita por excelência, principalmente devido à sua permanência, desejada em documentação importante. A facilidade da sua produção terá sido também um fator importante, onde a um extracto de galhas era adicionado sulfato de ferro e goma arábica, produzindo imediatamente uma tinta negra.

Até recentemente, têm sido descritas como complexos de ácido gálhico ou ácido tânico, o que parece simplificar a realidade de um extracto polifenólico, sendo que a sua complexidade química ainda não é conhecida [1]. Para determinar quais os compostos fenólicos presentes nos extratos de galhas, foram preparadas cinco tintas medievais ibéricas, dos séc. XV ao XVII, com a maior precisão histórica possível. As receitas variam no tempo de extração das galhas, no meio (vinho, água e vinagre), e noutros aditivos adicionados, como romã e índigo.

O objetivo principal deste trabalho foi identificar e quantificar os principais compostos fenólicos presentes nos extratos de galhas e avaliar a sua variação pela adição de sulfato de ferro e goma arábica ao produzir as tintas ferrogálhicas. Todos os extratos e tintas foram preparados em quintuplicado e analisados por HPLC-ESI-MS e HPLC-DAD [3]. A análise por HPLC-ESI-MS permitiu a identificação dos compostos fenólicos presentes em extratos e tintas. A análise por HPLC-DAD permitiu a quantificação destes compostos. As análises mostraram que a concentração relativa de ácido gálhico e seus derivados glucosilados varia consideravelmente com cada receita (Figura 1).

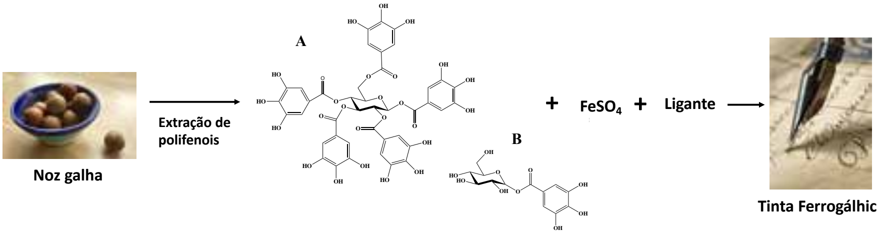

Fig.1. Receita base de uma tinta ferrogálhica. A-pentagalhoilglucose; B-monogalhoilglucose.

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What´s the water flavour?

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There is a general idea that people in Évora do not like tap water, although the water analysis complies with the limits stipulated by legislation. In this work, through the sensorial analysis of the population of Évora it is possible to confirm this idea, to perceive motives [1-2], detect problems [1-4] and suggest improvements.

A water blind test was performed, in which the population was invited to taste different bottled waters and Évora tap water, and answed a quiz. This test was made in an activity presented at the Feira de S. João (June 29, 2017), and the participation and enthusiasm of the population of Évora led us to deeper into this subject. To increase the number of answers, university students of Évora were also involved.

This work aims to contribute to the improvement of tap water quality in Évora through the sensorial analysis of the population and the university students of Évora.

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Improving Vibrational Mode Interpretation Using Bayesian Regression

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Making the assignment of signals found in the vibrational spectra to the atomic motions involved in each vibrational mode can be a cumbersome task. In general, this involves matching between experimentally recorded signals and those gathered from predictions made using first principles calculations. In a subsequent step, the atomic motions generated by the theoretical calculations must be interpreted, which is usually done either by visual inspection, or recurring to Potential Energy Distribution (PED) analysis. While the former technique is simple, it is highly prone to human error[1]. On the other hand, PED usually requires specialized human intervention in order to generate accurate description of the atomic motions[2]. However, such assignments provide valuable physical insights onto the structure and reactivity of matter at the molecular level.
In this work, we explore the viability of using Bayesian Linear Regression with Automatic Relevance Determination (ARD) in order to automate the process of describing the molecular motions associated to a given vibrational mode. For this purpose we developed a software application[3] which inner workings are detailed in Figure 1. The results from example applications[4] show that the VMARD is able to achieve assignments comparable to those of well established implementations of PED, without the need of prior human intervention (selection of internal coordinates).

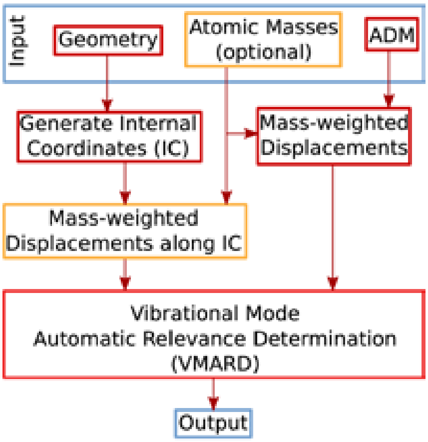

Fig.1. Legenda [Arial tamanho 10]

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Thermophysical study of the solvation of alcohols in ionic liquids

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In this work, recent results regarding thermodynamic studies of Solution/Solvation of alcohols in Ionic Liquids (ILs) will be presented. Due to alcohols and ILs similarities, these studies constitute an excellent path to probe the ILs solvation characteristics [1,2] which is of major importance to materialize the possibility of designing a specific IL or an IL-based system that combines a perfect set of properties for a specific application.

Enthalpies of solution of different alcohols in ILs, obtained by Isothermal Titration Calorimetry (ITC), at infinite dilution, and the derived enthalpies of solvation will be reported. Different combination of alcohols and ILs were selected exploring the ability of the alcohol's hydroxyl group to interact with the IL by dispersive or H-bonds interactions as well as of the non-polar tail to interact with the non-polar moieties of the IL.

The results reinforce the already known alcohol-anion H-bond interaction and suggest the preferential location of the alcohols at the interface between polar and non-polar domains of the ILs as it is reflected in the scheme of figure 1.

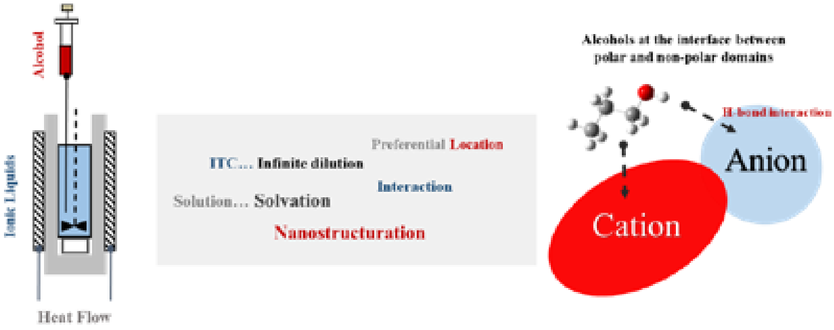

Fig.1. Schematic picture of the methodology and main conclusions.

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Interaction of biocompatible star-shaped block copolymers with 2D cell membrane models: a thermodynamic study

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The structure of the cell membrane as a lipid bilayer does not only serve the purpose of keeping the physical integrity of the cell, but changes in this structure have functional consequences, some of which are associated with severe pathological processes.
Among the vast range of biocompatible polymers, poly(ethylene oxide) – poly(propylene oxide) (PEO-PPO) block copolymers have shown to have biological activity in a variety of situations, both as individual chains (unimers) [1] and forming micellar aggregates which can be envisioned as delivery systems with advanced properties [2]. These amphiphilic copolymers may appear as linear triblock chains under the name of poloxamers, or in star-shaped varieties named poloxamines. The latter have an atypical structure with four PPO-PEO arms linked by an ethylenediamine ionisable centre.

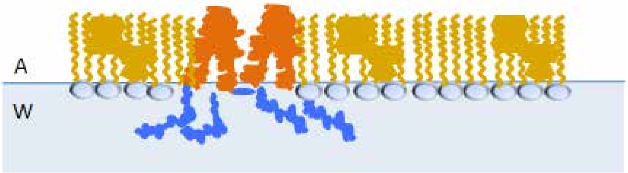

Figure 1: Part of a monolayer, featuring a poloxamine molecule and lipids.

This study focuses on the interaction between poloxamines with different EO content and lipid membrane models formed by phospholipids of different chain length and degree of insaturation, as well as cholesterol in different proportions. In order to gain information on this interaction, we spread mixed monolayers of these amphiphiles at the air/water interface (representing a membrane leaflet) and registered their compression, obtaining their surface pressure – area (π-A) isotherms. From these isotherms we performed thermodynamic calculations to obtain the excess ΔG function.
Results show the polymer – cell surface interaction depends on copolymer proportion in the system, as well as the existence of differences in the magnitude and kind of interaction as a function of the system composition.

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Selective vibrational excitation as a tool for conformational control

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Upon selective vibrational excitation, molecules can change their conformation [1]. However, under normal experimental conditions, the spectral signatures of different conformers overlap and selective vibrational excitation is difficult to achieve. In this work, we describe the low-temperature matrix isolation: an experimental method where guest molecules are immobilized in rigid and inert materials under cryogenic conditions. Infrared spectra of matrix-isolated species have typical bandwidths on the order of one wavenumber. This affords much valuable spectroscopic information, with a possibility to reliably distinguish individual spectroscopic signatures of different conformers. By using monochromatic light sources, one may envisage selective excitation of a chosen conformational state. Optical parametric oscillators (OPO), providing access to frequency-tunable narrowband light, brought this research field to a new level. Pettersson et al., by using the selective OPO excitation of the OH stretching overtone [2n(OH)] of the most stable conformer of formic acid, were able to generate a higher-energy conformer [1]. That reaction involved the internal rotation of the light H atom of the vibrationally excited OH group.

In the last few years there has been growing interest in discovering other patterns of vibrationally induced conformational control. Recently, we have demonstrated that selective vibrational excitation of the 2n(OH), 2n(NH) or 2n(NH_2) modes may lead to conformational isomerization of a remote fragment in a molecule (see Fig. 1) [2-5]. Our particular attention has been focused on the possibility of conformational control involving remote fragments with heavy atoms. To our knowledge, there are only three patterns of such reactivity reported up to the date. They involve remote isomerizations of methoxy (O–CH_3) [2, 3] or hydroxymethyl (CH_2–OH) [4] groups. Most recently, we proved possible to induce the conformational control of the aldehyde (CHO) fragment [5].

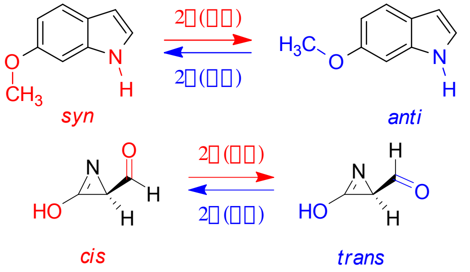

Fig. 1. Examples of conformational control: (left) induced in 6-methoxyindole by selective 2n(NH) exci-tations [2]; (right) induced in 2-formyl-2H-3-hydroxy-azirine by selective 2n(OH) excitations [5].

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Physical and Chemical characterization of anthocyanins from Purple-Fleshed Sweet Potato

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Anthocyanins represent one of the most amazing classes of compounds among polyphenols.

These molecules have unique characteristics such as their structural dependence on pH [1]. The kinetic and equilibrium network of anthocyanins has been widely assessed in order to understand their behavior and stability under different pH conditions.

Among the different types of anthocyanins, Purple-Fleshed Sweet Potato (PFSP) anthocyanins primarily exist as poly-acylated and poly-glycosylated structures derived from Peonidin and Cyanidin [2]. Acylation with various phenolic acids makes PFSP anthocyanins unique and also provides some advantages towards pH and heat resistance, light sensitivity, and overall stability [3], as anthocyanins are known to be reactive compounds that have their stability affected by oxygen, heat, light, pH and enzymes [4]. The study of their equilibrium network is therefore essential. Also, anthocyanins are reported to have poor light-emitting properties, however the scarce information on this matter was performed with monoglucosides and non acylated anthocyanins [5].

Thus, the aim of this study was to characterize the physical and chemical properties of anthocyanins from red wine. For that, a structural characterization of two main Purple-Fleshed Sweet Potato anthocyanins was performed using LC-MS and NMR techniques. The study of the equilibrium network was performed with the use of *pH jump* techniques and the fluorescence properties of the two isolated anthocyanins were also assessed.

The results suggested a higher stability at a broader range of pH values (with lower hydration and higher acidity constants) of the isolated anthocyanins when compared to the already published kinetic and equilibrium parameters of the parent non acylated anthocyanin. Also, unique fluorescence properties were reported for the anthocyanins of PFSP for the first time with an ex/em pair of l_{ex} 610 nm/ l_{em} 640 nm. A biological experiment was performed using gastric and intestinal cell lines, and PFSP anthocyanins intracellular localization with the use of fluorescence microscopy techniques.

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Thermal behavior investigation of hydrogenated waste cooking oil and beeswax for Phase Change Materials

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Energy efficiency is a very important goal in order to minimize the consumption of fossil fuels or the resources used in heating and cooling processes. One way to achieve this second goal is by using materials that absorb energy during a phase change and release it when the reverse transformation occurs. These materials are called Phase Change Materials (PCM) [1].

For a material to be considered a good PCM, a high transition enthalpy in the right temperature range for the application is crucial, as well as a low supercooling degree, high stability and low cost. Fatty acids and their esters are promising compounds for application as PCMs due to their high melting enthalpy and accessibility, but their cost can be a problem [2]. Vegetable oils are natural products made up essentially of triacylglycerides and fatty acids, with the main advantage of being a very economical source for esters of fatty acids, especially if waste cooking vegetable oils are considered.

In this work, fully hydrogenated waste cooking sunflower oil and mixtures with beeswax, also a natural product, were investigated by differential scanning calorimetry (DSC), in order to evaluate their potential for using as a PCM, for instance as latent heat thermal energy storage materials, LHTES, for solar water heating. For this application the desirable temperature range for the phase transition is 40 **ºC** ≤ T ≤ 80 ºC [3].

The fully hydrogenated oil melts between 45 and 75 ºC, onset temperature T_{onset} = 65 ºC, with an interesting enthalpy value, ΔH = 150 J·g^{-1}. Although some supercooling was observed for the solidification process, the temperature range where it takes place and the energy released, are of interest for its use in LHTES, for solar water heating. However, the polymorphic behavior of triacylglycerides [4] is clearly evident in the subsequent heating runs: most of the sample appears to be in two new solid forms, with an inadequate thermal behavior. Mixtures of hydrogenated oil and beeswax were investigated, in order to promote the nucleation of the desired polymorphic form. A 10% beeswax content mixture was found to have a promising thermal behavior: if the heating cycle has a 24 h period, the thermal behavior of the mixture is consistent with the observed in the first heating run, Figure 1.

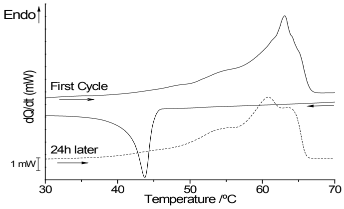

Fig.1. DSC thermogram obtained in the first heating cycle of a (9:1) mixture of hydrogenated oil with beeswax, and second heating run after 24 h; | β | = 10 ºC·min-1.

Acknowledgments
This work is supported by Coimbra Chemistry Center, CQC, through the Fundação para a Ciência e a Tecnologia, FCT, project PEST-OE/UID/00313/2013.

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Thermodynamic modelling of binary mixtures containing naturally occurring phenolic acids

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Phenolic acids are an important class of plant metabolites, widely studied due to their antioxidant, antitumor and antimicrobial activities [1]. A small fraction of these compounds is available in the free acid form whereas the remaining are bonded through ester, ether, or acetal bonds to other plant biomolecules (cellulose, lignin, flavonoids, terpenes, etc.) [2]. In the biorefinery context, the solubility of naturally occurring phenolic acids in different solvents is a key parameter in the design of the separation and reaction processes involving these valuable molecules.

Despite their relevance, solubility data even in common organic solvents and water are scarce. Following previous work, the solubility of three hydroxybenzoic acids in glycerol and a series of diols was measured and critically compared with the few literature data. Regarding the thermodynamic modelling of these mixtures, in general, classical activity coefficient models have been applied, with limited predictive capacity. Therefore, a different approach was followed by applying the nonrandom two-liquid segment activity coefficient (NRTL-SAC) model [3] and the Abraham solvation parameter model [4]. The solubility database used in the modelling task included the solutes represented in Fig. 1 and 13 solvents (water, methanol, ethanol, 1-propanol, 2-propanol, ethyl acetate, 2-butanone, dimethylformamide, acetonitrile, glycerol, 1,2-propanediol, 1,3-propanediol and 1,3-butanediol). Satisfactory results were obtained, allowing to estimate the solubility's order of magnitude. Thus, these thermodynamic tools can be used to support the development of the extraction, separation and purification processes of these complex and oxygenated biomolecules, in preliminary design stages.

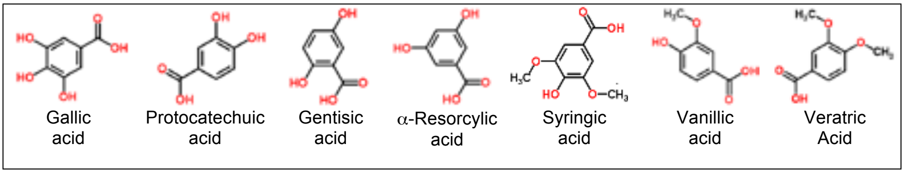

Fig.1. Chemical structure of the hydroxybenzoic acids studied in this work:

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Modelos teóricos para simular el efecto del potencial eléctrico sobre los desplazamientos de las frecuencias vibracionales de piridina adsorbida en un electrodo de plata

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El proceso de adsorción en una superficie produce cambios en la estructura electrónica de adsorbato y adsorbente, siendo de interés para entender fenómenos como la catálisis heterogénea o en dispositivos de electrónica molecular.[1] Una técnica particularmente útil para estudiar la adsorción sobre sustratos metálicos son los registros de los espectros SERS (Surface-Enhanced Raman Scattering) dependientes del potencial. Al modificar el potencial de electrodo, el proceso de adsorción cambia, tal como se observa en las frecuencias de las bandas vibracionales, que varían con el potencial aplicado. En este trabajo se han estudiado los desplazamientos de frecuencias vibracionales ($\boldsymbol{\Delta\bar{\upsilon}}$) de piridina (Py) adsorbida sobre un electrodo de plata. $\boldsymbol{\Delta\bar{\upsilon}}$ se obtiene experimentalmente como la diferencia entre la frecuencia observada para la Py adsorbida a cada potencial (V) menos la frecuencia de la disolución de Py ($\boldsymbol{\Delta\bar{\upsilon}} = \bar{\upsilon}(V)$- $\boldsymbol{\bar{\upsilon}}$(ref)). Para reproducir teóricamente el efecto del potencial, se han utilizado dos aproximaciones distintas. Por un lado, se ha utilizado el modelo de los *clústeres* metálicos cargados $[Ag_nPy]^q$, en los que el potencial de electrodo se simula con la densidad de carga $q_{eff} = q/n$ siendo n el número de átomos ($n = 2, 3, 5, 7$) y q la carga (±1 para n impar y 0 para $n = 2$). Este modelo se ha utilizado previamente proporcionando buenos resultados para diferentes propiedades [2,3]. Por otro lado, se ha utilizado un campo eléctrico externo y variable en la dirección del eje de la molécula adsorbida sobre un *clúster* Ag_2. Los cálculos de la estructura electrónica para ambas aproximaciones se han realizado con métodos basados en la teoría del funcional de la densidad (DFT) utilizando distintas bases y funcionales, mientras que el efecto del disolvente se ha simulado con el modelo implícito PCM (*Polarized Continuum Model*). Los resultados muestran que la variación de los desplazamientos son reproducidos por el modelo de los clústeres cargados al considerar el efecto disolvente, mientras que el modelo del campo eléctrico externo muestra un comportamiento parabólico (Fig. 1).

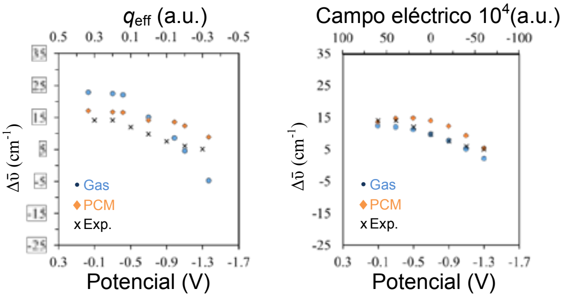

Fig. 1. Variación de $\Delta\bar{\upsilon}$ con V para la vibración 8a utilizando distintos modelos teóricos.

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Thermochemical study of *N*-(2-hydroxyethyl)morpholine

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Several morpholine derivatives have relevant applications in broad areas of the industry, namely as corrosion inhibitors, dye solvents, textile lubricants, ink eradicators and optical brighteners, in the pharmaceutical area as analgesics, local anaesthetic, antidepressants and antibiotic agents, as well as in the agriculture as bactericides, fungicides, herbicides and antioxidants. The morpholine, figure 1 (a), has a hexagonal saturated structure with two heteroatoms (oxygen and nitrogen in positions 1 and 4), which gives it a high flexibility with the consequent formation of several conformers.

Experimental and computational studies of *N*-(2-hydroxyethyl)morpholine were performed to evaluate and understand the energetic effect inherent to the substitution of the hydrogen in the amino group of the morpholine scaffold by hydroxyethyl, as depicted in figure 1 (b). This communication reports the standard energy of combustion and the standard enthalpy of sublimation of the morpholine derivative obtained from combustion calorimetry and Calvet microcalorimetry measurements, respectively. These data were used to derive the standard enthalpies of formation of *N*-(2-hydroxyethyl) morpholine, in the liquid and gaseous phases, at T=298.15 K. Computational calculations were performed using the G3(MP2)//B3LYP composite method.

Structural changes and the inherent energetic effects associated with the substitution of the hydrogen of the amino group by the hydroxyethyl substituent will be analysed in comparison with previous results. [1] It will also be presented a critical overview on the thermochemical studies of other with *N*-substituted morpholine derivatives, namely the *N*-(3-aminopropyl)morpholine [figure 1 (c)] already described in the literature. [2]

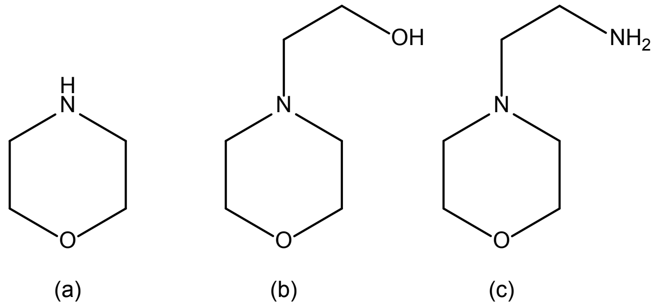

Fig.1. Structural formula of (a) morpholine, (b) N-(2-hydroxyethyl)morpholine and (c) N-(3-aminopropyl)morpholine.

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Vapour pressures and phase transition properties of 2,4,6-tribromo derivatives of anisole and of phenol

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2,4,6-Tribromoanisole (TBA) has been identified as a musty-smelling compound that contributes to off-flavours in wines [1]. TBA can be produced from its direct precursor, 2,4,6-tribromophenol (TBP), via *O*-methylation by bacterial microorganisms, and usually comes from sources related to the winery environment [2]. This brominated phenol is a synthetic intermediate of the most significant brominated flame retardants produced and has been used as a wood preservative [3].
The crystalline, liquid and supercooled liquid vapour pressures of TBA and TBP were measured in the following temperatures ranges: T = (336.5 to 401.7) K and T = (330.7 to 391.7) K, respectively, using a diaphragm manometer static method [4]. Moreover, the sublimation vapour pressures of 2,4,6-tribromophenol were also measured in the temperature interval T = (307.2 to 329.2) K, using a Knudsen mass-loss effusion technique [5]. The standard molar enthalpies, entropies and Gibbs energies of sublimation and of vaporization, at reference temperatures, were derived from the experimental results as well as the (p,T) values of the triple point of each compound. The thermal analysis of the two compounds was also performed using differential scanning calorimetry.

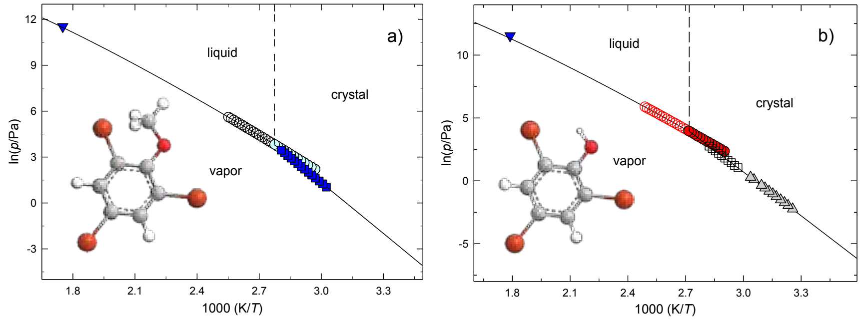

Fig.1. Phase diagrams of a) TBA and b) TBP.
Open circles, vaporization; closed circles, vaporization (supercooled liquid); squares, sublimation (static method); triangles, sublimation (effusion method); inverted triangles, standard ($p = 10^5$ Pa) boiling temperatures.

ACKNOWLEDGEMENTS:This work was developed within the scope of the projects UID/QUI/00081/2013, POCI-01-0145-FEDER-006980, and NORTE-01-0145-FEDER-000028 awarded to CIQUP, that were financed by Fundação para a Ciência e Tecnologia (FCT, Portugal) and co-financed in the framework of Operational Programme for Competitiveness and Internationalisation, COMPETE, with community funds (FEDER, Portugal) and national funds of MEC. ARRPA thanks FCT, European Social Fund (ESF, Portugal), and national funds of MEC for the award of the post-doctoral grant (SFRH/BPD/97046/2013).

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Volatility Study of 1-Alkylpyridinium Bistriflimide Ionic Liquids

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The vapor pressure of the 1-alkylpyridinium bis(trifluoromethylsulfonyl)imide series, $[C_nPy][NTf_2]$ (n=3, 5-9), was measured by a Knudsen effusion method combined with a quartz crystal microbalance. The experimental vapor pressure data were fitted to the integrated form of the Clausius-Clayperon equation and the enthalpies and entropies of vaporization were derived.

The thermodynamic properties of vaporization for the 1-alkylpyridinium bis(trifluoromethylsulfonyl)imide series, $[C_nPy][NTf_2]$ (n=5-9), are analyzed together with the results obtained previously for the shorter alkyl chain length $[C_nPy][NTf_2]$ [1], and the volatility of the imidazolium series $[C_nC_1im][NTf_2]$ [2], in order to evaluate the effect of the alkyl chain size of the cation and additional insights concerning the nanostructuration of ionic liquids.

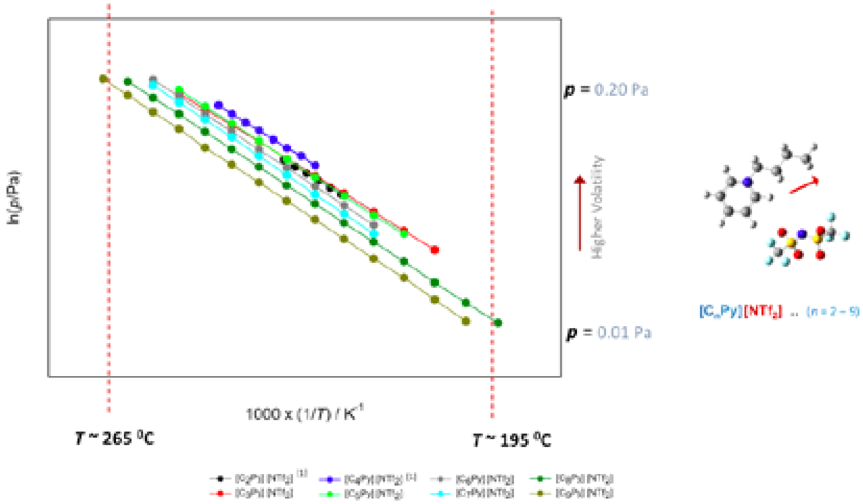

Fig.1. Volatility Study of $[C_nPy][NTf_2]$ (n = 2 – 9)

The $[C_nPy][NTf_2]$ series presents the lower volatility among the homologous series, with a trend shift at the Critical Alkyl Size (CAS n = 6-8), as a consequence of the nanostructuration of the ILs. The lower volatility of the alkylpyridinium derivatives is driven by their higher enthalpy of vaporization.

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A combined experimental and computational approach on the energetic and structural characterization of 2-cyclopentenone

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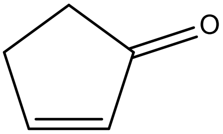
The thermochemical processes of biomass conversion are based on the conception of breaking down the biomass to smaller building block molecules from which new chemicals can be generated [1]. Although the understanding of the overall thermochemistry of those chemical transformations is essential, the thermodynamic characterization of the species involved in them remains a challenge. Thus, accurate knowledge of thermochemical data for those processes is crucial in guiding the experimental investigations to produce useful chemicals from biomass. In this context, our research group is involved in a systematic experimental and theoretical study over key compounds derived from biomass [2,3].

The present work involves an experimental and computational study of thermodynamic properties of 2-cyclopentenone, a compound existing in bio-oils, whose structural formula is presented in Fig. 1. The standard molar enthalpy of formation in the gaseous state, at $T = 298.15$ K, for the compound studied was derived from its standard molar energy of combustion and from its standard molar enthalpy of vaporization, obtained from static-bomb combustion calorimetry and high-temperature Calvet microcalorimetry, respectively. Using high level *ab initio* calculations, the gas-phase standard molar enthalpy of formation of this compound was also obtained. Additionally, a critical overview is provided on the energetics for the conversion of 2-cyclopentenone to longer chain alkane.



2-Cyclopentenone

Fig.1. Structural formula of the studied compound.

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Energetic characterization of the antioxidant activity hydroxycoumarin derivatives

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Coumarin itself and its derivatives have a large number of properties and applications that justify the interest in these compounds. Hydroxide derivatives have, as we may expect, antioxidant properties. We have previously studied the energetics of the 3-, 4- and 7-hydroxycoumarin isomers. [1,2].

The present work reports the experimental value of the standard molar enthalpy of formation of 6-hydroxycoumarin (Figure 1), in gaseous phase, at T = 298.15 K, obtained by combining the value of the standard molar enthalpy of formation, derived from combustion calorimetric experiments, and the value for the standard molar enthalpy of sublimation, obtained by Calvet microcalorimetry.

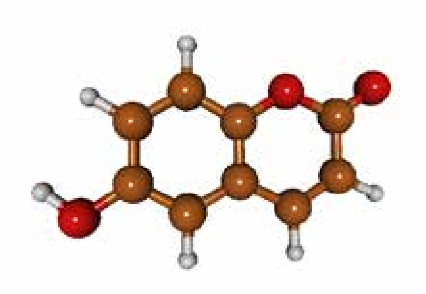

Fig.1: Molecular structure of 6-hydroxycoumarin

Additionally, very accurate quantum chemical *ab initio* calculations using the composite G3 and a domain based local pair natural orbital approach to coupled-cluster singles and doubles with perturbative triples correction, DLPNO-CCSD(T), have been conducted in order to accurately characterize the energetics of all the hydroxycoumarines and their radicalar related species. The results of such calculations allow us to support our experimental measurements as well as to adequately quantify and rationalize the antioxidant activity of these systems due to the -OH group.

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Interaction of antimicrobial peptides with model membranes

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Bacterial resistance against antibiotics has been one of the major concerns in public health in the past decades. One of the most studied alternatives to antibiotics are the antimicrobial peptides (AMPs), as their mechanism of action aims at the bacterial membrane, being thus less prone to induce resistance. It has been widely demonstrated that AMPs (native or constructed) have a large activity against bacteria, fungus and even cancer cells.[1]

This work is part of a larger study of AMPs from the bovine Lactoferrin family, characterizing their interaction with pathogens and model membranes with a composition that mimics bacteria's membranes, aiming at the understanding the mode of action of these AMPs [2-4].

Sometimes we need to include fluorophores in the peptides, *e.g.,* for localization studies by fluorescence microscopy. As such, we need to ascertain the effect of the fluorophore on the interaction. In present study we compared the peptide LFcin 17-30 with its marked forms LFcin 17-30-TAMRA-C, LFcin 17-30-TAMRA-N and D-LFcin 17-30-TAMRA-C. The technique used to assess their interaction with membranes was Differential Scanning Calorimetry (DSC).[5]

The different effect of the various peptides upon the membrane transition – profile and temperature – will be shown and discussed.

AKNOWLEDGEMENTS: Thanks are due to Fundação para a Ciência e Tecnologia (FCT), Portugal, for the financial support to Project UID/QUI/0081/2013.

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Influence of hydroxyl functional group on the structure and stability of xanthone: a computational approach

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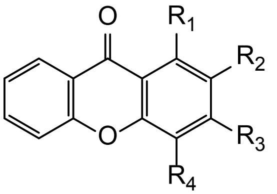
Hydroxyxanthones are abundantly found in many plants and are reported to have a great deal of biological activities including vasorelaxing, antimalarial and antioxidative effects. In particular, mangosteen (Garcinia mangostana), which is a rich source of natural hydroxyxanthones, has long been used to treat diarrheal illness in traditional medicine, and more recently is considered a natural chemopreventive agent.

The xanthone moiety has the potential to bind to a variety of targets, being the hydroxyl functional group [1] a very interesting one. Therefore, the knowledge of the influence of this substituent in the xanthone structure and stability is important to understand better the behaviour of this group of molecules – hydroxyxanthones – and to use such information to support the drug design of new derivatives.

In the present work, a computational study of the structural and thermochemical properties of four monohydroxyxanthones (1-hydroxyxanthone, 1OHXT, 2-hydroxyxanthone, 2OHXT, 3-hydroxyxanthone, 3OHXT, and 4-hydroxyxanthone, 4OHXT), whose general molecular formula is in Figure 1, through the use of the G3(MP2)//B3LYP composite method. The development of the experimental work for these compounds was not performed due to the scarce availability of samples in enough amount and purity.

The computational work is focused on conformational and tautomeric equilibrium analysis of the optimized molecular structures of the monohydroxyxanthone isomers and on the estimation of their standard ($p° = 0.1$ MPa) molar enthalpies, entropies and Gibbs energies of formation. The frontier molecular orbitals and the electrostatic potential energy surfaces are also addressed, together with the intramolecular hydrogen bonding energetics present in the 1-hydroxyxanthone isomer.



R_1 = OH, $R^2 = R^3 = R^4$ = H, **1-hydroxyxanthone**
R_2 = OH, $R^1 = R^3 = R^4$ = H, **2-hydroxyxanthone**
R_3 = OH, $R^1 = R^2 = R^4$ = H, **3-hydroxyxanthone**
R_4 = OH, $R_1 = R_2 = R_3$ = H, **4-hydroxyxanthone**

Fig.1. General molecular formula of the monohydroxyxanthones studied in this work.

ACKNOWLEDGEMENTS:
This research was developed within the scope of the projects UID/QUI/00081/2013, POCI-01-0145-FEDER-006980, and NORTE-01-0145-FEDER-000028 (Sustained Advanced Materials, SAM), awarded to CIQUP, financed by Fundação para a Ciência e Tecnologia (FCT), Lisbon, Portugal, and co-financed in the framework of Operational Programme for Competitiveness and Internationalisation, COMPETE, with community funds (FEDER) and national funds of MEC. VLSF thanks FCT, European Social Fund (ESF), and national funds of MEC for the award of the post-doctoral grant SFRH/BPD/78552/2011, and also to SAM project for the present post-doctoral grant

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2,4-Diaminopyrimidine as a model for trimethoprim co-crystallization?

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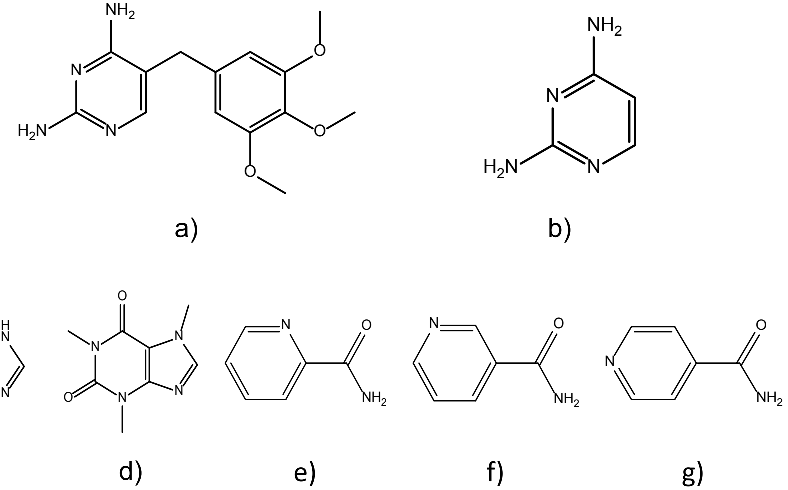
Co-crystals have emerged in recent years as attractive, alternative solid forms of active pharmaceutical ingredients (APIs) aiming at the optimization of their physicochemical properties and/or biopharmaceutical performance [1]. They are made up of the API and of one or more co-formers, all solid when pure at ambient conditions, joined together in a stoichiometric ratio in a new crystalline structure [1, 2]. The co-crystal components are associated in supramolecular synthons, most commonly linked by hydrogen bond interactions [1, 2].

Dihydrofolate reductase (DHFR) inhibitors, such as trimethoprim, Figure 1.a, iclaprim, pyrimethamine, metoprine, share a common 2,4-diaminopyrimide (24DAPM) core structure, Figure 1.b, [3]. In a co-crystallization experiment, although the same type of supramolecular synthons are expected for DHFR inhibitors and 24DAMP, the molecular complexity of the former may also play a role in the co-crystallization trial outcome.

In order to get insight on these effects, in this work results are presented and discussed for the ongoing investigation of co-crystallization of trimethoprim and of the core fragment 24DAPM with two types of co-formers, capable of giving rise to different supramolecular heterosynthons with the target molecules: the two xanthines, theophylline and caffeine, and the three isomeric pyridinecarboxamides, picolinamide, nicotinamide and isonicotinamide, Figure 1.



a) b)

c) d) e) f) g)

Fig.1. Molecular structure of a) trimethoprim, b) 2,4-diaminopyrimidine, c) theophylline, d) caffeine, e) picolinamide, f) nicotinamide, g) isonicotinamide.

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Thermal, optical and morphological properties for thin films of spiro-based materials

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Spiro compounds have been widely used as an important thin film layer in optoelectronic devices such as organic-light-emitting diodes (OLEDs) and organic photovoltaic cells (OPVs). The remarkable hole transporting properties of spiro-based thin films is due to their high hole mobility and low ionization potentials. In addition, these compounds exhibit an excellent thermal stability in the amorphous form [1,2].

This work focuses on two particular spiro compounds, namely Spiro-TAD and Spiro-MeOTAD (Fig. 1A). Comparatively to Spiro-TAD, the existence of functional groups methoxy in Spiro-MeOTAD is analyzed and discussed regarding its impact on the thermal, optical and morphological properties of bulk materials and thin films.

Homogenous and compact thin films of both materials were produced by a physical vapor deposition (PVD) procedure (Fig. 1B) [3]. Scanning electron microscopy (SEM) was used to explore the thin film topography (Fig. 1C). Differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) proved the high thermal stability in the amorphous state of both compounds. In addition, the optical properties, including optical band gaps, were obtained from UV-Vis spectroscopy, highlighting the semiconductor behavior of the aforementioned compounds.

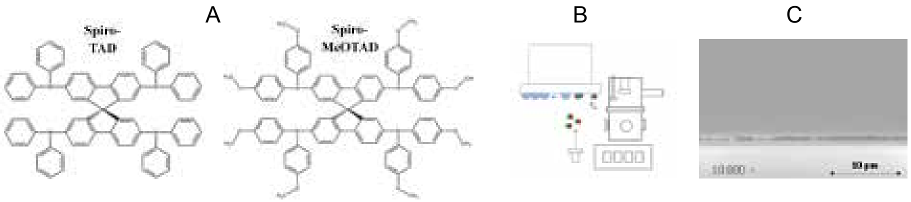

Fig.1. A – Molecular structure of Spiro-TAD and Spiro-MeOTAD; B – scheme of a physical vapor deposition apparatus; C – Micrograph of a vapor-deposited amorphous thin film.

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The authors thank Fundacão para a Ciência e Tecnologia (FCT), and FEDER (COMPETE 2020) for financial support to CIQUP, Faculty of Science, University of Porto (Projects UID/QUI/00081/2013 and NORTE-01-0145-FEDER-000028, Sustainable Advanced Materials, SAM).

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Sinergia/ competição entre os flavan-3-ois e derivados da lenhina para a estabilização da cor vermelha das antocianinas

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O objetivo deste trabalho foi estudar o efeito sinérgico ou de competição entre a (+)-catequina e um derivado da lenhina para a estabilização da cor vermelha das antocianinas. Os resultados obtidos a pH 1 e 3.5 usando técnicas de espectroscopia do UV-Visível mostram que a presença de (+)-catequina reduz significativamente a interação entre a malvidina-3-glucósido e a lenhina.
Por outro lado, utilizando a metodologia de fluorescência foi possível verificar que a interação da lenhina com a malvidina-3-glu**cósido** (K=1.6x10^4) **é muito maior do que a observada entre a lenhina e a** (+)-catequina (K=1.6x10^2).

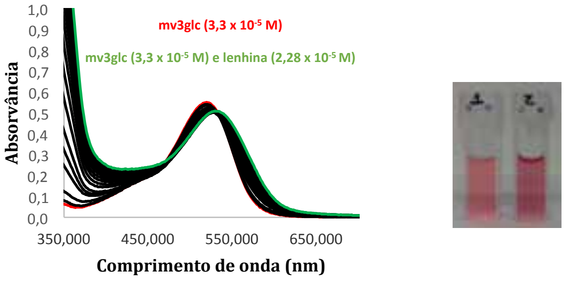

Fig.1. Espectro de absorção da mv3glc com diferentes concentrações de lenhina a pH 1. Cuvetes (1) mv3glc 3,3x10-5 M; (2) mv3glc (3,3x10-5 M) e lenhina (5,80x10-5 M).

Tabela 1. Efeito da concentração da (+)-catequina na constantes de associação entre a malvidina-3-glucósido e a lenhina a pH 1,0.

Concentração (+)-catequina (M)	*n*K
0	9,4x10^4
1	7,8x10^4
50	4,7x10^4
100	3,4x10^4
150	1,9x10^4

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Interaction of Self-Assembling Cyclic Peptide Nanotubes with model membranes as followed by DSC, ATR-FTIR and MD

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The use of intelligent materials that form active species when in contact with bacterial membranes has been studied in recent years, with various applications. Cyclic Peptides (CP) of planar conformation are one promising application of these smart materials. The orientation of their amide group perpendicular to the ring plane facilitates the formation of Self-assembling Cyclic Peptide Nanotubes (SCPNs) when in contact with membranes. With appropriate amino acid composition, they are currently seen as very promising antimicrobial candidates, due to their robust secondary structure and proven activity [1], combined with a high resistance to protease degradation.

We are using different biophysical experimental techniques (DSC, SAX, DLS, ATR-FTIR) together with an in-silico approach to study the interaction of some antimicrobial SCPNs with model membranes, aiming at characterizing their membrane interactions, to unveil their mechanism of action.

Preliminary Molecular Dynamics (MD) studies with coarse-grained resolution for different model membranes will be shown and compared with results from DSC experiments. The results from ATR-FTIR provide information on the structural features of these systems.

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Photochemistry of matrix isolated benzimidazole

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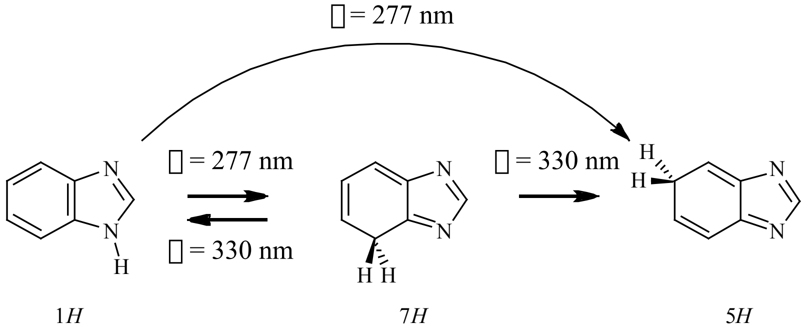
There is a considerable interest in the tautomerism, structure, and photochemical properties of benzimidazole and related compounds, which can be attributed to their wide application as drugs, herbicides, and dyes [1]. The tautomerism [2], photophysical properties [3], and photochemistry of benzimidazole in solution media have been discussed elsewhere [4]. To the best of our knowledge, the unimolecular photochemistry of benzimidazole as isolated species has not yet been reported, and it is the focus of the present investigation.

It has been theoretically predicted that excited state hydrogen atom detachment in heteroaromatic compounds similar to benzimidazole (such as pyrrole and indole) [5], might lead to radical formation, and should play an important role in their photochemical behavior. The matrix isolation method provides experimental conditions where instable species, such as radicals or high-energy tautomers, can be generated photochemically, *in situ*, stabilized, and then characterized spectroscopically, making this technique ideal to the proposed study.

In this work, we present the photochemistry of monomeric 1*H*-benzimidazole trapped in a cryogenic argon matrix. We provide identification of two new prototropic tautomers (7*H* and 5*H*, see Scheme 1), and discuss the mechanism of their formation, which strongly suggests intermediacy of the benzimidazolyl radical. Quantum chemistry calculations give theoretical support for interpretation of the experimental data.



Scheme 1. Experimental observations on the UV - induced photochemistry of monomeric 1H-benzimidazole isolated in an argon matrix

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Empleo de clústeres lineales de plata para el estudio de procesos de transferencia en el SERS de 2-2'-Bipiridina

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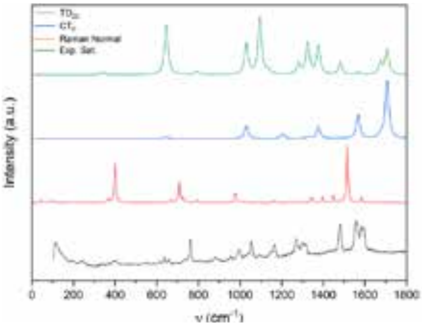
Gracias a la espectroscopía SERS (Surface-Enhanced Raman Scattering) se puede detectar la presencia de procesos de transferencia de carga fotoinducidos entre metales y moléculas adsorbidas.[1,2] En este trabajo se ha aplicado la metodología ya utilizada en el caso de piridina, pirazina[3] o metilpiridinas,[4] para el estudio de un sistema molecular más complejo como es la 2,2'-bipiridina (BPy). A causa de la tensión entre los dos anillos aromáticos flexibles, la BPy puede adoptar varias conformaciones.[5] Aunque su forma trans es la más estable en disolución, se ha seleccionado la forma cis-BPy debido a las capacidades electrodonadoras de la Bpy al unirse al metal a través de los dos nitrógenos.

Experimentalmente se han registrado los espectros SERS sobre un electrodo de plata a tres longitudes de onda (473, 532 y 785 nm). Las intensidades relativas indican la presencia de procesos de transferencia de carga metal-molécula (Fig. 1). La modelización teórica se ha llevado a cabo mediante cálculos el DFT simulando el efecto de potencial mediante clústeres lineales de átomos de plata con diferentes longitudes y cargas unido a la Bpy por ambos nitrógenos (Ag_nBPy^q, con q = 0 para n = 2 y q = ±1 para n = 3, 5, 7). Se observa la intensificación selectiva de la banda de 1550 cm^{-1} en el rango de potenciales -0.6 y -1.2V que está relacionada con la transferencia fotoinducida de un electrón desde el HOMO del metal a orbitales vacantes (CT0 o CT1) de la molécula de BPy (Fig. 2).



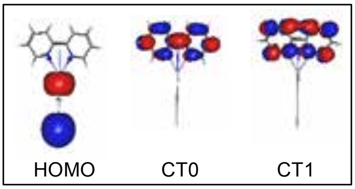


Fig.1. Espectros (Ag3Bpy)- M06HF/LanL2DZ calculados y SERS experimental.
Fig.2. Orbitales del complejo Ag3Bpy- : HOMO, CT0 y CT1.

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Study of the Viscosity of mixtures *n*-Nonane + 1-Alcohol

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There are currently numerous articles on the viscosity of binary mixtures of *n*-alkanes + 1-alcohols [1-7]. In this work the behavior of the viscosity of binary mixtures n-nonane + 1-alcohol at temperatures of 288.15K, 298.15K and 308.15K and at atmospheric pressure is analyzed.
To measure the viscosity, an Anton Paar AMV 200 viscometer [8] was used, which is kept at a constant temperature by means of a Poly-Science thermostatic bath.
The dynamic viscosity increases as the number of atoms in the alcohol chain increases and decreases with increasing temperature.
In the work the behavior of the viscosity is analyzed with the prediction equations: Grunberg-Nissan [9], McAllister [10], Auslander [11], Teja-Rice [12].

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Sublimation vapour pressures of three di-chlorobenzoic acids

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Due to their extensive application, pesticides became an environmentally concern issue. Being produced and applied to protect plants and humans from diseases, their biological effects constitute an environment ecotoxicological interest. Many of them include in their composition di-halogenated benzoic acids, such the 2,4-dichlorobenzoic acid (2,4-DBA), 2,5-dichlorobenzoic acid (2,5-DBA) and 2,6-dichlorobenzoic acid (2,6-DBA), which present a slow degradation rate in both anaerobic and aerobic conditions [1]. The sublimation vapour pressures of the three dichlorobenzoic acids were measured at different temperatures using the Knudsen mass-loss effusion technique [2]: 2,4-dichlorobenzoic acid between (335.2 and 357.2) K, 2,5-dichlorobenzoic acid between (332.1 and 354.3) K, and 2,6-dichlorobenzoic acid between (321.1 and 343.3) K. From the experimental results, the standard (p^o = 10^5 Pa) molar enthalpies and Gibbs energies of sublimation, at chosen reference temperatures, were derived. The onset temperature and the molar enthalpy of fusion of the three compounds studied were determined by differential scanning calorimetry. The contributions of carboxylic and chlorine substituents to the sublimation properties of the acids studied as well as the eventual interactions between these groups in *ortho*, *meta* and *para* positions are discussed.

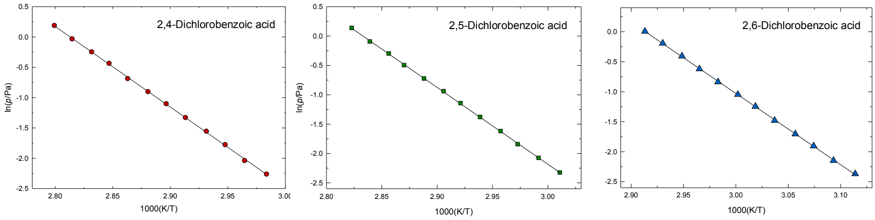

Fig.1. Plots of the vapour pressures against reciprocal temperature for the three di-chlorobenzoic acids studied.

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Entalpías de cambio de fase de hidrocarburos aromáticos policíclicos (PAH´S) determinadas por D.S.C. y termogravimetría

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Los hidrocarburos aromáticos policíclicos (PAH's) se forman en los procesos de combustión incompletos de gasolinas, aceites, gas, madera, carbón y petróleo crudo; así como en procesos de pirolisis de material orgánico. Los PAH's generalmente se encuentran en mezclas, esto provoca que algunas de estas mezclas se potencialicen entre ellas causando un mayor daño a la salud [1]. Las exposiciones a mezclas de compuestos aromáticos policíclicos como lo es el humo del cigarro, las emisiones de coque, los vapores de alquitrán y los gases de la combustión de derivados del petróleo, se asocian con efectos nocivos en la salud humana ya que tienen efectos cancerígenos, mutágenos y teratógenos [2]. Debido a que los PAH's se generan en un sinfín de procesos realizados por las actividades humanas y al efecto negativo que tienen estos compuestos en la salud, resulta necesario e interesante conocer algunas de sus propiedades fisicoquímicas y termoquímicas. En este trabajo se estudiaron cinco hidrocarburos aromáticos policíclicos a saber, dibenzo[a,c]antraceno, dibenzo[a,h]antraceno, perileno, fluoranteno y benzo[b]fluoranteno, los cuales se muestran en la figura 1. Se utilizó calorimetría diferencial de barrido para determinar la pureza, la entalpía y la temperatura de fusión. También se aplicó termogravimetría para determinar la dependencia de la presión de vapor con la temperatura y las entalpías de vaporización y sublimación de cada hidrocarburo policíclico. Los resultados de dicho estudio se discutirán en la presentación.

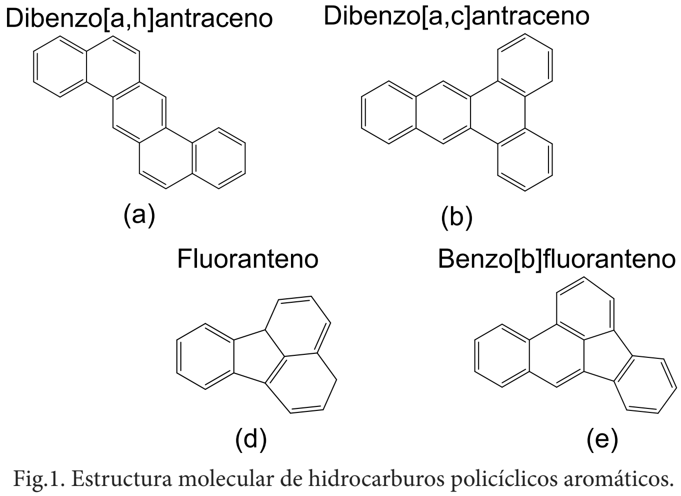

Fig.1. Estructura molecular de hidrocarburos policíclicos aromáticos. (a) Dibenzo[a,h]antraceno, (b) Dibenzo[a,c]antraceno, (c) Perileno, (d) Fluoranteno, (e) Benzo[b]fluoranteno.

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Vapour pressures and thermodynamic properties of phase transitions of the phenyl derivatives of maleic anhydride

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Maleic anhydride is a highly reactive intermediate commonly used in industrial settings. It is an important building block for key copolymers, such as styrene and ethylene copolymers [1,2], and also grafted into nonreactive polymers for added reactivity [2]. Additionally, some maleic anhydride derivatives are fluorescent and used as fluorescent labels.

In the present work, we explored the relative volatilities and thermodynamic properties of phase transition of the phenyl derivatives of maleic anhydride: 2-phenyl and 2,3-diphenylmaleic anhydride. The sublimation vapour pressures of these compounds were measured experimentally by means of a Knudsen effusion apparatus [3], and the respective thermodynamic properties (standard molar enthalpy, entropy and Gibbs energy) of sublimation were determined from the vapour pressure dependence with the temperature. The enthalpies and temperatures of fusion were determined using differential scanning calorimetry.

These results were then rationalized in terms of enthalpic increments resulting from the addition of the phenyl rings in adjacent positions of maleic anhydride and of the *ortho* interaction between them (fig. 1).

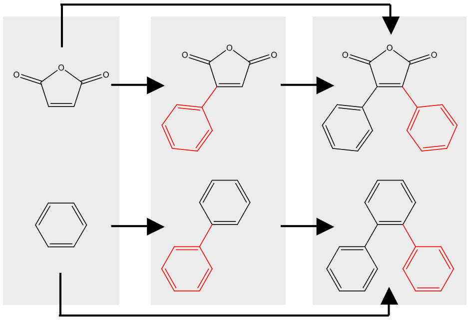

Fig.1. Schematic representation of the enthalpic increments associated to the insertion of the phenyl groups to maleic anhydride and benzene molecules.

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Phase behavior of binary mixtures of fames and alkanes

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Biodiesel blends with mineral diesel, although improving many characteristics of the fuel and lowering its environmental impact, is detrimental to the low temperature behavior of the diesel. The understanding of the phase behavior of binary mixtures of the main FAMEs present in biodiesel with alkanes in mineral diesel is for great importance to understand, and eventually improve these properties in commercial diesel. This work studied the phase behavior of 6 binary mixtures of a saturated methyl ester with alkanes.

These systems show a very complex behavior, with the formation of co-crystals, peritectic reactions, metatectic transitions and the formation of solid solutions. The results here reported show for the first time that in mixtures with equal alkyl chain a co-crystal is formed and the mixtures with an alkane alkyl size two carbon bigger than the FAME lead to the formation of a solid solution increasing the cloud and pour point of the mixture.

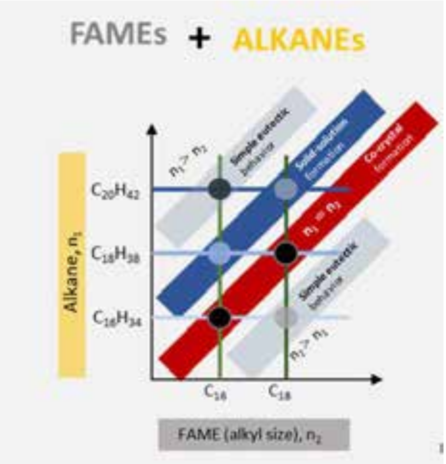

Fig.1. Resume of work plan and results.

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High pH Reversed-Phase Preparative Chromatographic Separation of Nadolol Racemates using C18 Adsorbents

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In recent years, the continuous improvement of preparative liquid chromatographic techniques, make easier the resolution of complex multicomponent chiral drugs, into single pure stereoisomers, by means of combining different strategies and using chiral and achiral adsorbents. Nadolol is one representative beta-blocker pharmaceutical drug prescribed worldwide for relieve of several diseases related with the cardiovascular system. This pharmaceutical chiral drug represents a very interesting case-study since it is composed by four stereoisomers, being a mixture of two racemates, i.e., a mixture of two pairs of enantiomers. The complete separation of all the four nadolol stereoisomers can be achieved using alternative strategies, different types of separation sequences and techniques, such as, the use of different adsorbents (chiral and achiral stationary phases), and the correspondent mobile phase optimization at both normal and reversed-phase modes [1-3].

In this work, a large set of experimental results will be presented for the separation of the two nadolol racemates using a commercial Azura preparative HPLC system, equipped with two 250 mL/min pump heads. The fixed-bed separation was carried out through a sequence of multiple injections, optimized by taking into account the retention time of both racemates using an XBridge Prep OBD C18 column with preparative dimensions (250mm ID x 30mm L) and with a particle size diameter of 10 mm [4]. Experimental results will show the optimization of the mobile phase composition and injection time. The experimental results presented in this work stresses out the advantage of using a first achiral reversed-phase chromatographic separation step to perform the separation of the two nadolol racemates.

ACKNOWLEDGEMENTS: This work is a result of project "AIProcMat@N2020 - Advanced Industrial Processes and Materials for a Sustainable Northern Region of Portugal 2020", with the reference NORTE-01-0145-FEDER-000006, supported by Norte Portugal Regional Operational Programme (NORTE 2020), under the Portugal 2020 Partnership Agreement, through the European Regional Development Fund (ERDF), and of project POCI-01-0145-FEDER-006984 – Associate Laboratory LSRE-LCM funded by ERDF through COMPETE2020 - Programa Operacional Competitividade e Internacionalização (POCI) – and by national funds through FCT - Fundação para a Ciência e Tecnologia.

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Innovative photonic crystals and phosphors based coatings for wood

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Wood is a natural resource and sustainable building material that is the basis of one of the most traditional Portuguese industrial sectors with a strong economic impact [1]. In order to open new markets, the natural properties of wood and wood-basis materials should be broadened while maintaining their intrinsic and unique properties.

Ferreira Martins & Filhos S.A., in collaboration with CIQ(UP), is developing new coatings to provide the wood unique aesthetic characteristics. These new wood coatings will allow the development of products that do not paint the wood, maintaining its natural characteristics and, also, providing two different attributes: a butterfly effect and phosphorescent properties based on photonic crystals and phosphorescent pigments.

Photonic crystals (PC) [2] are responsible for iridescent characteristics of butterflies' wings, being iridescence classified as the process in which the color of a surface varies depending on the angle and observation and source of illumination. Thus, the use of PC in wood will provide an iridescent effect to this natural material.

On the other hand, coatings that provide emission of light without any electric source have had a growing demand. A wood oil with phosphorescent pigments was also developed [3]. This new product will give phosphorescent properties to wood emitting light at night without electricity source.

This communication will show the latest results about new wood coatings based on PC and phosphors.

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Surface Tension for the ternary system dimethyl carbonate + *p*-xileno+ n-decane in function of the temperature (288.15 K – 308.15 K)

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Presents work study of experimental surface tension for the ternary system dimethyl carbonate + *p*-xylene +*n*-decane binary system[1-2], in the temperature range from 288.15 K to 308.15 K and at atmospheric pressure. The surface tension values were fitted by a third degree polynomial[1-3].

Diethyl carbonates are useful in organic solvents due to the fact that the chemical used as solvent extraction processes, as well as battery technology[4-5]. In some occassions molecules carbonate containing an aromatic and aliphatic portions are interested in several uses as gasoline additives and as lubricants in the replacement of chlorofluorocarbons with new refrigerants hydrofluorocarbons[6-9].These industrial uses are the most important reason to considerate an increase in theoretical and experimental investigations of dialkyl carbonates and mixtures there of with other compounds[9-11], so our research group has also focused on the study, such as measurements and models of mixtures containing carbonate molecules.

The interest in the study of this mixture lies in the fact that dimethyl carbonate[3,12]. has been considered as a replacement of traditional oxygenated gasoline additive, because it is a non-toxic and environmentally friendly product capable of reducing pollutant emissions as carbon monoxide.

The experimental surface tension in this system for both temperatures shows similar behavior. Highest temperature the surface tension is fewer than a low temperature.

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Alginate fraction from *sargassum muticum* obtain by ultrasound assisted extraction techonology

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The invasive brown seaweed *Sargassum muticum* was proposed to extract biopolymeric compounds of interest. A negative impact on ecology, fishing and recreate activities was associated to this invasive alga. For this reason, searching a revalorization for this raw material is necessary. Alginate (composed for mannuronic and guluronic acids), laminaran and fucoidan are the main compounds of brown seaweeds. These compounds can present gelling or bioactive properties such as antioxidant, antiviral, antitumoral, anticoagulant or anti-inflammatory [1]. The gelling and biological features can be dependent on several factors: algal species, harvesting, life cycle, extraction and purification conditions [2]. In this context, this work was aimed to the characterization of the alginate fractions after different times of sonication.

S. muticum was collected manually in Praia A Mourisca (Pontevedra, Spain) in July 2014. At laboratory, *S. muticum* was washed with tap water and stored at -18°C until use. The raw material was exposed to ultrasounds assisted-extraction with distilled water with a liquid:solid ratio of 20:1 (w/w, d.b.) at room temperature at sonication times below 30 minutes [3]. The suspension was separated by centrifugation and different fractions were obtained: liquid [3], alginate and a residual solid. The impact of sonication time on the physicochemical, mechanical and biological features of the extracted alginate were studied.

Results indicated that ultrasound assisted-extraction could be a suitable technology to extract fucoidans and alginates from *S. muticum* with acceptable extraction yields. The lowest molecular weights (< 80 kDa) of the alginates were dropped with sonication time. The used sonication conditions (< 30 min) led to the formulation of alginate gels with intermediate strength (US5 > US10 > US15) and soft (US20 > US25 > US30) mechanical properties. The sonication time had a positive impact on the tumoral cell growth inhibition. This research provided a pallet of alginates with suite gelling behaviour, resulting from seaweed treated under different sonication times.

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Subcritical water extraction as a green technology to recover high valuable compounds from *mastocarpus stellatus* red seaweed

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Mastocarpus stellatus is a carrageenophyte red seaweed (Rhodophyta) present in the Northwest coast of Spain. Hybrid carrageenans extracted from this model seaweed are highly demanded as a gelling, thickener, suspending, stabilising or texturing agents for a broad range of industrial applications [1]. A particular type of hybrid carrageenans isolated here are kappa/iota hybrids with improved mechanical properties [2]. Bioactive and biological activities have been also reported for this kind of biopolymers [3]. The objective of this study was to evaluate the possibility of using a green technology as subcritical water extraction to recover high valuable compounds from *M. stellatus*.

The raw material was kindly provided by Portomuiños (A Coruña, Spain) and it was stored at -18°C until further use. A subcritical water extraction technology was used to obtain biopolymeric fractions from this red seaweed. Liquid:solid ratio 30:1, and the temperature from 70 to 190 °C in a pressurised stainless steel reactor were the experimental conditions carried out. After the hydrothermal processing, the solid and liquid phases were separated by filtration, and the liquid phase was preliminarily studied. Yields, molecular weight distributions and bioactive properties were determined following the procedures previously reported [4].

The results obtained presented promising yields extractions, molecular weight distributions with high molecular profiles and high values of sulfate content and intermediate magnitudes of phoroglucinol content and antiradicalar properties, when compared with other similar seaweeds. The environmentally friendly technology used could be an attractive alternative to conventional alkali extraction methods, allowing the extraction without a previous drying stage and also could be suitable to be applied to other red seaweeds.

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Preparação de filmes de PVC e PVA contendo partículas de compostos de carbono

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Para o trabalho desenvolvido no âmbito do projeto FAMEST é importante a obtenção de dados relativo à resistência térmica e elétrica de polímeros e dos seus compósitos para a sua posterior utilização em impressoras 3D.

Com esse objetivo começou-se por preparar filmes de PVC [1] com diferentes quantidades de diferentes compostos de carbonos, como grafite, grafeno e óxido de grafite. Para comparação com os filmes previamente mencionados preparou-se também filmes de PVA e seus compósitos.

Com os filmes já preparados realizaram-se os ensaios para a medição da resistência da corrente utilizando o *TREK Model 152 Resistance Meter* e para os ensaios de medição da resistência térmica utilizou-se o equipamento descrito na norma EN 13521:2001 - Footwear – Test methods for uppers, lining and in socks – Therma linsulation.

Com o estudo feito até agora concluiu-se que a espessura dos filmes não foi a mais indicada para os ensaios para a medição da resistência térmica, sendo necessário fazer novos ensaios para a preparação de filmes mais espessos.

Nos ensaios para a medição da resistência térmica não foi possível determinar a influência da concentraç**ão** de partículas dispersas, pelo que também **é** necessário estudar uma outra alternativa para melhor homogeneizar os compósitos.

AGRADECIMENTOS: Ao projeto FAMEST - Footwear, Advanced Materials, Equipment's and Software Technologies, financiado por Programa COMPETE 2020 e que é composto por um consórcio de 23 empresas e 9 entidades de I&I.

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On the kinetics of methanol dehydration over ZrO2 supportedcarbon-derived catalysts

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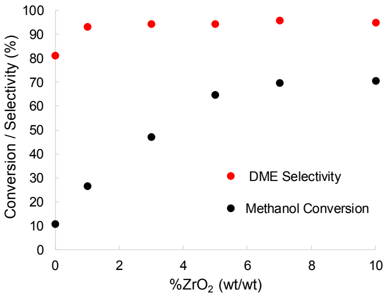
Dimethyl ether (DME) is being deeply studied as a potential renewable substitute for petroleum derivative. The preparation of biomass-derived carbon-based catalysts via chemical activation of olive stone with phosphoric acid, their modification with different ZrO2 loads and their application as methanol dehydration catalysts have been studied. The catalytic results showed that the best methanol conversion and selectivity towards DME were achieved with the carbon catalyst prepared with an impregnation mass ratio value (H3PO4/carbon precursor) of 2 and an activation temperature of 800 ºC, loaded with a 7 % (wt) (Fig.1). This catalyst exhibits high steady state methanol conversion values, keeping a selectivity to DME higher than 96%, even at temperatures as high as 400 ºC (XCH3OH= 80%, 0.1 g·s/μmol, PCH3OH= 0.08 atm in helium). The effect of oxygen in the reaction atmosphere was also analyzed. In this sense, an increase of 15 % in the DME yield was obtained when using air instead of helium as reaction atmosphere (350 ºC, 0.1 g·s/μmol, PCH3OH= 0.04).

A kinetic study has been carried out on this catalyst in which two mechanisms Eley Rideal and Langmuir Hinshelwood for methanol dehydration have been analysed (Fig. 2). The models proposed also consider the presence of oxygen in the reaction media. The active centers of the catalyst seem to be C-P-O-Zr-C groups, present on the surface of the carbon-derived catalyst.



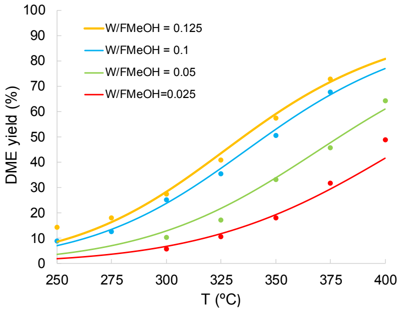


Fig 1. Methanol conversion and DME selectivity as a function of the ZrO2 loading (W/FMeOH =0.1 g·s/μmol, T = 400 ºC, PCH3OH= 0.02 atm)

Fig 2. Experimental and simulated DME yield as a function of reaction temperature at different spaces times (W/FMeOH). PCH3OH= 0.04 atm

ACKNOWLEDGMENTS: We gratefully thank MINECO (Project CTQ2015-68654-R) for financial support. J.P.J. thanks MECD for a FPU fellowship (FPU13/02413).

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On the deactivation of ZrO2 supported-carbon-derived catalysts during methanol dehydration

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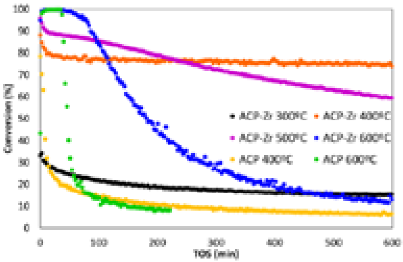
Dimethyl ether (DME) is being deeply studied as a potential renewable substitute for petroleum derivative. Lots of papers search for the best operating conditions of many catalysts to DME production. However, addressing how the catalyst deactivates, mainly by coke deposition, is also an issue of great interest in order to allow optimizing the catalyst synthesis for the best DME production process conditions.

Physical (CO_2; AC) and chemical carbon-based materials (H_3PO_4; ACP) were prepared from olive stone and studied as catalysts and catalyst supports for methanol to DME reaction. AC and ACP were loaded with $ZrO(NO_3)_2$ to get a 7% of ZrO_2 (wt/wt) (AC-Zr and ACP-Zr). The methanol to DME reaction experiments were carried out in a laboratory fixed bed reactor at a partial pressure of 0.04 atm and at several space times (from 0.05 to 0.1 g·s/µm) and temperatures (from 300 to 600°C).

At low temperatures, ACP shows an almost total conversion of methanol to DME1, but as temperature grows up, methane conversion rises (Fig. 1). ACP-Zr has shown to be a highly active and selective (Fig. 2) catalyst for methanol dehydration to DME, but it deactivates relatively fast at temperatures higher than 500 °C. The catalyst seems to present two kinds of active sites, which are deactivated at different rates. One of them loses their activity fast (even at the lowest temperature studied) and is related to phosphorus-carbon surface groups, while the other one does not lose activity at the studied temperatures, starting to deactivate only at temperatures above 400°C, and it can be associated to zirconium phosphate species.



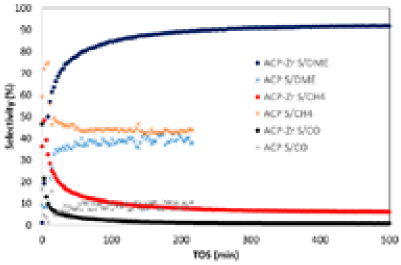


Fig 1. ACP and ACP-Zr conversion profiles with reaction time at 500 °C for methanol dehydration.
Fig 2. ACP and ACP-Zr selectivity profiles with reaction time at 500 °C for methanol dehydration.

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Valorisation of de-starched pulp from regional wastes as a feedstock for potato flakes production

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The Galician province of Ourense is known for its potato production, being the second largest producer in Spain and representing 2% of the European production. Potato harvest has a high degree of discarding (up to 30%), which currently has a low added value being used primarily for animal feed. The losses produced by the peeling of the potatoes may vary between 15 and 40%, depending on the procedure used [1]. Another massive waste from the potato industry is the pulp remaining from the starch extraction. In this context, this work is part of a research which aims at the valorisation of this regional product using sustainable approaches.

Three potato varieties (Kennebec, Neiker and Agria) were supplied by INORDE (Instituto Ourensán de Desenvolvemento Agroindustrial), selected based on its potential starch and bioactive content. After starch extraction [2], the remaining pulp was subjected to a controlled drying process at 100 °C or 130 °C in order to extend its shelf life, and as a consequence, to obtain crunchy potato products with different potential applications. Drying kinetics were controlled and modelled.

Results indicated that de-starched pulp needed drying times lower than 140 min to achieve final moisture content comparable to those of commercial snacks. All drying kinetics were nicely fitted (R2 > 0.98) by Page model. The preliminary obtained outcomes showed that potato flakes with promising colour and sensorial features could be obtained with de-starched pulp from the three tested potato varieties dried at 130 °C. Snacks industry could be an attractive alternative to these residual wastes.

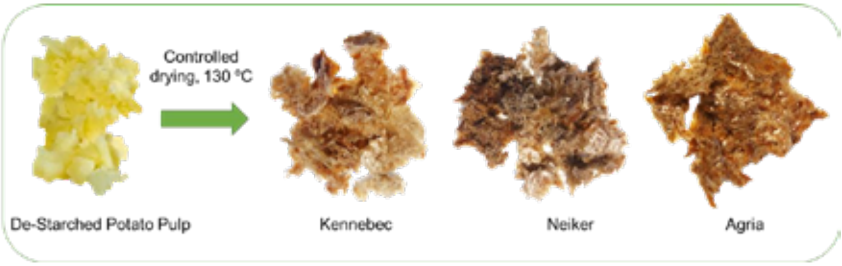

Figure 1: Potato flakes from de-starched pulp recovered from tested potato varieties.

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Potato starch-based formulations for bioactive biofilm preparation using local disposal resources

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An intense search for new renewable sources to produce natural biopolymers for edible coatings or biodegradable films is observed as they offer lower environmental costs [1]. The objective of this work was to investigate the use of potato starch extracted from local disposal resources, as an alternative to commercial ones, in new biofilm formulations enriched with bioactive compounds recovery from potato peels.

Two potato varieties harvested in Galicia (Agria and Neiker), kindly supplied by the Instituto Ourensán de Desenvolvemento Agroindustrial, were picked based on its starch and bioactive features, respectively. Potato starch was extracted from Agria potato variety and used for gel making at 70°C (previously optimized, [2]). Potato peel from Neiker variety was subjected to subcritical water extraction (autohydrolysis) in order to obtain a liquid extract (liquor) with bioactive properties. Using both the liquor and the starch extracted (10%, w/w), biofilms were developed by casting method [1], using glycerol as plasticizer.

It should be highlighted that thin, flexible, and transparent biofilms with attractive functional properties were obtained from extracted potato starch. Films forming solutions produced using the liquid autohydrolisis fraction as solvent allowed the improvement of the bioactive properties, providing comparable mechanical properties to those formulated using distilled water as solvent. Thus, extracted potato starch from local disposal resources proved to be a promising material for the production of edible coatings or biodegradable films.

Figure 1: Potato starch biofilms with bioactive features from disposal resources.

ACKNOWLEDGEMENTS:: Authors acknowledge the financial support (INOU 2018) to the Diputación Provincial de Ourense and University of Vigo. M.D. Torres thanks the Ministerio de Economía, Industria y Competitividad for her postdoctoral grant (IJCI-2016-27535).

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Rectifying heat flows with polyoxometalate anisotropic structures

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Valves and diodes break inversion symmetry defining a forward and a backward direction. Solid-state materials with such behavior are valuable since they perform unique tasks in flow and information control. Controlling heat flows at reduced sizes inspired by the manipulation of electric currents, has received much attention during the last decade, focusing mainly on theory and simulation. The impact of such control is expected to be ubiquitous, since chemical, physical and biological processes are intrinsically determined and controlled by temperature. However, while the cases of electric flow control is highly successful, their thermal counterpart is at its infancy, mainly due to the low number of solid-state materials displaying an absence of inversion symmetry in thermal properties.

Here we present bottom-up strategies for the spontaneous formation of anisotropic polyoxometalate hybrid structures with variable shapes and sizes and with thermal conductivity that depends on the heat flow direction across a surface. We focus in the case of the microsized harpoons shown below, where a complex thermal rectification behavior can be explored for logic operations. We show that the basic ingredients for this complex behavior are the harpoon geometry and preferential heat conduction on the longitudinal direction. The anisotropic structures shown here can impact the design and the efficiency of solid-state devices for thermal and energy management as well as the development of all-thermal information processing devices.

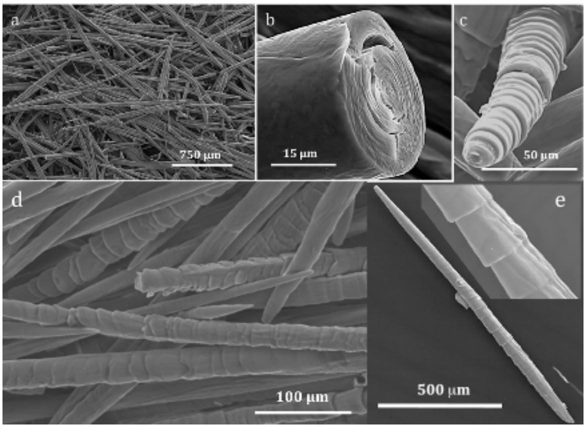

Fig.1. Scanning electron microscope images of the harpoons obtained in an open system. (a) overview; (b) cross-section; (c) a view from the backside; (d) view over several harpoons; (e) image of the harpoon whose thermal behavior was investigated.

We acknowledge Tera Analysis for providing us a professional version of QuickFieldTM. This work was developed within the scope of the projects ThermoPOMs P2020-PTDC-QEQ-QIN-5975-2014 and CICECO-Aveiro Institute of Materials, POCI-01-0145-FEDER-007679 (FCT Ref. UID /CTM /50011/2013), financed by national funds through the FCT/MEC and co-financed by FEDER under the PT2020 Partnership Agreement. NJOS and FLS acknowledge FCT for the IF/01533/2015 and IF/00222/2015 grants.

Optimization of the synthesis of imprinted hollow TiO_2 microspheres

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Hollow TiO_2 microspheres have been widely studied because they present unique properties of multiple reflection and diffraction of light, surface permeability, light capturing capacity, surface area, low density, among others, that make them attractive in different areas, namely in photocatalysis [1]. The molecular imprinting founded on microstructures based on TiO_2 has been attracting attention for selective photocatalysis. A few preparation methods and template molecules have already been employed to produce imprinted TiO_2. As far as we know, only 4 reports refer to the preparation of TiO_2 structures with molecular imprinting in the particulate form [2-5], none of them as hollow microspheres.

This work aims at the optimization of synthesis procedures leading to new hollow TiO_2 microspheres imprinted with bilirubin, with higher photonic efficiency and high photocatalytic selectivity. The optimization results were scrutinized under the perspective of a factorial analysis design. It was possible to reach a synthesis method with controllable parameters allowing adjustable surface areas and particles sizes distribution. The controlling synthesis parameters were the temperature, precursor and solvent. In this way it was possible to obtain bilirubin-imprinted hollow TiO_2 microspheres with particle diameter in the range 800-1500nm, shell thickness in the range 37-170nm, surface area in the range 50-145 m^2/g and mesoporosity (pore size> 3.4nm).

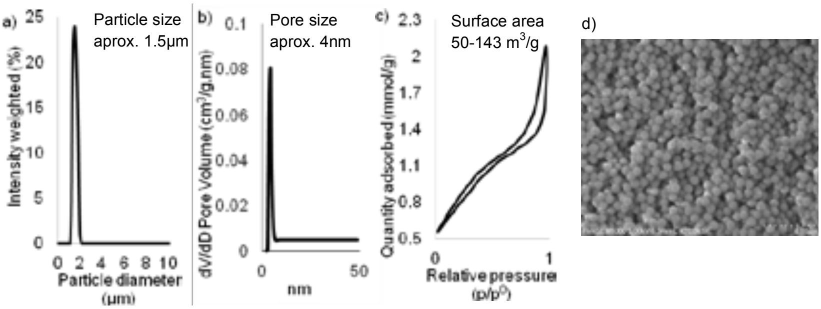

Fig.1. Characterization of bilirubin-imprinted TiO_2 hollow microspheres: a) Particle size distribution, b) Pore size distribution, c) Isotherms BET and d) SEM micrograph of the bilirubin-imprinted hollow TiO_2 microspheres imprinted TiO_2 microspheres.

AGRADECIMENTOS: This work was financed by the Pest-C./QUI/UI0081/2013 project (FEDER/COMPETE and Portuguese Foundation for Science and Technology (FCT)) and by Projeto CVMar+i, INTERREG V-A Espanha – Portugal (POCTEP) 2014-2020, nº de Exp. 0302_CVMAR_I_1_PVF is grateful to the FCT for the scholarship SFRH/BD/126642/2016.

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Multifunctional Porphyrin-based Nano-Metal-Organic Frameworks

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MOFs constitute an outstanding class of crystalline materials [1]. These materials are prepared from metal ions, or cluster nodes, and organic linkers, and because to the endless number of potential combinations, it is easy to imagine the sizeable structural diversity which can be attained. In this regard, the use of porphyrins as linkers in the construction of MOFs has shown great promise in recent years, mainly due to two fundamental driving forces: on the one hand, Pors have intrinsically remarkable properties; on the other hand, their pivotal role in Nature in diverse biological functions is also well-known [2, 3]. In recent years, our research group has been focusing on the development of new MOFs based on linkers bearing phosphonic acid groups coordinated to lanthanide cations [4]. Herein, we describe our most recent efforts to extend our research to porphyrins to prepare novel materials with a wide array of capabilities such applications. Herein, we present one of these materials with tremendous versatility regarding different applications: photo-degradation of a sulphur mustard simulant, chemosensing of nitro-aromatics and in heterogeneous sulfoxidation catalysis (Figure 1) [5].

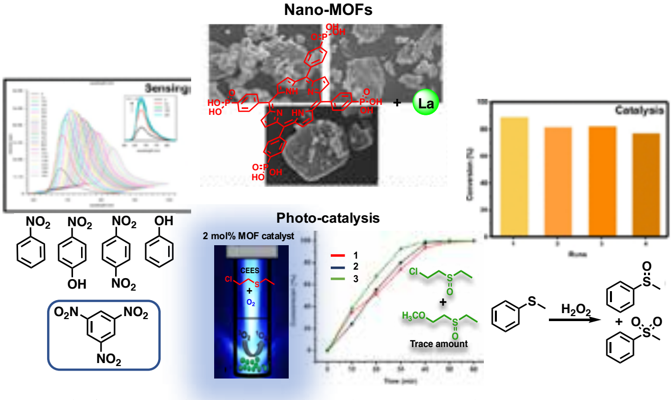

Fig.1. Multifunctional Porphyrin-based Nano-Metal-Organic Frameworks

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Functional lamellar coordination polymers

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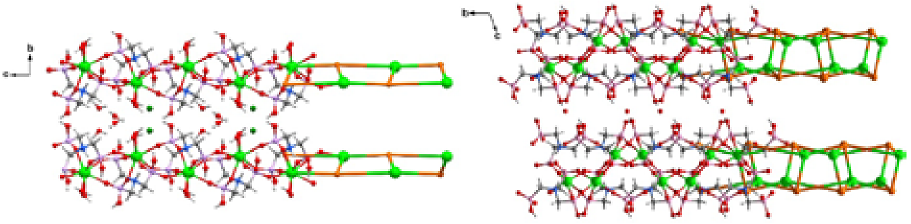
Research on Metal-Organic Frameworks (MOFs) and Coordination Polymers (CPs) is currently driven by the need to employ such materials in important technological areas for society by taking advantage of their high structural versatility. Over the last few years our research group has been focusing on the design of novel networks based on polyphosphonic acid ligands and rare-earth cations. This combination of building units, particularly the use of phosphonic acid chelating units, has been found to induce the formation of highly robust dense networks, some of which exhibit true multifunctionality (*e.g.*, photoluminescence combined with catalytic activity).

In this work we describe our most recent efforts to design and prepare novel crystalline layered CP materials based on gadolinium metal centres and the flexible triphosphonic-based molecule nitrilotri(methylphosphonic acid) (H_6nmp). Small changes in the experimental conditions allowed the preparation of two similar materials with different applications: $[Gd(H_4nmp)(H_2O)_2]Cl{\cdot}2H_2O$, a positively charged CP, exhibits remarkable activity as a heterogeneous catalyst in four different reactions (alcoholises of styrene oxide, acetalization of benzaldehyde, ketalization of cyclohexanone and acetalization of cyclohexanaldehyde) [1], and $[Gd(H_4nmp)]{\cdot}xH_2O$ shows promising results as proton conductor, with conductivities reaching 0.51 Scm^{-1} being the highest value reported so far for this kind of materials [2].



$[Gd(H_4nmp)(H_2O)_2]Cl{\cdot}2H_2O$ $[Gd(H_4nmp)]{\cdot}xH_2O$

Fig.1. Schematic representation of the crystal structures of [Gd(H4nmp)(H2O)2]Cl·2H2O and [Gd(H4nmp)]·xH2O.

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Protective effects of Mn(III)-Schiff base-dicyanamide complexes on H_2O_2-induced oxidative stress: catalase mimics or radical scavengers?

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Oxidative stress involves different damages to biological macromolecules and tissues, and subsequently, causes numerous diseases and aging [1]. Catalases, glutathione peroxidases and superoxide dismutases constitute the major antioxidant defense systems against the dangerous reactive oxygen species (ROS), generated as by-product of aerobic respiration. Manganese(III)-Schiff base complexes may behave as artificial mimics of these enzymes. To gain insight into the kinetic and mechanistic details of the peroxidase-like activity of this type of complexes, we selected two new Mn(III)-Schiff base-dicyanamide complexes. During the course of the work we observed that spectral scanning experiments with solutions containing ABTS, H2O2, and one of the complexes at concentrations typically used in the ABTS test, yield systematically different results depending on the instrument used (Fig. 1).

A detailed study of this effect, including the use of a 455 nm cut-on long pass filter, showed that formation of ABTS●+ does not necessarily indicate that the Mn(III) mimics have peroxidase or catalase activity but they can be involved in radical processes. In particular, the capability of these complexes, including EUK-134, to act as ●OH scavengers must be considered when explaining the mechanism of their biological activity.

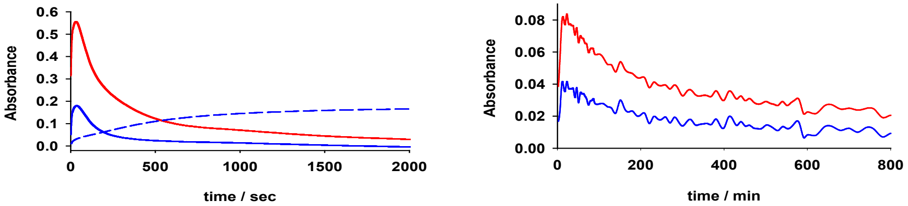

Fig. 1. Kinetic traces at 400 (red) and 750 (blue) nm obtained for the ABTS peroxidase test using compound [Mn(3OMe-*salen*)(DCA)] with a conventional spectrophotometer (right) and with a stopped-flow instrument provided with a diode-array detector (left). The blue dashed line corresponds to a stopped-flow experiment using a 455 nm cut-on long pass filter.

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From molecular to supramolecular catalysts for water splitting

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Decomposing water is the more direct way to produce hydrogen, which can be stored and utilized as a transportable fuel or converted into energy-rich organic molecules, to cope with the intermittent character of the solar radiation. The Oxygen Evolving Complex (OEC) is the native enzyme that catalyzes the oxidation of water in natural photosynthesis to release oxygen. This constitutes one of the half reactions of water splitting. The creation of biomimetic systems to reproduce the basic chemistry of this process gives us more insight into better understanding this crucial natural reaction which is responsible of the atmospheric oxygen that we breathe [1-2].

In this communication we report the ability of a number of manganese complexes to split water, which has been studied by means of water photolysis experiments. The synthetic models to be presented show different structural features: monomers (complexes **1**-**2**), m-aquo dimers (complexes **4**-**6**), m-phenoxo dimer (**2**), dimer-of-dimers (complex **7**) and tetrameric (complex **8**) complexes. The discussion concerning the photolytic behaviour encompasses the advances made in the new insights on the structural features ascertained through the development of characterization techniques. Supramolecular interactions arise as a key factor to enhance the ability of these systems to split water. A dimer-of-dimers manganese complex, described in this work, appears as a precursor of an extremely active photolytic catalyst.

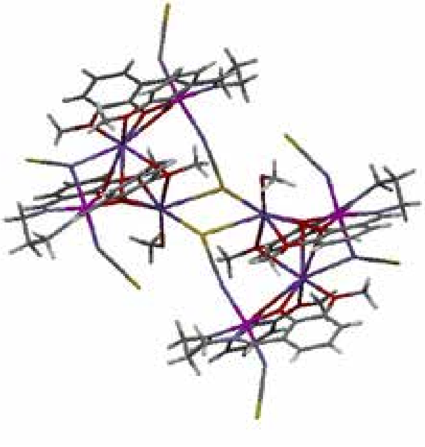

Fig. 1. X-ray crystal structure for the dimer-of-dimers model **7**.

ACKNOWLEDGEMENTS: The authors are grateful for the financial support given by the Xunta de Galicia (GRC2014/025 and METALBIO Network ED431D 2017/01).

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A novel platinum(II) porphyrin for photodynamic therapy

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Several palladium and platinum metalloporphyrins have shown important photophysical properties that allows them to be used as chemosensors for oxygen detection [1]. Besides the fact that platinum is more abundant in the earth's crust than palladium, the platinum complexes also exhibit phosphorescence at room temperature, which makes them more suitable for oxygen detection. Unfortunately, these complexes are typically susceptible to photodegradation, which can be avoided by the use of halogen *meso*-substituted porphyrins [2, 3].

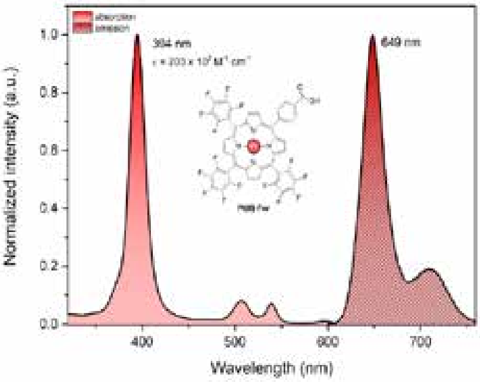

Fig.1. Absorption (left) and emission (right) spectra of **Pt(II)-Por** in DMF.

Herein, a new platinum(II) complex of 5-(4-carboxyphenyl)-10,15,20-tris(pentafluorophenyl) porphyrin Pt(II)-Por was synthesized. The carboxyphenyl group was introduced as a functional group to allow the linkage of other cytotoxic and anti-inflammatory drugs. The characterization of this complex was performed by UV-Vis, fluorescence, ^{1}H, ^{13}C and ^{19}F NMR spectroscopies and by MALDI-TOF spectrometry. These results, as well as singlet oxygen generation studies, will be presented and discussed.

ACKNOWLEDGMENTS: The authors gratefully acknowledge "Cooperação Científica e Tecnológica FCT/DAAD-2017/2018" through the project "Novel ligand–porphyrin conjugates for targeted photodynamic therapy of cancer". This work also received financial support from the European Union, FEDER (Fundo Europeu de Desenvolvimento Regional) through PT2020 and by national funds through FCT (Fundação para a Ciência e a Tecnologia), QREN, and COMPETE, NORTE-07-0162-FEDER-000048, UID/QUI/50006/2013 (LAQV/REQUIMTE) and project M-ERA-NET/0005/2014. The authors acknowledge the financial support by the FCT through the Post-doctoral (SFRH/BPD/85793/2012 – A. Leite) and PhD (PD/BD/142868/2018 – J. Almeida) grants.

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Breathing Metal-Organic Frameworks Based on a Polyphosphonate Organic Linker

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Studies on solid-state matter are intimately associated with the innate rigidity of compounds. These “traditional” concepts have recently been challenged with the rise of porous coordination polymers (PCPs) or Metal-Organic Frameworks (MOFs) and their intrinsic properties. Dynamic structural transformations of MOFs triggered by external stimuli, are some of the examples that have recently received particular interest, mainly because they retain the same topology than those of more rigid structures and, at the same time, show important flexibility.

This communication reports our recent findings in phosphonate yttrium-based Metal-Organic Frameworks (MOFs), formulated as $[Y(H_5btp)]\cdot 5.5H_2O$ (**1**), $[Y(H_5btp)]\cdot 2.5H_2O$ (**2**), $(H_3O)[Y_2(H_5btp)(H_4btp)]\cdot H_2O$ (**3**) and $[Y(H_5btp)]\cdot H_2O\cdot 0.5(MeOH)$ (**4**), which were prepared using a “green” microwave-assisted synthesis methodology to promote the self-assembly of the tetraphosphonic organic linker [1,1’-biphenyl]-3,3’,5,5’-tetrayltetrakis(phosphonic acid) (H_8btp) with Y^{3+} cations. This new family of functional materials, isolated in bulk quantities, exhibits a remarkable breathing effect. Structural flexibility was studied by means of X-ray crystallography, thermogravimetry, variable-temperature X-ray diffraction and dehydration and rehydration processes, ultimately evidencing a remarkable reversible Single-Crystal to Single-Crystal (SC-SC) transformation solely through the loss and gain of crystallization solvent molecules. Porous materials **2** and **3** were further studied to ascertain their performance as heterogeneous catalysts and proton conductors, respectively, with outstanding results being registered for both materials. Compound **2** showed a 94% conversion of benzaldehyde into (dimethoxymethyl)benzene after just 1h of reaction. The protonic conductivity of **3** at 98% of relative humidity (2.58×10^{-2} Scm^{-1}) was among the highest registered among MOFs, with the great advantage of the material to be prepared using a simpler and sustainable synthesis methodology.

AGRADECIMENTOS: I wish to give a personal and heartfelt “thank you” to all the collaborators and students involved in the research in my group over the past years. All contributed immensely with work and discussions to the great body of results. This body of work was developed within the scope of the project CICECO-Aveiro Institute of Materials, POCI-01-0145-FEDER-007679 (FCT Ref. UID /CTM /50011/2013), financed by national funds through the FCT/MEC and when appropriate co-financed by FEDER under the PT2020 Partnership Agreement. Fundação para a Ciência e a Tecnologia (FCT, Portugal) is also gratefully acknowledged for funding this research and dissemination of the results.

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Crown ether palladium compounds: a strategy for encapsulating potassium cations in crown ether rings

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Cyclometallated compounds are commonly used as catalysts and anticancer agents [1], especially those derived from palladium and platinum. This is due to their air and thermal stability. On the other hand, it is known that crown ethers show as one of their most salient application the size-selective interaction towards cations [2]. Thus, by combining these two functionalities into the same molecule [3] it is possible to attain a new kind of structures that include the stability of cyclometallated compounds in cooperation with the size-selective entrapping ability of crown ethers. This should give rise to the formation of new sensors pertaining to the family of main group metal/transition metal compounds.

In this communication, we present the synthesis of the first palladacycle able to entrap a potassium cation through bonding to two 15–crown–5 ether rings in a single molecule, confirmed by X-ray crystallographic data [4]. The preparation is not only reproducible, but it also allows to obtain a similar structure arising from a cyclometallated platinum species.

ACKNOWLEDGMENT:
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Study of the reactivity of functionalized palladacycles with phosphines

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The aim of this work is the design, synthesis and characterization of a series of phenylboronic cyclometallated derivatives bearing different phosphines. Palladium cyclometallated compounds have proved to be useful as catalysts in cross coupling reactions [1, 2]. In particular, palladacycles with a boronic acid function may lead to further modifications applicable to the Suzuki-Miyaura reaction [3], thus modifying the properties of the compounds. Reactivity towards phosphine ligands provides different structures [4] that modulate the applicability to the coupling reaction.

The compounds were prepared by reaction of cyclometallated species with different phosphine ligands and they were characterized by IR, ^{1}H and ^{31}P NMR spectroscopy.

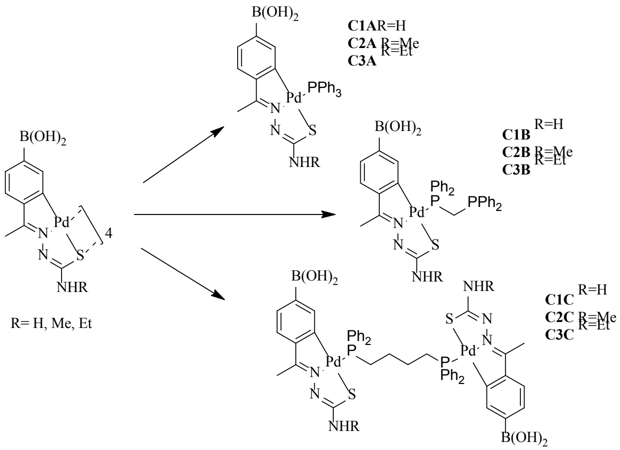

Fig.1. Reaction scheme

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Chelate-to-bridging shift of phosphane dipalladacycles

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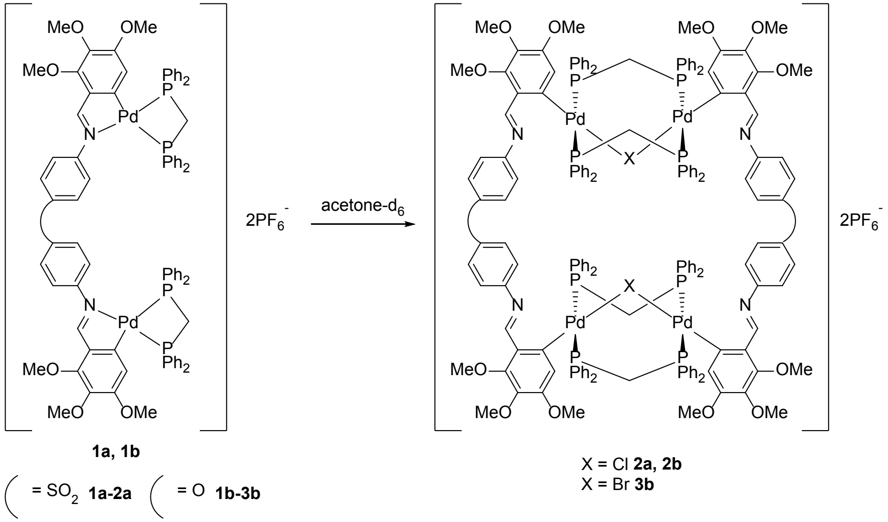
The chemistry of cyclometalated compounds[1] has attracted much research interest in past years. They are known for their ample applications in numerous fields: organic synthesis[2], photochemistry[3], catalysis[4], and as potential biologically active materials[5]. We now report a chelate-to-bridging shift which occurs spontaneously in solution even at low temperature in palladacycles bearing Ph2PCH2PPh2-P,P, (dppm). Palladacycles of the type [Pd2(Ph2PCH2PPh2–P,P)2(C,N:C,N)] (C,N:C,N = bis(N–2,3,4–trimethoxybenzylidene)–4,4´–sulfonyldianiline or –4,4´–oxydianiline) can undergo a spontaneous slow chelate–to–bridging diphosphine coordination shift in solution. Following this strategy a tailor-made synthetic procedure was devised that culminates in isolation of the first crystallographically characterized tetranuclear palladium double A–frame structures hosted in a single molecule.



Scheme 1: Reaction sequence leading to the synthesis of the double A–frame complexes.

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Self-assembly of polyoxometalate hybrids into anisotropic structures

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It is now well established that the combination of inorganic and organic components into a single material at the molecular and nanometer level results in a material that benefit from the properties of both components and often from their synergistic interactions.[1] Introducing an organic moiety into an inorganic polyoxometalate (POM) is a promising way to enhance the adaptability and properties of POM-based materials. The majority of POM-hybrids can be classified into two groups, the hybrids with weak interactions (e.g. electrostatic interactions, hydrogen bonding, or van der Waals interactions etc.) and the hybrids with strong interactions (e.g. covalent bonds) between the inorganic and organic components.[2] In recent years, considerable attention has been given to the preparation of POM hybrid structures through surfactant encapsulation mainly by exploring the electrostatic interactions between POM and surfactant molecules.[3]

Here we present bottom-up strategies for the spontaneous formation of anisotropic polyoxometalate hybrid structures with variable shapes and sizes. By varying the experimental conditions such as solvent mixtures & ratios, temperature and hybrid concentration we can control the assembly of POM-hybrids in a way that different morphologies are obtained (shown bellow). Among the different morphologies obtained, conical and harpoon structures are of particular interest due to their symmetry breaking structures and also due to the different chemical and physical regions of contact accessible at inner-outer surfaces and at their ends (in the case of the cones).

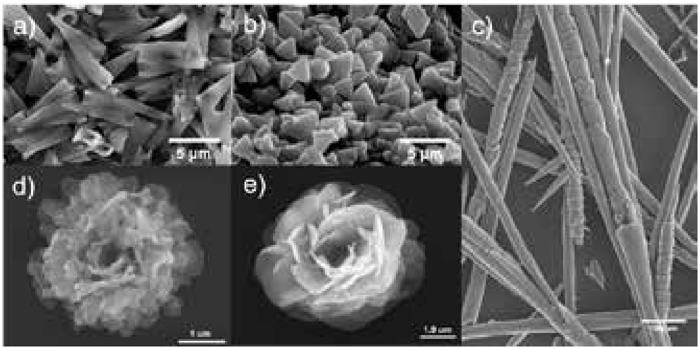

Fig.1. Scanning electron microscope images of the a) and b) cones with different sizes, c) harpoons, d) and e) flowers with distinct features.

This work was developed within the scope of the projects ThermoPOMs P2020-PTDC-QEQ-QIN-5975-2014 and CICECO-Aveiro Institute of Materials, POCI-01-0145-FEDER-007679 (FCT Ref. UID /CTM /50011/2013), financed by national funds through the FCT/MEC and co-financed by FEDER under the PT2020 Partnership Agreement. NJOS and FLS acknowledge FCT for the IF/01533/2015 and IF/00222/2015 grants.

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QUÍMICA INORGÂNICA

POSTER

Strategies to obtain enhanced rhodamine-based materials for sensing metal ions and NO_2 gas

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The design of fluorescent chemosensors for a broad range of environmental and biological analysis is an expanding field of research. These sensors are gaining special attention due to their high sensitivity and selectivity, quick response and simplicity of measurement [1]. On the other hand, the design of materials with optical and mechanical properties suitable for sensing applications depends on the preparation of fluorescent molecules with structural features for efficient immobilization in polymeric supports or binding matrixes [2], [3].

The preparation of a series of rhodamine dyes (Figure 1A) and the study of their photophysical properties is reported. Dyes containing catecholate or isophthalate receptors were tested as metal ions sensors in biological media, particularly for iron(III). [3] The isophthalate-based dyes were immobilized (infiltrated in TiO_2 thin films) [3c] and their photophysical properties were accessed by UV-Vis and photoluminescence, and compared to those in solution. Finally, a rhodamine derivative containing a $-CO_2H$ substituent was immobilized and tested as a NO_2 gas sensor. [4]

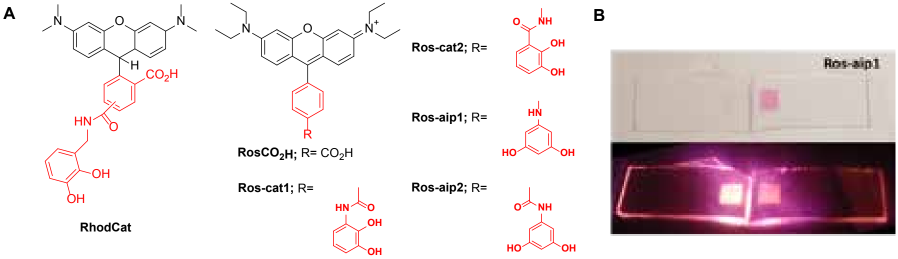

Fig.1. A - Structures of rhodamine-based fluorescent chemosensors; B - TiO2 thin films infiltrated with Ros-aip1 at naked eye (top) and collected emission (down) for 8.8 mM, (left) and 147 mM (right).

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A new dipalladacycle with an hexadentate [C,N,S:C,N,S] imine

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Up to now extensive work has been published on double cyclometallated complexes containing two independent metallated phenyl rings. [1-4] In spite of such an extensive range of publications, relatively few studies deal with double metallation on the same phenyl ring. In order to make this posible, it is necessary that the ligand contains two substituents with potentially donor atoms –nitrogen, sulfur…–, wich allow the formation of two five –or six– membered chelate rings.

This communication describes the preparation, characterization and structural study of novel tridentate [*C*,*N*,*S*] bys-cyclopalladated complexes with ligands derived from the condensation of a primary amine –2-(methylthio)aniline– with the corresponding aromatic dialdehyde –terephthaldehyde–.The compound is also interesting due to their close-to-planarity arrangement and to the presence of seven fused rings in their structure.

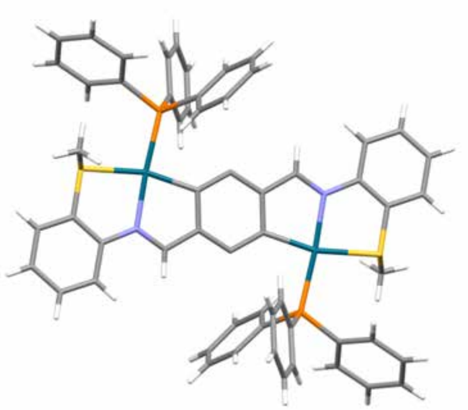

Fig.1. Crystal structure

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Effect of the hydrolysis of a *tris*thiosemicarbazone ligand on the structure of a Cd(II) helicate

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Thiosemicarbazones are highly versatile skeletons that have been widely used as ligands in coordination chemistry.[1] Our reseach group has extensive experience on the assembly of *bis*thiosemicarbazone helicates. We have demonstrated that we can selectively obtain mesocate or helicate architectures following a simple metal ion recognition strategy using tetradentate *bis*thiosemicarbazone ligands.[2] Interestingly scarce metallosupramolecular structures derived from *tris*thiosemicarbazone ligands have been reported in literature.[3]

To check whether a further binding domain in the thiosemicarbazone would change the discrete helical structure, we have performed the electrochemical synthesis of a cadmium complex using the *tris*thiosemicarbazone H_3L (Figure 1, left). The resulting compound was fully-characterized as $[Cd_2(HL)_2]\cdot 3H_2O$. Recrystallization of the later from the mother liquors yielded X-ray quality crystals of $[Cd_2(L')_2]\cdot 3CH_3CN$, where L' is a new ligand formed after hydrolysis of an imine bond during the crystallization process. Herein we propose a mechanism to explain the partial hydrolysis of the Cd(II) helicate that resulted in minimum changes in the helical structure.

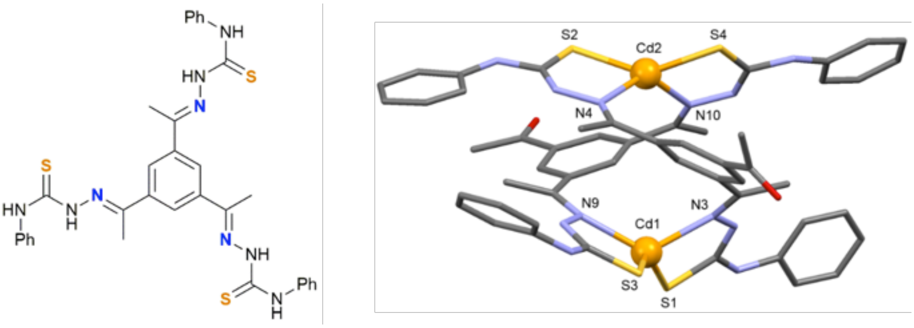

Fig.1. Tristhiosemicarbazone ligand H3L (left) and sticks diagram of the Cd(II) helicate obtained after hydrolysis of the coordinated tristhiosemicarbazone ligand (right).

ACKNOWLEDGEMENTS: Financial support by the Xunta de Galicia (GRC2014/025 and METALBIO Network ED431D 2017/01) is acknowledged.

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Thermal rectification in microsized harpoons made of polyoxometalate hybrids

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Harpoons are probably the first manmade tools where inversion symmetry is broken, resulting in a notable difference in their aerodynamics when moving in opposite directions, defining unequivocally a forward and a backward direction. While breaking inversion symmetry in the shape of solid-state materials is often achieved by top-down or additive approaches, breaking inversion symmetry spontaneously using bottom-up wet chemical routes involves a much more subtle design, typically offering in return easier processability and scalability.

Here we report the development of polyoxometalate-based microsized harpoons obtained by wet-chemical routes, we show their complex thermal behavior rectifying heat flows and working as a magnitude comparator and we show that the basic ingredients for this behavior is the harpoon geometry and a preferential heat conduction on the longitudinal direction. These thermal magnitude comparators can impact the design and the efficiency of solid-state devices for thermal and energy management as well as the development of all-thermal information processing devices.

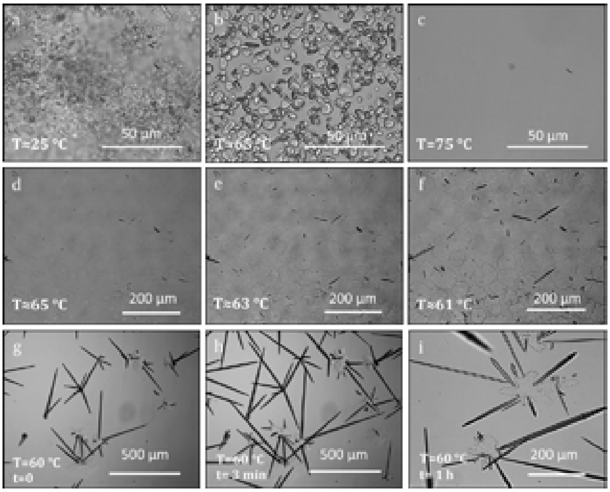

Fig.1. Optical images obtained during the heating and cooling procedures of PW12O40. DODA system leading to the formation of the harpoons. Panels (a) to (c) correspond to the heating stage, panels (d) to (f) correspond to the cooling stage and panels (g) to (i) correspond to an aging stage at T=60 °C.

We acknowledge Tera Analysis for providing us a professional version of QuickFieldTM. This work was developed within the scope of the projects ThermoPOMs P2020- PTDC-QEQ-QIN-5975-2014 and CICECO-Aveiro Institute of Materials, POCI-01-0145-FEDER-007679 (FCT Ref. UID /CTM /50011/2013), financed by national funds through the FCT/MEC and co-financed by FEDER under the PT2020 Partnership Agreement. NJOS and FLS acknowledge FCT for the IF/01533/2015 and IF/00222/2015 grants.

Obtención de un *meso*-helicato de cobre(I) derivado de un ligando fosfino-tiocarbohidrazona

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Los complejos metalosupramoleculares están formados por ligandos orgánicos que se coordinan de forma espontánea a iones metálicos dando lugar a diferentes tipos de estructuras entre las que destacan los *meso*-helicatos o mesocatos.

Por otra parte, la química de coordinación de los ligandos tiocarbohidrazona ha despertado gran interés no sólo por su versatilidad como sistemas donadores, sino también por su potencial aplicación en el campo de la biomedicina [1]. La introducción de átomos de fósforo en los dominios enlazantes de las tiocarbohidrazonas podría permitirnos la estabilización de iones M(I), M= Cu, Ag, Au. Así, los complejos de Cu(I) derivados de éste tipo de ligandos podrían presentar actividades antimicrobianas interesantes, de forma similar a las que presentan sus análogos derivados de tiosemicarbazona, de cara a futuras aplicaciones biológicas [2].

En este trabajo se describe la síntesis y caracterización de un mesocato dinuclear dicatiónico de cobre(I) derivado de un ligando fosfino-tiocarbohidrazona H_2L. La estructura cristalina del mesocato $[Cu_2(H_2L)_2](PF_6)_2$ ha sido determinada por difracción de rayos X de monocristal (Figura 1).

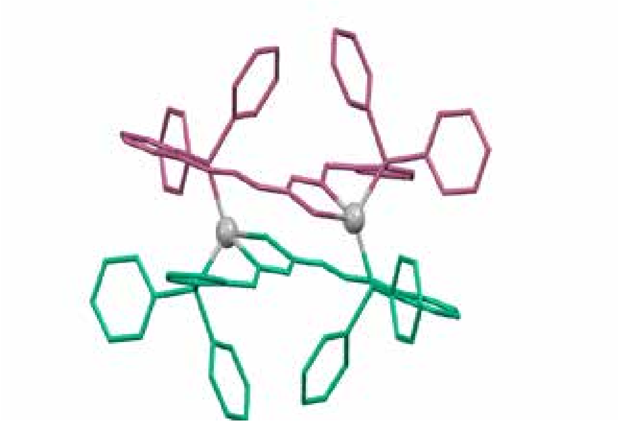

Fig.1. Estructura cristalina del mesocato dinuclear [Cu2(H2L)2](PF6)2.

AGRADECIMIENTOS: Xunta de Galicia (EM2014/018, GRC2014/025, ED431/2017/01 Networks) y MINECO (CTQ2015-70371-REDT MetDrugs, CTQ2015-71470-REDT H2BioCatO2, CTQ2017-90802-REDT MetalBIO).

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Towards the tunable design of assembled structures of polyoxometalates and ionic liquids

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Self-assembled structures containing polyoxometalates (POMs) are currently a hot topic in supramolecular chemistry and materials science. POMs are known to form organic-inorganic hybrids with cationic surfactants through electrostatic interactions. To date, the self-assembled structures reported in rely mainly on the use of cationic surfactants with localized point charges such as dimethyldioctadecylammonium (DODA) where the hybrid structure formation is driven by the surfactant aggregation in organic solvents. Through careful selection of the POM structure and counterion, a wide range of well-defined structures has been developed, including, but not limited to, cones, spheres, flowers, vesicles. [1-4]

Herein, we present an aqueous "one-pot" approach for the synthesis of a variety of novel structures with unique arrangements derived from the combination of the $\{Mo_{72}Fe_{30}\}$ "Keplerate" with the ionic liquids (ILs). The nature of ILs used offer a flexible way to explore different structures by varying the ratio of electrostatic to Van der Waals forces through the increase of the IL alkyl chain length and/or changes in the cationic structure. Optical microscopy and scanning electron microscopy (SEM) measurements show that the obtained assemblies have markedly different morphologies as the length of the IL alkyl chain and the IL to POM ratio are varied. To the best of our knowledge, this research represents the first 'one-pot' synthesis attempted using the giant $\{Mo_{72}Fe_{30}\}$ directly from aqueous media. [5] Hydrophilic IL stand out as interesting additives for the simple, environmentally friendly and tailored design of POM structures with predefined properties.

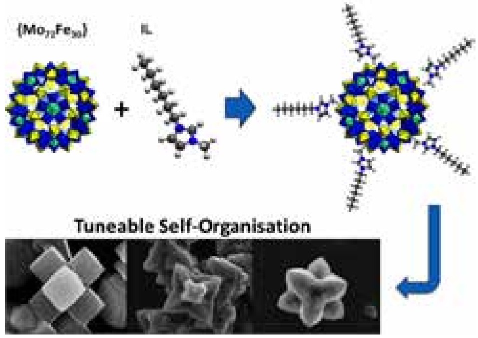

Fig.1. Schematic illustration of the self-organization of POM and ILs

This work was developed within the scope of the projects ThermoPOMs P2020-PTDC-QEQ-QIN-5975-2014 and CICECO-Aveiro Institute of Materials, POCI-01-0145-FEDER-007679 (FCT Ref. UID /CTM /50011/2013), financed by national funds through the FCT/MEC and co-financed by FEDER under the PT2020 Partnership Agreement. NJOS and FLS acknowledge FCT for the IF/01533/2015 and IF/00222/2015 grants.

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high stable metal-organic frameworks for sustainable oxidative desulfurization of diesel fuels

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Oxidative desulfurization (ODS) is one of the most promising sustainable and cost-effective methods for the deep desulfurization of diesel fuel, corresponding to the need for lower emission of sulfur which results from its combustion [1]. ODS processes allows the efficient removal of the most refractory sulfur-containing compounds leading to near zero sulfur fuels under mild conditions, namely low temperature and pressure.

Following our research efforts on functional crystalline materials, we have been developing novel catalytic systems for efficient ODS processes resorting on Metal-Organic Frameworks (MOFs) as active heterogeneous catalysts. MOFs are highly organized coordination polymers that are often crystalline and porous. UiO-66(Zr) is a highly stable MOF based on $Zr_6O_4(OH)_4(CO_2)_{12}$ secondary building units and, due to its high surface area and exceptional chemical, thermal and mechanical stability, was applied as heterogeneous catalyst in ODS processes.

Using strategic economical preparative methodologies, active catalysts were prepared following solvothermic and microwave-assisted synthesis, which enabled the preparation of active MOFs after only 15 minutes of reaction [2]. All the materials were characterized by various techniques, such as PXRD, FTIR-ATR spectroscopy and SEM. High catalytic efficiency was found for some of the prepared MOFs, ensuring near total desulfurization of model diesels and relevant results for real diesel samples after few hours, under sustainable conditions. To promote their recyclability after the third catalytic cycle, we developed a novel reactivation process, enhancing the potential of these materials for the catalysis of ODS reactions.

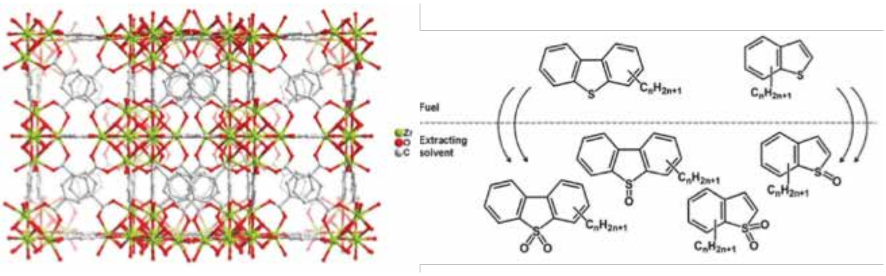

Fig.1. 3D framework of UiO-66(Zr) (left) and the ODS process in a diesel fuel (right).

AGRADECIMENTOS: The work was co-financed by UE, FEDER - Fundo Europeu de Desenvolvimento Regional and COMPETE 2020 – POCI (POCI-01-0145-FEDER-007265) through PT 2020 and by national funds through the FCT / MCTES for the research centre REQUIMTE - LAQV (UID/QUI/50006/2013) and project PTDC/CTM-CTM/31983/2017; additional thanks to the FCT/MCTES for the PhD fellowship SFRH/BD/95571/2013 (to SR), and the Post-doctoral grant SFRH/BPD/111899/2015 (to LCS).

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Crown ether palladium complex: effective strategy for encapsulating potassium cations

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Crown ethers are ligands that interact with metal ions selectively, depending on the size of the cavity. According to this, they have shown a wide variety of applications related to sensors or membrane ion transport, among others [1]. On the other hand, cyclometalled compounds also display interesting properties as metallomesogens or catalysts [2]. Thus, the combination of both functionalities in the same structure, have been widely studied in order to combine their ample set of applications [3]. However, only in one case were both functionalities combined in the same structure [3b].

In this communication we present the first palladacycle able to entrap a potassium cation through bonding to two 15–crown–5 ether rings in a single molecule. In addition, both moieties where placed on the same aromatic rings, so that the cyclometallated moieties forced the approach of the macrocyclic ligands. This new structure was confirmed by X-ray crystallographic data [4]; thus, giving rise to a new family of main group / transition metal compounds.

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2-ARYL-4-CHLORO-2*H*-CHROMENE: A KEY INTERMEDIATE IN THE SYNTHESIS OF CHROMENE HYBRIDS

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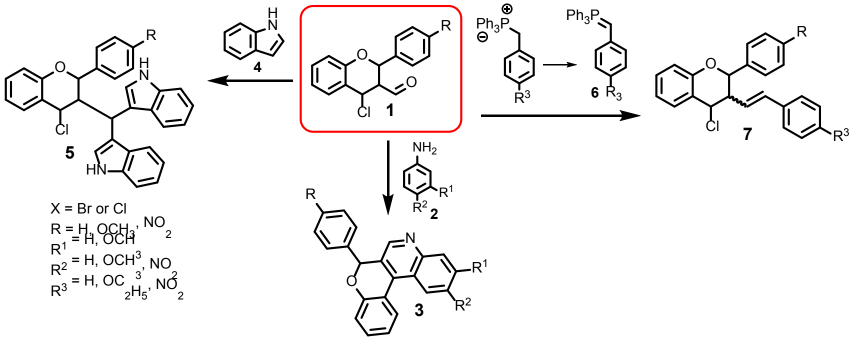
2*H*-Chromenes (2*H*-1-benzopyrans) represents a common scaffold in numerous natural or synthetic biologically active compounds. Some derivatives exhibit a wide spectrum of biological properties, such as antibacterial, antifungal and antitumoral activities [1].

3-Styryl-2*H*-chromene derivatives are synthetic compounds recently highlighted by their antitumoral properties [2]. On the other hand, the nitrogen heterocyclic compounds such as quinolines and indoles are found in nature and present vast applications as pharmaceuticals [3]. Moreover, hybrid molecules constitute a privileged scaffold for many pharmaceuticals [2], [4].

6-Aryl-6*H*-chromene[3,4-*c*]quinolines **3**, 3,3'-[(2-aryl-4-chloro-2*H*-chromen-3-yl) methylen]bis(1*H*-indoles) **5** and 4-chloro-2-aryl-3-styryl-2*H*-chromenes **7** were synthesized using 2-aryl-4-chloro-2*H*-chromenes **1** as starting materials (Scheme 1). In this communication, the recent developments in the methodologies for their synthesis as well as their NMR characterization will be presented and discussed.



Scheme 1

ACKNOWLEDGEMENTS: Thanks are due to University of Aveiro and FCT/MEC for the financial support of the QOPNA research unit (FCT UID/QUI/00062/2013) through national founds and, where applicable, co-financed by the FEDER, within the PT2020 Partnership Agreement, and to the Portuguese NMR Network. D. H. A. Rocha (SFRH/BD/68991/2010) also thanks FCT for their PhD grant.

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(*E,E*)-CINNAMYLIDENEACETOPHENONES AS TEMPLATES FOR THE ONE-POT SYNTHESIS OF ISOQUINUCLIDINES

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Isoquinuclidines (2-azabicyclo[2.2.2]octanes) are found widely in natural products namely in iboga-type indole alkaloids and are also valuable intermediates in the synthesis of other alkaloids and in medicinal chemistry [1]. One of the most well-established routes to isoquinuclidines is the Diels-Alder reaction of 1,2-dihydropyridines (1,2-DPHs) with dienophiles [2]. However, the synthesis of 1,2-DHPs can be very difficult due to the high instability of these compounds. In this work an effortless synthetic pathway to prepare highly substituted isoquinuclidines from easily available (*E,E*)-cinnamylideneacetophenones was achieved.

A sequential one-pot synthesis was performed under MW irradiation and comprises, primarily, the synthesis of 2,6-diaryl-1,2-dihydropyridines by a 6π-azaelectrocyclisation involving an intermediate α,β,γ,δ-diunsaturated imines, obtained by condensation of (*E,E*)-cinnamylideneacetophenones with amines. A second step involves the diastereoselective Diels-Alder reactions of the formed 1,2-DHP with *N*-methylmaleimide affording highly substituted isoquinuclidines in good chemical yield (30-50%) [3]. This procedure easily converts unstable 2,6-diaryl-1,2-dihydropyridines to, otherwise inaccessible, isoquinuclidines without any kind of manipulation.

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Synthesis and biological evaluation of β-functionalized porphyrin with cationic heterocyclic units

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Due to their unique properties, particularly synthetic versatility, thermal stability, large π-electron systems and photochemical and photophysical properties [1], porphyrins are receiving a special attention from the scientific community; this is due to their high success in different fields like catalysis, medicinal drugs, electronic materials and sensors [2]. An important field of application is related with their potential to be used as photosensitizers (PS) in the Photodynamic Inactivation of Microorganisms (PDI) by oxidative stress, after their activation by light in the presence of molecular oxygen. This approach is considered to be an efficient alternative to conventional therapeutic approaches in the inactivation of viruses, fungi and bacteria, namely, due to the low probability of microorganisms to develop resistance [3,4]. Herein, we report the synthesis and characterization of a series of beta cationic porphyrins bearing imidazole and terpyridine units in one of their β-pyrrolic positions and their ability to photoinactivate the *Gram*-negative bacterium *Escherichia coli* [5,6].

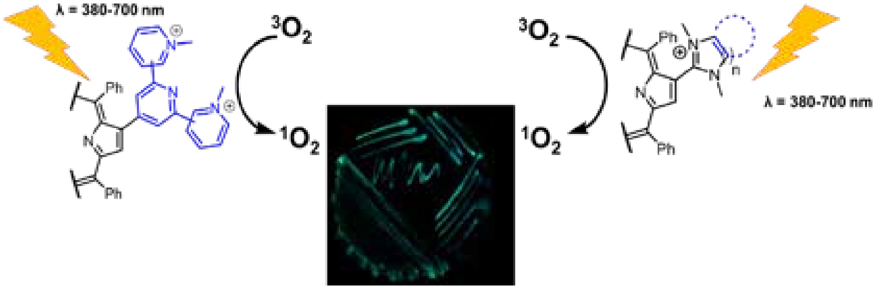

Fig 1. Representation of the *E. coli* photoinactivation by β-functionalized cationic porphyrins.

ACKNOWLEDGEMENTS: Thanks are due to FCT/MEC for the financial support to the QOPNA research Unit (FCT UID/QUI/00062/2013), to the CESAM (UID/AMB/50017/2013), through national funds and when applicable co-financed by the FEDER, within the PT2020 Partnership Agreement and "Compete" 2020, and also to the Portuguese NMR Network. PROTEOMASS Scientific Society (Portugal) and the Associate Laboratory for Green Chemistry LAQV (FCT/MEC (UID/QUI/50006/2013) and PT2020-POCI-01-0145-FEDER-007265) for general funding. NMM Moura thanks FCT for his postdoctoral grant (SFRH/BPD/84216/2012).

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Simple Strategies in the β-Functionalization of *meso*-Tetraaryporphyrins Via Nitro and Formyl Substituents

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Meso-tetraarylporphyrins with formyl and nitro groups are considered excellent platforms for further synthetic manipulations affording new systems with adequate physicochemical features to be used in the development of sensors, electronic materials and medicinal drugs [1]. In this communication it will be discussed simple synthetic strategies developed in our group giving access to benzoporphyrins, porphyrin-chalcone type derivatives, porphyrins bearing oligopyridine units and porphyrins fused to isoxasole units [2-5]. The ability of some of these systems substituted at β-pyrrolic positions to coordinate metal ions and their biological evaluation towards microorganisms will also be discussed.

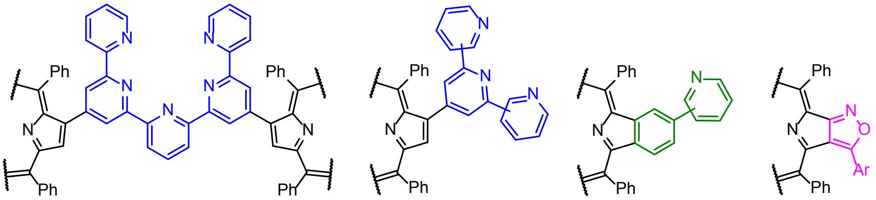

Fig 1. Some structural features of synthetic products that will be discussed in this communication.

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[5] Unpublished results.

Afinidade e seletividade de porfirinas e ftalocininas catiónicas para diferentes estruturas de ADN: *screening* competitivo

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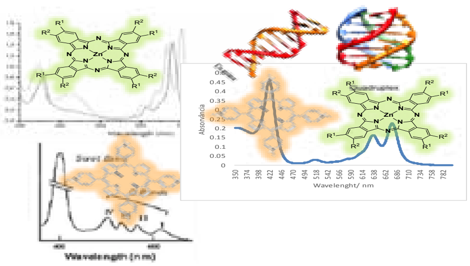
Os telómeros são estruturas existentes nas extremidades dos cromossomas que lhes conferem estabilidade e asseguram que toda a informação genética é perfeitamente copiada quando a célula é duplicada.[1] O tamanho dos telómeros vai diminuindo a cada ciclo celular e a enzima telomerase é a responsável pela manutenção do tamanho destas estruturas. No entanto, esta enzima é também responsável pela proliferação descontrolada das células cancerígenas, pois nestas células ela encontra-se sobre-expressa.

As sequências de ADN ricas em guanina podem associar-se formando estruturas estáveis designadas por G-quadruplexes. A formação de G-quadruplexes, e a sua estabilização por ligandos, como porfirinas e ftalocianinas, permite a inibição da ação da telomerase e o potencial controlo da proliferação das células cancerígenas. Para tal é necessário que estes ligandos sejam seletivos para as estruturas dos G-quadruplexes quando na presença de grandes quantidades de ADN de cadeia dupla.

As porfirinas e as ftalocininas apresentam bandas de absorção características na região do visível o que possibilita a utilização da espectroscopia de UV-Vis para investigar a estabilidade, a seletividade e o tipo de interações estabelecidas entre estes potenciais ligandos e estruturas de ADN como duplexes e G-quadruplexes. Quando ocorre interação entre o ligando e o G-quadruplex (ou ADN de cadeia dupla) verifica-se um deslocamento destas bandas caraterísticas e a análise da magnitude desse deslocamento permite avaliar a força e o tipo de ligação que ocorre entre as estruturas de ADN e os ligandos.[2]

De forma a avaliar a seletividade de ligandos, para o G-quaduplex ou ADN de cadeia dupla foram estudadas individualmente as interações de várias moléculas, incluindo duas ftalocianinas catiónicas e a já amplamente estudada 5,10,15,20-tetra(N-metilpiridinium-4-il)porfirina (TMPyP) [3], com o G-quadruplex AG3(TTAGGG)3, sequência existente nos telómeros humanos. Os resultados obtidas nas experiências anteriores e o facto das porfirinas e das ftalocianinas terem máximos de absorção em regiões distintas permitiu desenvolver um método de screening competitivo. Com este método torna-se possível, recorrendo a pequenas quantidades de ADN e de ligando, e num muito curto espaço de tempo, aferir a afinidade e a seletividade de vários ligandos para diferentes estruturas de ADN.



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Photochromism of fused-naphthopyrans

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Photochromic molecules change their colour upon absorption of UV light. For naphthopyrans the phenomena are thermally reversible and thus after ceasing the irradiation the system returns spontaneously to the initial colourless state. The UV light promotes the cleavage of the pyran C(sp_3)-O bond affording a mixture of two coloured photoisomers which have different thermal stability. Thus, when the light source is removed, the major photoisomer (TC) fades quickly to the initial uncoloured form but the minor one (TT, responsible for 10-20% of the colouration) in thermally more stable and returns slowly to the uncoloured form yielding a persistent residual colour. Therefore, the complete return to the initial uncoloured state is actually quite slow and takes more than 5 minutes [1,2].

One way to avoid the formation of this unwanted slow-fading coloured photoisomer and overcome the problem of the residual colour, is to prevent the C=C isomerization of the short-lived TC isomer to the more stable TT isomer. We have found a solution to this problem by incorporation an alkyl bridge between the pyran double bond and the naphthalenic ring. These new fused-naphthopyrans have different photochromic properties than the common ones used in the production of photochromic lens [3]. As anticipated, UV irradiation of these uncoloured fused-naphthopyrans, in solution or dispersed in polymeric matrices, leads to the formation of only one coloured photoisomer that returns quickly, and completely, to the uncoloured state in few seconds/minutes. [4]. By eliminating the slow decay photoisomer we can thus improve the ON/OFF switching performance of these lenses

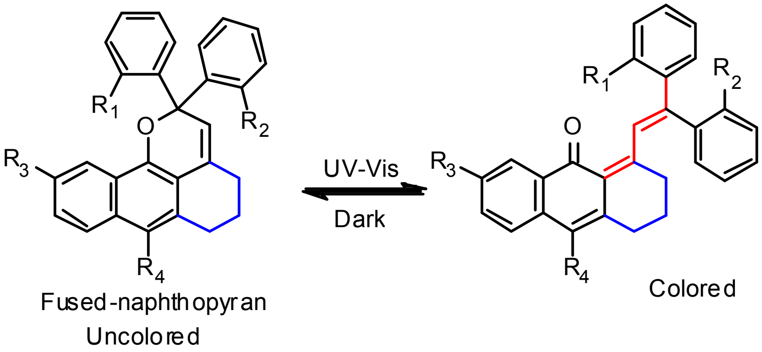

Figure 1. Photochromic Equilibrium for a Fused-Naphtho[1,2-b]pyran

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A new route to thiazolo[5,4-c]isoquinolines

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Thiazoloisoquinolines are heteroaromatic compounds that can exist in various isomeric structures that differ by the relative orientation of the thiazole ring regarding the isoquinoline moiety [1]. The potential of some of these isomers has been investigated in the medicinal field, namely as antiinflammatory agents [2].

Thiazolo[5,4c]isoquinolines were synthesised for the first time in 1966, through a multi-step procedure that ultimately involved the acidcatalysed cyclisation of 4-amino-3-thiocyanato-isoquinolines [3]. It is quite interesting to note that these compounds immediately found application as stabilizers and fog inhibitors for photographic silver halides [4].

In 1975 Winters and Di Mola found that, at very high temperatures (270–280 °C), some electronrich heterocyclic compounds containing urea units can undergo a thermal cyclization on the vicinal phenyl group to afford isoquinolinones [5]. Three years late the same authors patented the synthesis of both pyrazolo[3,4-c] and thiazolo[5,4-c] isoquinolines, and their potential application as antiinflammatory, CNS-depressant and anti-anxiety agents [6]. As far as we know, since then nothing else has been reported in the literature related to this type of compounds.

In this communication we describe a one-step approach to 2arylthiazolo[5,4c] isoquinolines. The synthesis, structural characterization and the properties of these compounds will be discussed.

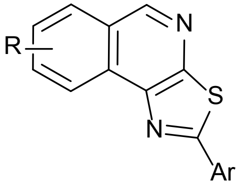

Fig.1. Basic-structure of the thiazolo[5,4-c]isoquinolines synthesised in this work.

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Halogen bonding and luminescence in supramolecular architectures

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Halogen bonding (XB) is a supramolecular interaction that plays an important role in diverse fields including chemistry, biology and crystal engineering. After hydrogen bonding (HB), XB are the most studied weak interactions. These two types of intermolecular bonding have received much attention from the scientific community because their competition or complementarity determines the crystal packing of organic halogen compounds. The development of new synthons using XB is a difficult but important step in the design of supramolecular architectures.[1]

In the search for efficient all-organic solid-state luminophores, XB that promote the inter-systems crossing through the heavy atom effect and, thus, induce phosphorescence have emerged as an important factor.[2] The combination of XB and the aggregation-induced emission enhancement (AIEE) effect that promote fluorescence in solid state has been our strategy to develop new luminescent organic materials.[3,4]

Here, we present a case study combining these two approaches. We have designed, synthesized and characterised three different families of organic compounds (chalcone, benzophenone and benzimidazole derivatives) decorated with electron-donating substituents and halogen atoms. The occurrence of XB, its complementary or competition with HB, the contribution of both in determining the compound's crystal packing, and their influence on the luminescence properties will be discussed.

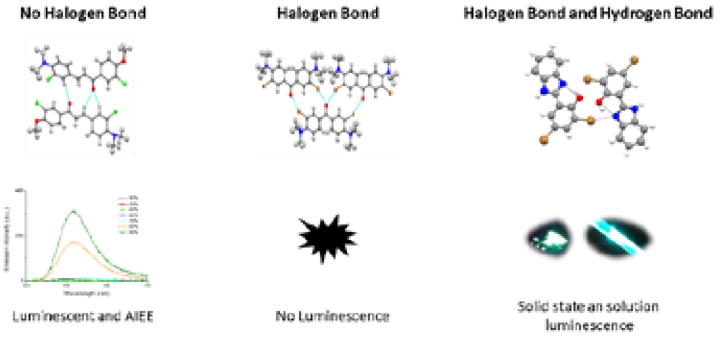

Fig.1. Study of halogenated chalcones, benzophenones and benzimidazoles

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Novel porphyrin-flavone conjugates: synthesis and photophysical characterization

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Flavonoids are a large group of secondary metabolites present in many fruits and vegetables and with interesting pharmacological effects [1]. Although 2-styrylchromones are less common in nature, their pharmacological effects are also remarkable [2]. The possibility to combine this type of molecules to porphyrins, known as good photosensitizers (PS) for Photodynamic Therapy (PDT), can be considered an innovative and promising alternative in the development of effective PSs [3,4].

Therefore, the aim of this work was to construct novel porphyrin-flavone conjugates from porphyrins and flavones or 2-styrylchromones and to evaluate their potential as PSs for PDT.

In this communication will be reported the synthetic strategy used and the structural characterization of new conjugates obtained from 5,10,15,20-tetrakis(pentafluorophenyl) porphyrin and the chromones **1**-**3**. The analysis of their photophysical properties will be also a subject of discussion.

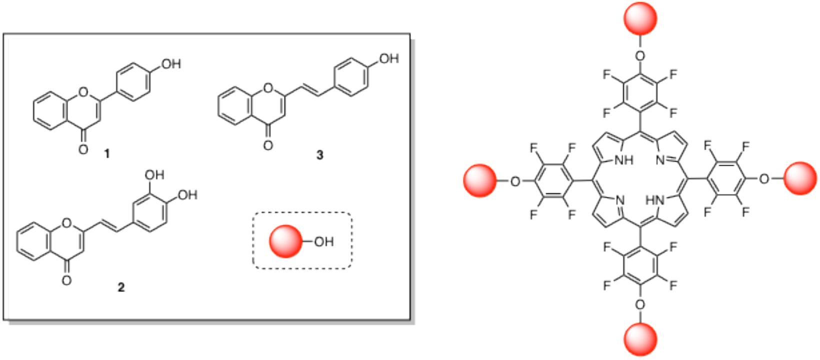

Fig.1. General structure of the porphyrin-flavone conjugates obtained from the flavone derivatives **1-3.**

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New routes for the synthesis of marine xanthones with antimicrobial activity

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The marine environment has been an important source of new chemical entities with relevant biological activities [1]. In the last years, several new marine natural products have been discovered showing biological activities such as, antitumor, antidiabetic, anticoagulant, anti-inflammatory, and particularly antibiotic and antifungal [2]. The need for new antimicrobials is a very important issue, mostly due to the increasing emergence of resistant bacteria and fungus. Marine environment is an excellent source of novel hits/leads against pathogenic agents, that complement and constitute alternatives to the existing therapy [3].

From the different marine natural products with antimicrobial activity, substances with the xanthone scaffold are quite promising [4]. Extraction from marine resources provides low quantities of the active xanthone derivatives. To overcome this problem, the total synthesis is the way to get enough quantities to study and to use these bioactive substances.

The aim of this work was to synthesize new marine derived xanthones with antimicrobial activity. Total synthesis of the xanthone derivatives was performed through benzophenone route, applying new synthetic strategies. Important building blocks and key intermediates were also synthetized leading in addition to the desired compounds. Different methodologies were applied in order to achieve shorter reactions times, more selectivity, lower costs and less environmental damages. All the synthetized compounds were purified, and their structures elucidated using chromatographic and spectrometric techniques (FTIR, GC-MS and NMR (^{1}H,^{13}C, HSQC and HMBC)).

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Bioguided study in the search for natural antifungal components in the Brazilian Biomas

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A bioguided phytochemical study of an *M. caesalpiniifolia* [1,2] leaf extract with antifungal activity allowed the elucidation of twenty eight compounds. Apigenin-6-*C*-β-boivinopyranoside(**1**); apigenin-8-*C*-β-oliopyranoside(**2**); (E)-6-(2-carboxyethenyl) apigenin(**3**); (E)-8-(2-carboxyethenyl)apigenin(**4**) and 7,5”-anhydroapigenin 6-*C*-α-(2,6-dideoxy-5-hydroxy-*arabino*-hexopyranoside (**5**) have not been described previously. The structures of the new compounds were determined by comprehensive spectroscopic analysis, including one- and two-dimensional NMR techniques and mass spectrometry. The compound **3**, showed promising activity and selective for *C. krusei* (15 μg/ml), which has also presented resistance to the azoles. On the other hand, the association of mayor components,3-*O*-D-β-glucopyranosylsitosterol (**6**) and ethylgallate (**8**) was synergistic against *C. krusei,* especially the IC values of the compound **6**, which suffered reduction of more than 100 times.

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Synthesis of new quercetin-based derivatives with potential antioxidant activity

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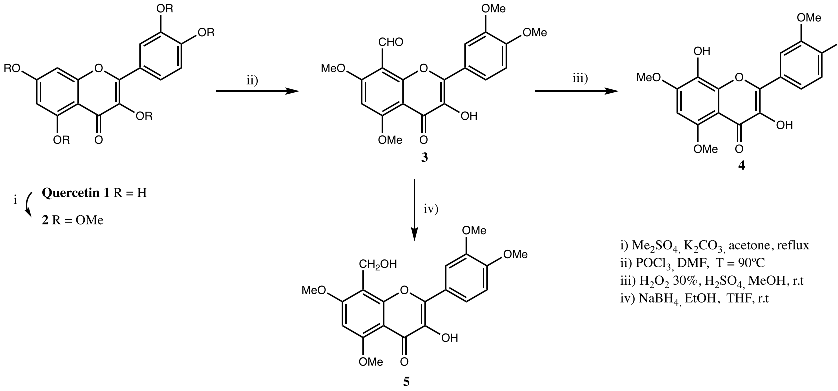
Flavonols, as polyhydroxylated phenolic substances, present important biological and pharmacologic activities strongly dependent on their structural features, namely the degree of hydroxylation or other substitutions and conjugations. Selective hydroxylation can thus permit the establishment of new structure-activity relationships. Quercetin (**1**) behind its natural occurrence and being one of the most abundant flavonols in plants and plant-derived food, is well-known for its prominent antioxidant capacity.
Herein we will present the results on the synthesis of novel quercetin-based derivatives using well-known transformations allowing the introduction of new hydroxyl groups (Figure 1). Generally, all the transformations were achieved in good yields and all products have been fully characterized by ^{1}H and ^{13}C NMR and mass spectrometry.



i) Me_2SO_4, K_2CO_3, acetone, reflux
ii) $POCl_3$, DMF, T = 90ºC
iii) H_2O_2 30%, H_2SO_4, MeOH, r.t
iv) $NaBH_4$, EtOH, THF, r.t

Figure 1: Developed synthesis to novel quercetin-based flavonols

ACKNOWLEDGEMENTS: Thanks are due to University of Aveiro, FCT/MEC for the financial support to the QOPNA research Unit (FCT UID/QUI/00062/2013) through national funds and where applicable co-financed by the FEDER, within the PT2020 Partnership Agreement, and also to the Portuguese NMR Network. Thanks are also due to project AgroForWealth (CENTRO-01-0145-FEDER-000001), funded by Centro2020, through FEDER and PT2020. Sónia Pires thanks to AgroForWealth project for her Pos-Doc grant (BPD/UI89/4413/2017).

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Halogen-exchange and amination of chlorinated thioxanthones

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Thioxanthones are heterocyclic compounds with a dibenzo-γ-thiopyrone scaffold. Their capability to display multiple biological properties, as well as their proneness to chemical modifications, make thioxanthones privileged structures [1]. Relevant biological activities which have been described for these compounds are antischistosomal, antitumor, and efflux pump inhibition [2].

Taking a chlorinated thioxanthone as starting material, halogen exchanges were attempted, in order to improve yields of following reactions. Chlorine exchange by bromine was performed [3] using potassium bromide in the presence of phosphoric acid, nitrobenzene at 200° C for 24 hours. The reaction was then washed and extracted, and repeated for another 24 hours. Chlorine exchange for fluorine was also attempted [4], in the scope of structure-activity relationship studies, but only traces of the wanted derivative were obtained.

The amination of thioxanthones was performed using a copper-catalysed Ullmann type C – N coupling (**Figure 1**). With this, we expect to obtain a library of novel aminated thioxanthones with potential antitumor activity and able to inhibit efflux pumps and revert multidrug-resistance.

The structures of the synthetized compounds were determined by ^{1}H, ^{19}F, and ^{13}C NMR. Furthermore, GC-MS was used to identify and quantify the obtained brominated thioxanthone.

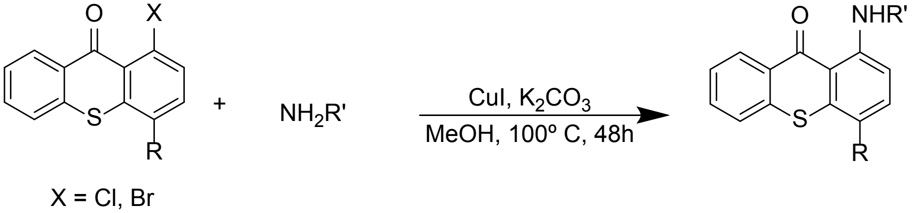

Fig. 1 Synthetic approach used for the synthesis of aminated thioxanthones.

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Synthesis and characterization of ammonium-photosensitizers

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QUÍMICA ORGÂNICA

POSTER

Nowadays, the development of new photosensitizers (PSs) for photodynamic inactivation of microorganisms (PDI) has been considered a main goal in photobiology due to the increasing microbial resistance to actual antibiotics. In the PDI approach the activation of the PS by light in the presence of oxygen mediates the production of cytotoxic reactive oxygen species (ROS) responsible for microbial cell damage of vital components [1]. In this important alternative to current microbial infections the presence of positive charges in the PS core showed to be an important requirement for an efficient inactivation of Gram-negative bacteria without the presence of membrane disrupting agents [2,3]. Taken this into account, in this communication it will be reported and discussed the synthesis, structural and photophysical characterization of cationic porphyrins (**1**, **1a**) and chlorins (**2**, **2a**) as free-bases and coordinated with zinc(II) bearing ammonium substituents.

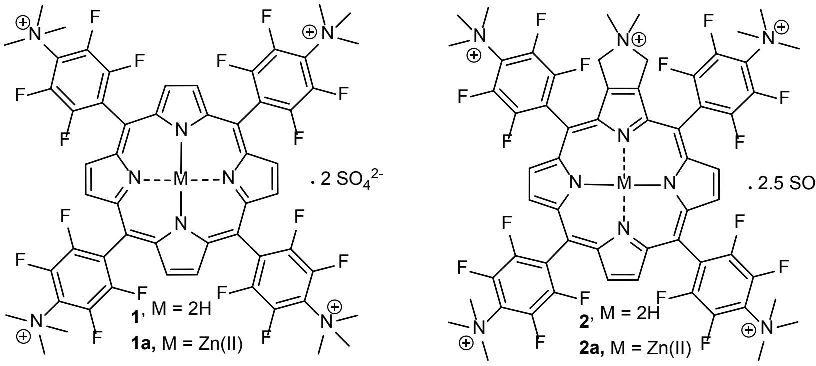

Figure 1: Structures of cationic porphyrins (1, 1a) and chlorins (2, 2a) bearing ammonium substituents.

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New pyrrole-based fluorophores: Synthesis, structures and luminescent properties

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Pyrroles scaffold is broadly found in natural products and it is known to be involved in many biological processes [1]. Fluorescent properties are also found in some derivatives of pyrrole [2]. Moreover, they can be used as molecular probes or biomarkers, and are commonly used as intermediates in the synthesis of pharmaceuticals, agrochemicals, dyes, photographic chemicals, and perfumes. As a consequence, a great attention has recently been devoted to the synthesis of pyrroles [3].
Herein we report the synthesis and characterization of five new pyrrole derivatives, bearing phenyl rings on the positions 1, 2 and 4, with electron-donating groups at the periphery. Photophysical properties were also evaluated. Their crystal structure has been also studied in order to have a clear understanding of the properties of the molecules in the crystalline state.

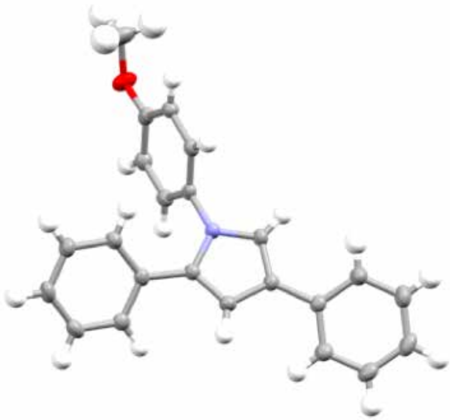

Fig.1. Molecular structure of 1-(4-methoxyphenyl)-2,4-diphenyl-1H-pyrrole.

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Click chemistry synthetic approach for discovery of new potential bioactive chalcones

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Chalcones have long been recognized for their wide range of biological activities [1]. Click-chemistry approaches based on Huisgen's cycloaddition reaction are particularly attractive and have received enormous attention due to their utility in preparing compounds with diverse applications, especially in drug discovery [2]. The 1,2,3-triazoles formed by this methodology are very stable under both metabolic and chemical degradations. They also show diverse biological activities such as anticancer, antibacterial, and antiviral [3].

In the present work we propose a versatile 'click-based' approach to synthesize potential bioactive chalcone derivatives. Firstly, chalcone derivatives were synthesized by Claisen Schmidt condensation of previously obtained propargylated acetophenones with substituted benzaldehydes in basic medium. Afterward, these compounds were submitted to microwave assisted Copper (I)-catalyzed azide alkyne cycloaddition with diverse azides in order to obtain the desired triazole derivatives. The structure of all synthesized compounds was established by NMR techniques.

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#Authors contributed equally to this work.

Initial steps of the total synthesis of neofiscalin A, a natural antimicrobial alkaloid

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Neofiscalin A (**1**) is an alkaloid containing a pyrazino[2,1-*b*]quinazoline-3,6-dione core linked to an indole moiety, that was isolated from the soil and marine fungus *Neosartorya siamensis*. This secondary metabolite showed potent antimicrobial activity against methicillin-resistant *Staphylococcus aureus* (MRSA) and vancomycin-resistant *Enterococcus faecalis* (VRE) as well as exhibited an enormous potential as an antibiofilm agent. [1]

Herein, we present the initial synthetic steps towards the total synthesis of neofiscalin A (**1**) starting with the synthesis of the tryptophan-derived scaffold **2** [2], which can then be coupled to the anthranilic acid (**3**) and the protected L-valine (**4**) through a microwave-promoted three-component one-pot reaction [3], obtaining the desired neofiscalin A (**1**).

Synthetic details as well as structure characterization (by 1D and 2D NMR studies) of the new synthesized compounds will be presented and discussed.

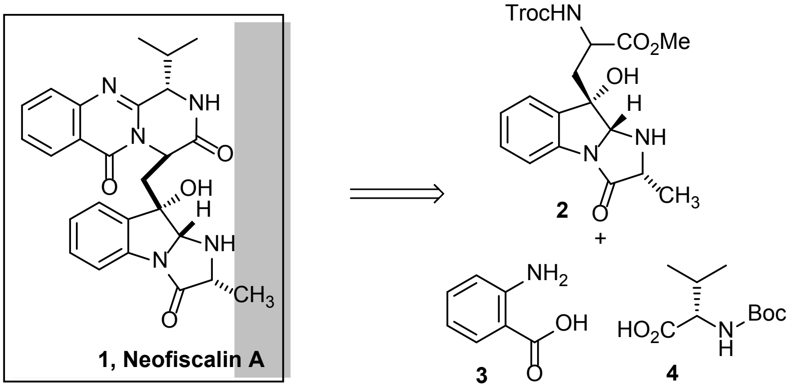

Fig.1. Retrosynthesis of neofiscalin A.

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Synthesis, characterization and photophysical properties of thioglycerol-porphyrins and -phthalocyanines

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Porphyrins (Pors) [1] and phthalocyanines (Pcs) [2] belong to a class of compounds with high molar absorptivity and fluorescence quantum yields, which can be used as building units to design (multi)functional Metal-Organic Frameworks (MOFs). The structural modification of Por and Pc cores can promote good electron-donating materials, attending to the central metal ion and to the peripheral substituent groups [3]. In this communication we report the synthesis and spectroscopic characterization of novel tetra-substituted thioglycerol Por **1**, and tetra- and octa-substituted thioglycerol Pcs **2** and **3**, respectively (**Figure 1**).

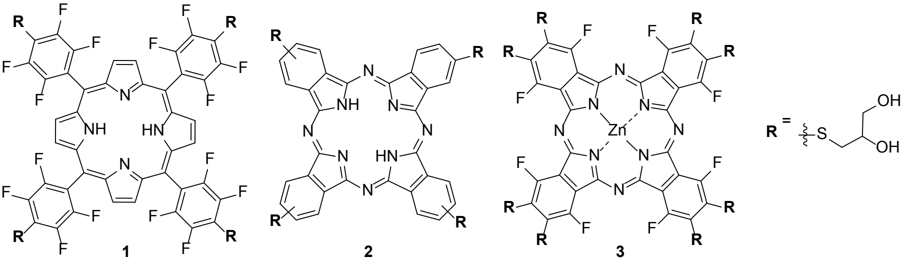

Figure 1: Thioglycerol Por 1 and thioglycerol Pcs 2 and 3.

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Synthesis of dipyrrolic compounds for fluoride detection

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Over the past decades, considerable attention has been devoted to the synthesis and development of new analytical methods for the reliable detection of target species such as anions [1]. The detection, differentiation and visualisation of these entities are crucial challenges for the design of selective optical chemosensors [1]. Nonetheless, the synthesis of materials that behave as selective optical chemical sensors is still a challenge in organic chemistry. In this area, pyrrole units are particularly attractive since the N–H protons remain in place over a wide pKa range making possible their use as a hydrogen bond donor group within a large pH window. Also, the reasonably easy functionalization and incorporation into elaborate cyclic and acyclic systems are reasons to have into account when synthesising this kind of receptors [2]. More recently, attention has turned towards acyclic receptors using a push-pull chromophore approach on the **β**-position of pyrrolic moieties giving rise to a colourimetric effect towards different anions [3]. Herein, we report a methodology to functionalize the α-positions of dipyrromethane compounds through Knoevenagel reactions with indane-1,3-dione and malononitrile. The corresponding products (1 and 2) were evaluated as optical anion chemosensors and revealed high selectivity for fluoride (Figure 1).

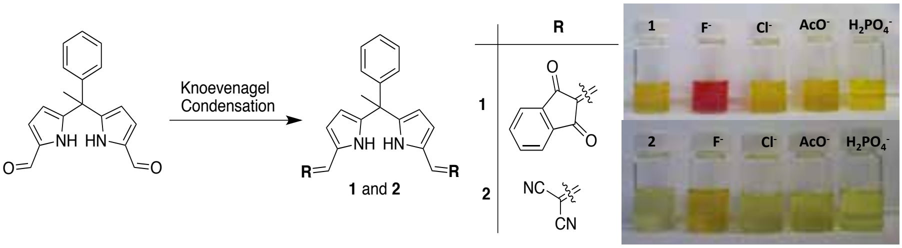

Fig.1. Preparation of dipyrromethanes and colour variation upon addition of fluoride as tetrabutylammonium salts.

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Desenvolvimento de Novos Conjugados do GPE com Propriedades Potencialmente Sinérgicas

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As doenças neurodegenerativas resultam da degeneração progressiva e/ou morte dos neurónios, tendo como consequência perturbações ao nível do movimento (ataxias) ou no funcionamento cerebral, causando demência, sendo que a estimativa para 2020 é de existirem cerca de 48,1 milhões de pessoas no mundo com demência.[1]

O Ácido Glicil-L-Prolil-L-Glutâmico (GPE, *Fig. 1*), é um neuropéptido obtido pela clivagem do *N*-terminal do fator de crescimento insulínico tipo 1 (IGF-1) localizado no cérebro.[2] Embora o seu *modus operandi* permaneça desconhecido, estudos *in vitro* e *in vivo* demonstraram que este tripéptido é capaz de estimular a libertação de acetilcolina e de dopamina, proporcionando ainda neuroprotecção contra diversos agentes neurotóxicos, estando por isso patenteado pela farmacêutica *Neuren* com o nome *Glypromate*®. No entanto, o GPE apresenta propriedades farmacocinéticas desfavoráveis, nomeadamente baixa absorção oral, razão pela qual este potencial fármaco não avançou além da fase III de ensaios clínicos.[2,3]

Assim, este trabalho contém como principais objetivos a síntese e a avaliação biológica de novos conjugados do GPE, aumentando a sua lipofilicidade pelo encobrimento dos grupos polares expostos e pelo acoplamento de aminas neuroativas de forma a criar um potencial efeito sinérgico de ação neuroprotetora e ainda tornar os conjugados finais mais estáveis, proporcionando assim um aumento da permeabilidade através da barreira hematoencefálica destes compostos.

Uma vez que se sabe que o GPE é metabolizado por carboxipeptidases,[4] foi inicialmente realizada a funcionalização do glutamato no ácido carboxílico, na cadeia lateral ou na posição-a, realizando um acoplamento peptídico com o aminoindano (**a**), amantadina (**b**) e memantina (**c**) (*Fig. 1*). De seguida, os glutamatos funcionalizados foram acoplados aos restantes resíduos constituintes do GPE usando um método de síntese peptídica *One-pot* desenvolvido pelo nosso grupo de investigação.

Os conjugados propostos (12 compostos finais) foram sintetizados com sucesso estando atualmente na etapa dos ensaios biológicos no i3S, com a finalidade de determinar a atividade neuroprotetora utilizando o teste de viabilidade celular MTT, aplicado em células CADs sob condições de *stress* oxidativo induzido por H_2O_2.

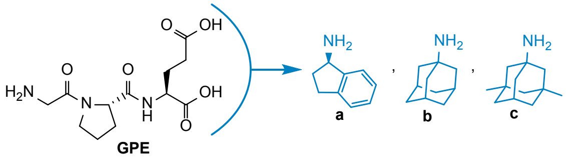

Fig.1. GPE e aminas bioativas utilizadas para a síntese de conjugados.

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QUÍMICA ORGÂNICA

POSTER

Identification of organic compounds, beyond fatty acids, from terrestrial and aquatic species by gc-ms

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Gas chromatography coupled to mass spectrometry (GC-MS) is a sensible, reliable and robust chromatographic technique that allows the separations, identification and quantification of a great diversity of secondary metabolites in complex extracts from aquatic and terrestrial species [1]. Sample processing for GC-MS-based metabolite profiling include solvent extraction, concentration to dryness, derivatization and consecutive analysis. Detectable compounds include very often many secondary metabolites [like fatty acids (short and long fatty acids, saturated, MUFA and PUFA), fatty alcohols, alkanes and sterols] whose fragmentation patterns are widely described in the literature and whose identification is greatly facilitated by the use of commercial or public available MS searchable databases and libraries.

However, some species contain a significant amount and diversity of other constituents such as alkaloids, halogenated compounds, sugars, sugar alcohols/acids, aminoacids, terpenoids, etc whose identification constitutes a major challenge. In these cases, a careful and thorough study of their mass spectra and fragmentation mechanisms is often necessary.

We will describe own results from plant and seaweeds research to exemplify the applicability of GC-MS in the identification of alkaloids, halogenated compounds and other organic natural compounds beyond the fatty acids.

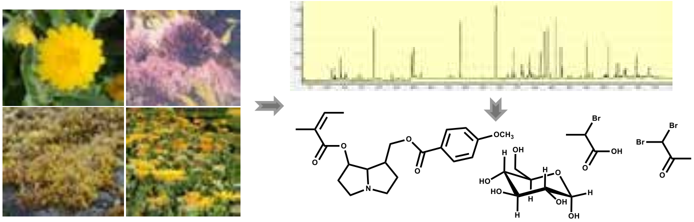

Figure 1. GC-MS analysis of Calendula and Asparagopsis secondary metabolites.

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Aggregation-induced emission enhancement of chiral boranils

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Four-coordinate organoboron complexes have emerged as new materials for optoelectronics including organic light-emitting diodes (OLEDs). For applications in OLEDs, although a large number of red and green emitters have been developed, showing good electroluminescence performance, efficient blue emitters are still missing, in particular, deep blue emitters for electroluminescent devices.[1]

A large number of four-coordinate organoboron complexes exhibit excellent fluorescence properties in dilute solutions, however, examples of solid-emissive dyes are limited because of aggregation-caused quenching (ACQ). Nevertheless, some dyes present a behavior opposite to ACQ, i.e., aggregation-induced emission (AIE) or aggregation-induced emission enhancement (AIEE).[2] In such cases, the dyes exhibit strong fluorescence upon aggregation. Based on many theoretical and experimental studies, the restriction of intramolecular rotation (RIR) has been proposed as the main cause for this phenomenon. These materials may emit in the solution and aggregate state and for these reasons they are of much interest.[3]

The very few examples of chiral boron complexes reported are based on polymeric systems.[4] In our work, chiral ligands were introduced into the difluoroboron complexes and, herein, the synthesis and comparative study of two enantiomeric boranils and a similar but achiral boranil are presented. All three compounds exhibit a bright blue fluorescence in both solution and solid state and present a strong AIEE effect, which has been rationalized through the study of their crystalline structures.

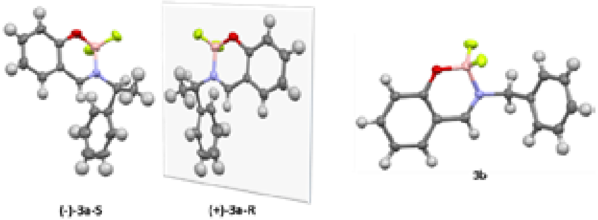
(-)-3a-S (+)-3a-R 3b

Fig.1. – Structure of compounds **(-)-3a-*S***, **(+)-3a-*R*** and **3b** revealed by single-crystal X-ray diffraction.

ACKNOWLEDGEMENTS: Thanks are due to University of Aveiro, FCT/MEC for the financial support to the QOPNA research Unit (FCT UID/QUI/00062/2013) and CICECO–Aveiro Institute of Materials (POCI-01-0145-FEDER-007679; FCT–UID/CTM/50011/2013), through national funds and where applicable co-financed by the FEDER, within the PT2020 Partnership Agreement, and also to the Portuguese NMR Network. This work was also supported by the Integrated Programme of SR&TD "pAGE – Protein aggregation Across the Lifespan" (reference CENTRO-01-0145-FEDER-000003), co-funded by Centro 2020 program, Portugal 2020, European Union, through the European Regional Development Fund. PV thanks the FCT for a doctoral grant (SFRH/BD/99809/2014).

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Síntese e Avaliação da Fotocitotoxicidade de Corantes Aminoesquarílicos Conjugados com Colesterol

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Atualmente, uma das principais causas de morte são as doenças de foro oncológico. As terapias convencionais (cirurgia, radioterapia e quimioterapia) têm como inconveniente a falta de seletividade que resulta, por norma, em efeitos secundários diversos. Assim, existe a necessidade de explorar terapêuticas alternativas, surgindo desta forma a terapia fotodinâmica (PDT, do inglês, *Photodynamic Therapy)* [1]. Esta tem por base a fotocitotoxicidade de diferentes fotossensibilizadores (FS) que se acumulam, preferencialmente e de forma seletiva nas células tumorais, e que surge apenas após excitação com luz de comprimento de onda adequado [2].

A PDT tem como base processos fotodinâmicos, em que a luz absorvida pelo fotossensibilizador gera um estado eletrónico excitado que, por sua vez, pode transferir a sua energia para o oxigénio no estado fundamental, produzindo assim oxigénio singuleto citotóxico. Este, dá origem a uma cascata de processos bioquímicos conducentes à morte das células tumorais [3]. Uma classe de compostos que tem suscitado bastante interesse como FS são os corantes esquarílicos devido às propriedades específicas que apresentam [4].

Neste trabalho, foram sintetizados alguns corantes aminoesquarílicos catiónicos derivados do 2-metilbenzotiazole e da 2-metiquinolina, adequadamente substituídos no anel central com uma molécula de colesterol (figura1), como estratégia para potencialmente melhorar a permeabilidade celular, e feita a respetiva caracterização estrutural. A (foto)citotoxicidade dos corantes sintetizados foi testada *in vitro* em várias linhas celulares tumorais humanas (carcinomas da mama, pulmão, cervical e fígado) e comparada com a dos corantes isentos de colesterol. A citotoxicidade dos corantes também foi avaliada numa linha de células primárias não tumorais de fígado de porco, na presença e ausência de luz. Foi igualmente avaliada a capacidade de produção de oxigénio singuleto dos corantes sintetizados. Assim, neste trabalho pretendeu-se desenvolver novos compostos com absorção no IV próximo e boa permeabilidade celular que possam ser potenciais fotossensibilizadores para terapia fotodinâmica.

Os resultados obtidos mostram que os corantes sintetizados não apresentam praticamente citotoxicidade no escuro, nas concentrações usadas; contudo, sob radiação os corantes que possuem o elemento de reconhecimento celular não parecem mostrar desempenho significativamente melhor que o dos mesmos corantes sem o colesterol.

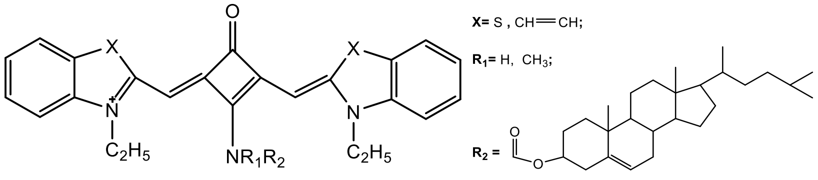

Fig.1. Estrutura química dos corantes sintetizados.

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Synthesis and characterization of *tris(*3-Hydroxy-4-pyridinonate) gallium(III) complexes

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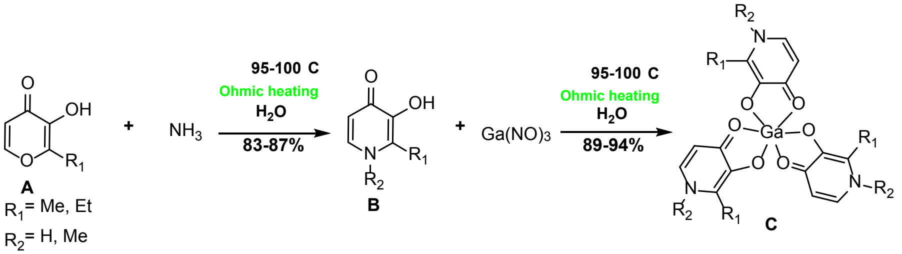
In the past decade our group has worked on the design and synthesis of chelators and metal chelates for biomedical, environmental and agriculture applications. In the context of agriculture applications, Fe(III)-chelates have proved to be useful to correct Iron Deficiency Chlorosis (IDC) in plants.[1] We recently investigated and compared three specific Fe(III)-chelates, namely $[Fe(mpp)_3]$, $[Fe(etpp)_3]$ and $[Fe(dmpp)_3]$ and analysis of the biological response, compound $[Fe(mpp)_3]$ proved to be a strong candidate as a new iron fertilizer to correct IDC. In order to understand the mechanism of action of these complexes, we want to see how the chelates interact with liposomes, usually accepted as simple model membranes. NMR spectroscopy is a useful methodology for studying inter-molecular interactions, such as association processes between drugs and the cellular membrane.[2][3] For that reason and since Fe(III)-chelates are paramagnetic, we synthesised the isostructural and diamagnetic Ga(III)-chelates to perform the NMR studies.

In this work we report the synthesis of the Ga(III) complexes (scheme 1) which includes two steps: the ligand synthesis (when necessary), **B**, and the complexation, **C**. The Hdmpp (R_1, R_2=Me) is a commercial ligand and the other ligands [Hmpp (R_1=Me, R_2=H) and Hetpp (R_1=Et, R_2=H)] are synthesised through the conversion of **A** into **B** by a nucleophilic attack of NH_3, followed by ring opening, elimination of water and ring closure. For this synthesis, Ohmic heating was used as more efficient heating method (previous studies). [4][5] Complexes were characterized by HR-MS, UV/Vis, elemental analysis and ^{1}H-NMR in D_2O solution (diffusion-ordered ^{1}H-DOSY and spin–lattice relaxation rates (T1)).



Scheme 1 - Synthesis of 3-Hydroxy-4-pyridinone Gallium(III) Chelates.

ACKNOWLEDGEMENTS:UID/QUI/50006/2013-POCI/01/0145/FEDER/007265;PTDC/AGRPRO/3515/2014-POCI-01-0145-FEDER-016599.

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Towards the synthesis of a polyoxygenated xanthone

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Several approaches towards the synthesis of polyoxygenated xanthones have been reported [1], based on the interested associated to the diversity of their biological activities. From the more usual methods, Friedel–Crafts acylation/cyclization protocols are the most commonly used. Based on previous structure-activity relationship studies, a polyhydroxylated xanthone was proposed as a promising antioxidant agent, and its synthesis was attempted through three differing approaches: i) via a benzophenone intermediate, ii) via the Grover, Shah and Shah (GSS) method and via Eaton's reaction (**Scheme 1**). These three approaches failed to yield compounds with the wanted scaffold. Herein, we present two synthetic pathways towards the synthesis of the polyoxygenated xanthone (**Scheme 1**): iii) via an ester intermediate following a Smiles rearrangement and iv) through acyl radical intermediates.

Structure elucidation of the intermediates was established by infrared (IR) and nuclear magnetic resonance (NMR). Both intermediates and the target compound will be assessed for their antioxidant activities.

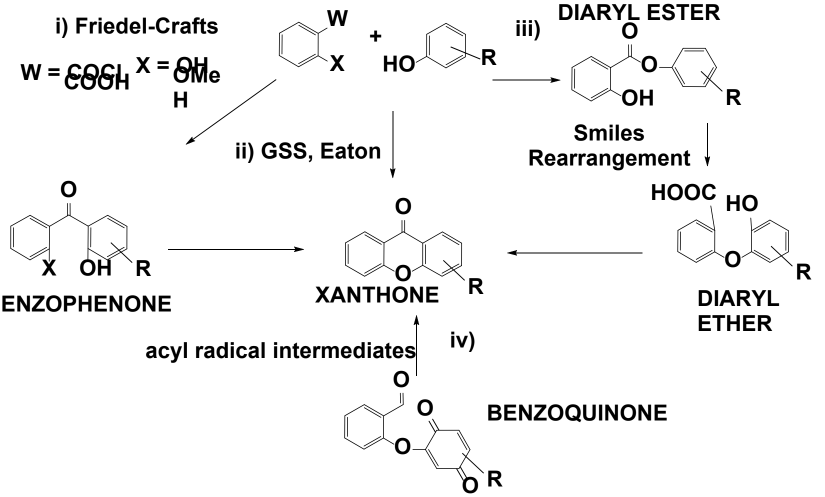

Fig.1. Synthetic pathways to obtain the target xanthone.

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Synthesis of functionalized tetrahydroquinolines, and its further transformation into hexahydropyrroloquinoline-2,3-diol by aminocyclization.

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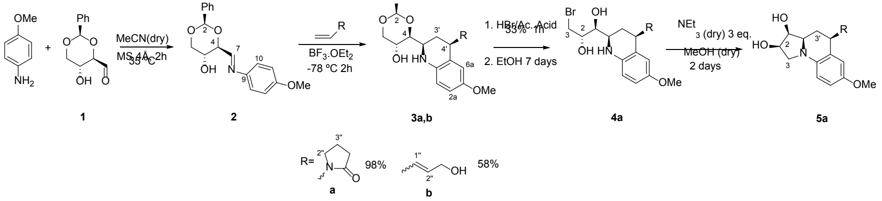
The main objective of this work was the synthesis of a new tetrahydroquinoline (THQ) by reaction of imine 2 obtained from reaction of a D-erythrose aldehyde (1) derivative and *p*-anisidine with 1-vinyl-2-pyrrolidone or 2,4-pentadien-1-ol. The adducts (3) were obtained by inverse electron-demand Diels-Alder cycloaddition, in presence of Lewis acid, which was then subjected to acidic hydrolysis affording the respective triol in protonated and deprotonated forms. Various attempts have been made to cyclize the triol with formation of a five-membered heterocyclic ring by bromination of terminal hydroxyl group (4a) and intermolecular cyclization (5a). Final compounds may represent of possible candidate to Golgi α-mannosidade II inhibitor, a biological target for anticancer agent, due to structure similarity with swainsonine. All products were characterized by NMR spectroscopy and mass spectrometry.



Scheme 1: Synthesis of THQ adducts.

Avaliação química da *Phyllanthus welwitschianus* Müll.Arg

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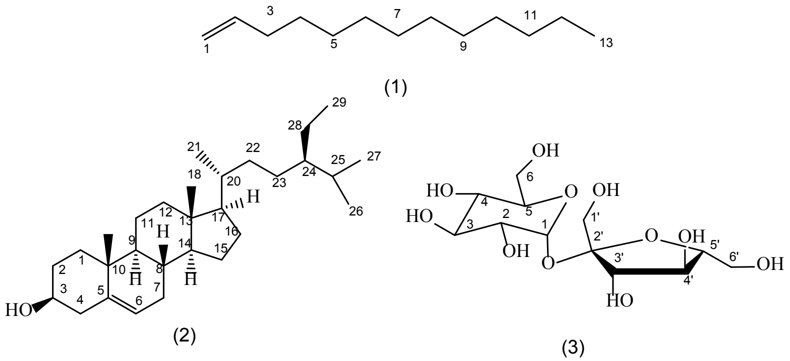
Em Angola, como em outros países, as populações dependem da medicina tradicional para assegurar cuidados de saúde. A flora Angolana é rica em plantas medicinais, mas o estudo das mesmas é muito limitado.

A *Phyllanthus welwitschianus* Müll.Arg pertence à família Phyllanthaceae [1] e em Angola as suas folhas são usadas como curativo para feridas [2].

As folhas da planta foram recolhidas, secas e reduzidas a pó, esse material foi depois macerado em metanol durante uma semana e o metanol eliminado por evaporação, o processo de extração foi repetido 5x. Uma parte do extrato de metanol foi depois submetido a cromatografia em coluna tendo-se obtido 10 frações de diferentes polaridades.

As diferentes frações foram sucessivamente cromatografadas e como resultado foram obtidos três compostos. O tridec-1-eno foi obtido na fração de hexano-acetato de etilo 9:1, o b-sitosterol foi isolado a partir da fração hexano-acetato de etilo 1:1 e por último a sacarose foi obtida depois de tratamento da fração acetato de etilo-metanol 1:1.

Os compostos obtidos foram caracterizados por métodos espectroscópicos de IV, RMN 1D e 2D e comparados com dados bibliográficos [3,4,5].



(1)

(2)

(3)

Fig.1. Compostos isolados na Phyllanthus welwitschianus.

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Preparação das formas enantiomericamente puras do ácido 2-azanorbornano-3-exo-carboxílico através de reacções de aza-Diels-Alder assimétricas

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Neste trabalho é apresentado um estudo integrativo para a preparação do ácido 2-azanorbornano-3-exo-carboxílico nas suas formas enantiomericamente puras através de reações de aza-Diels-Alder diastereoselectivas usando dois auxiliares quirais: (-)-8-fenilmentol (8PM) e o (+)-8-fenilneomentol (8PnM).

O passo-chave baseia-se na transproteção do grupo 1-feniletilo pelo grupo terc-butiloxicarbonilo (Boc) usando Pd/C e H2 para os dois cicloadutos precursores diastereoisomericamente puros. Em termos mecanísticos aceita-se que o processo de transproteção em condições redutivas ocorre em duas etapas: 1) N-C hidrogenólise, formando a amina secundária e 2) proteção da amina resultante através do tratamento o dicarbonato de di-terc-butilo (Boc2O), para formação do respetivo carbamato.1,2 Contudo, os resultados experimentais obtidos excluem este cenário uma vez que na ausência de Boc2O a hidrogenólise não ocorre.

Experiências in silico realizadas para as reações de hidrogenólise assistida por Boc2O suportam a formação de um carbamato carregado como sendo um provável intermediário para o mecanismo de transproteção.

Conceptualmente, estes resultados sugerem um mecanismo complementar para a transproteção do grupo 1-feniletilo pelo grupo Boc sob condições redutivas oferecendo uma alternativa mais suave para obtenção de aminas secundárias N-Boc protegidas a partir de aminas terciárias impedidas, destacando o papel do Boc2O neste processo.

A partir dos cicloadutos N-Boc protegidos foi possível obter-se as correspondentes aminas secundárias sob a forma de trifluoroacetatos de amónio, aliaviando o impedimento estérico para correspondente recuperação dos auxiliares quirais 8PM e 8PnM e, consequentemente, a formação dos dois equivalentes enantioméricos do ácido 2-azanorbornano-3-exo-carboxílico.

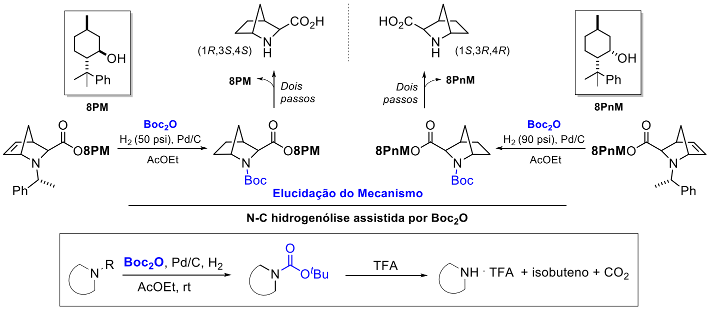

Fig.1. Preparação dos ácidos 2-azanorbornano-3-exo-carboxílicos enantiomericamente puros evidenciando o mecanismo de N-transproteção via carbamato carregado.

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METAL-ORGANIC FRAMEWORK BASED MATERIALS TWOARDS SUSTAINABLE PROCESSES

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Metal–organic frameworks (MOFs), also known as porous coordination polymers, have been proven to be outstanding candidates for bridging the gap between zeolites and mesoporous silica. MOFs are formed by metal ions/clusters and organic linkers and have captured widespread interest, achieving an explosive development over the past two decades. The crystalline nature, structural diversity, and tailorability, as well as ultrahigh surface area make MOFs find their potential applications in diverse areas, such as gas sorption and separation, chemical sensing, proton conductivity, biomedicine and catalysis. However, in numerous MOFs the structural stability and performance limits their practical applications, relatively to other porous materials. Consequently, distinct strategies have been used to prepare MOF based materials and overcome these disadvantages.[1, 2]

The modification and derivation of MOFs, and their utilization as platform, template or subtract opens up an avenue to the preparation of diversified porous materials with unique advantages in comparison to traditional pristine materials. Following our interest in the development and application of functional MOFs towards sustainable processes an overview of interesting MOF-based materials prepared and investigated in our research group is reported.

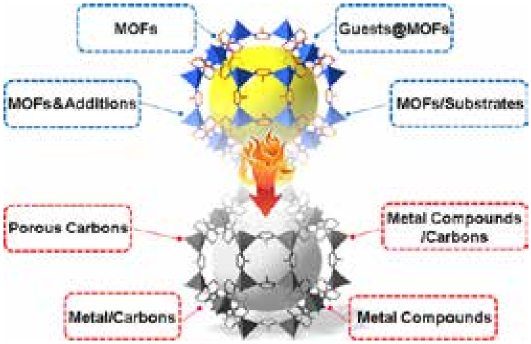

Fig.1. Illustration of the preparation of diverse porous materials from MOFs and MOF-based composites as templates/precursors. [2]

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Utilização de uma Metodologia Superfície-Resposta para Maximizar a Extração de Ácido Rosmarínico

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O crescente interesse dos consumidores pelos alimentos que consomem aliado à maior taxa de literacia, está a revolucionar a indústria alimentar, nomeadamente no sentido de um menor processamento de alimentos e na utilização de aditivos alimentares de origem natural. Entre esses aditivos, o ácido rosmarínico (AR), extraído do alecrim (*Rosmarinus officinalis* L.), é usado como conservante em muitas matrizes alimentares, estando já aprovado pela *European Food Safety Authority* (EFSA) com o número de acesso E 392. Dada a longa e pouco económica extração deste aditivo a partir do alecrim, outras plantas que ofereçam rendimentos razoáveis devem ser equacionadas para a produção de extratos naturais com poder conservante.

Neste trabalho, uma extração hidroalcoólica assistida por calor com diferentes variáveis, como percentagem de etanol (*S*, 0 - 100%), temperatura (*T*, 25 - 85°C) e tempos de extração (*t*, 20 - 120 minutos) foi aplicada às folhas de três plantas aromáticas e medicinais diferentes, nomeadamente alecrim, manjericão (*Ocimum basilicum* L.) e salvia (*Salvia officinalis* L.). Posteriormente, foi aplicado uma metodologia de superfície-resposta com vista a encontrar a resposta máxima de ácido rosmarínico, um dos compostos fenólicos mais importantes na atividade conservante do extrato de alecrim. Este modelo utilizou um desenho central composto de três variáveis com cinco níveis diferentes. Os resultados da extração foram expressos em três valores de resposta Y: Y1) mg de AR, determinados por HPLC-DAD, expresso por grama de folha (F) seca (mg AR/g F massa seca (ms)), usada para analisar especificamente a quantidade de AR presente nas folhas; Y2) miligramas de AR obtidas do resíduo seco (mg RA/g R) de forma a medir a pureza (P) do resíduo; e Y3) em g R/g ms, que oferece informação relativa ao rendimento da extração. No caso do alecrim, as condições ótimas de maximização da extração foram de 87±7 minutos, 85±8 **°C** e 39,1±0,8% de etanol, produzindo cerca de 23,3±0,7 mg AR/g F ms (Y1), 82±4 mg AR/g R (Y2), e 0,31±0,02 g R/g ms (Y3). Para o manjericão, estes valores situaram-se em 98±4 min, 85,0±0,8 °C, e 45±4% de etanol, resultando em 29±1 mg RA/g F ms (Y1), 112±11 mg AR/g R (Y2) e 0,32±0,04 g R/g ms (Y3). Finalmente, para a salvia os resultados foram de 120±6 minutos, 85±2 **°C** e 47,2±0,8% de etanol, resultando em 29±2 mg AR/g F ms (Y1), 127±5 mg AR/g R (Y2) e 0,33±0,03 g R/g ms (Y3).

Estes resultados permitem concluir que o alecrim demonstra a maior quantidade de AR, mas que tanto o manjericão como a salvia permitem um rendimento aceitável, podendo ser de interesse para a indústria alimentar.

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Novel choline amino acids ionic liquids based aqueous two-phase systems for the purification of DNP-amino acids

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In the biotechnological industry, the purification or recovery of biomolecules requires the use of the liquid-liquid extraction technique, which generally uses organic solvents. However, organic solvents can affect the biological activity or chemical structure of the biomolecule and promote the denaturation of these biomolecules [1]. For this reason, the biocompatibility is a crucial topic in the design of these separation processes. In this context liquid-liquid extraction making use of aqueous two-phase systems (ATPS) can be a greener option in this field [2].

In the mid-1950s, Albertsson [2] proposed the use of aqueous two-phase systems as an alternative to traditional liquid-liquid equilibria (LLE) separation. The ATPS is an extraction technique that presents several advantages versus to the conventional liquid-liquid extraction, such as: environmentally friendly media, low cost and easy of scaling-up since the ATPS consists of two immiscible aqueous-rich phases based on polymer-polymer, polymer-salt or salt-salt combinations and are a clean replacement because they are mostly composed of water (up to 70% in the overall systems).

The first work that reports the use of ionic liquids on ATPS was published by Rogers *et al.* in 2003 [3]. In this study, Rogers *et al.* describe the formation of ATPS by the addition of K_3PO_4 salts to aqueous solutions of butylmethylimidazolium chloride ionic liquid (IL). Since then, the use of ILs as alternative phase-components in ATPS has been widely studied; most of the ILs used are derived from imidazolium and pyridinium cations with halides as anions. However, these ILs are toxic and poorly biodegradable. In recent years choline amino acids ionic liquids (CAAILs) showed an excellent biodegradability and low toxicity [4], and amino acids are adequate candidates as anions and provide a suitable separation media for biomolecules.

For this reason the use of ATPS with compounds as new biodegradable ionic liquids (CAAILs) and salts is a promising option for this type of processes and therefore the aim of this work is to evaluate the viability of the use of ATPS based on CAAILs and salts as an extraction method for amino acids.

In this essay the partition coefficients of DNP-glycine, DNP-L-alanine, DNP-L-valine and DNP-L-leucine in {choline alanine (1) + K_2HPO_4 (2) + water (3)} ATPS and the binodal curve and tie-lines compositions of this ATPS were measured at T=298.15 K and atmospheric pressure, aiming to evaluate the influence of the structure of the DNP-amino acids on the partition coefficients.

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Valorization of wood wastes from the agro-food industry – a sustainable approach to obtain cosmeceutical products

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The valorization of wastes from the wine and fruit industry represents an increasingly important research area from an environmental and economic point of view, as these sectors exerts a huge influence in Portuguese economy. Traditionally, these wastes have been used in low added value applications, such as firewood, left in the field as organic material or incinerated [1]. The aim of the present study was the *in vitro* characterization of pruning wastes from vine and apple tree for further potential use as a source of phenolic compounds [2, 3]. For this purpose, environmental-friendly techniques, namely microwave-assisted extraction (MAE) and subcritical-water extraction (SWE), were employed. The phenolic composition, antioxidant and biological activities from the obtained extracts were quantified by spectrophotometric and chromatographic techniques.

According to the obtained results, vine and apple tree pruning wastes could be used as a source of phenolic compounds, and the highest concentrated extracts were obtained by the SWE technique. Concerning the differences in the vine shoot varieties, *Touriga Nacional* from Douro region presented the highest total phenolic content (35.2 ± 1.7 mg GAE/g dry sample), as well as the highest antioxidant activity. Regarding the results obtained for the apple tree wood wastes, the highest total phenolic content was reported for *Fuji* extract (52.9 ± 3.4 mg GAE/g DW). Work is in progress to evaluate the potential contamination of polyphenols extracts with pesticides. However, the previous results demonstrated the potential of Portuguese pruning wastes from vine and apple tree to be used as a promising source of phenolic compounds with antioxidant activity, for further application in cosmetic and/or pharmaceutical industries. In fact, preliminary assays for cytotoxicity showed that vine shoot subcritical water extracts presented the lowest cytotoxic effect for skin cells.

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High throughput nmr methodology for ionic liquid screening: Extracting polyphenols

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Matcha green tea is a powdered superfood, rich in polyphenols that is more and more popular each day. [1] Polyphenols extracted from plants have considerable significance as bioactive compounds with several pharmacological applications. [2]
Catechins, which are present in green tea, have a crucial role in preventing diabetes, cardiovascular diseases, cancer and obesity. They also have an anti-inflammatory, antiarthritic, antibacterial, antioxidative, antiviral, neuroprotective and antidental caries effects. [3]
The extraction of polyphenols can be made through traditional methods such as impregnation, maceration extraction, Soxhlet technique, solid-liquid extraction through solvent application followed by leaching, among others. However, these techniques have some disadvantages due to excessive consumption of time, energy and polluting solvents. [2,4] Consequently, there is an urgent need for improved and sustainable extraction techniques. In the last two decades, a new type of greener solvents has emerged - the ionic liquids (IL). [5,6]
Our approach relies on avoiding a slow process of trial and error. So, we highlight the importance of nuclear magnetic resonance spectroscopy (NMR) to understand the molecular details of the IL interactions towards polyphenol-like compounds. Nuclear Overhauser effect (NOE) can be used to distinguish and quantify the intermolecular interactions. From these experiments, emerged the most successful IL structural features able to provide a solvent like behavior.
This methodology allowed the rational development of alternative solvents for polyphenol compounds, however it may easily be extrapolated to other types of materials. [7]

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A greener approach to obtain sulfur-free fuels based on the Venturello catalyst and a solvent-free system

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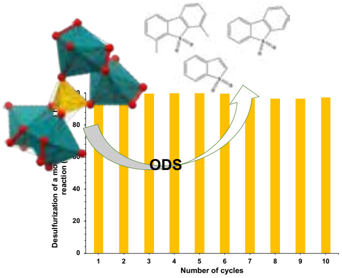
The overuse of fossil fuels during the last century has resulted in undesirable effects on the environment. In order to reverse or decrease our footprint on the planet some sulfur reduction policies have been imposed on diesel and gasoline. However, severe conditions are required to remove the refractory sulfur compounds from the fuels by the desulfurization process currently applied in the refining industry, affecting the economic viability and fuel specifications. Therefore, the development of alternative desulfurization technologies is necessary, but still a challenge for both academia and industry.[1] Oxidative desulfurization (ODS) is one of the most promising processes and is based on two fundamental steps: (i) oxidation of the sulfur compounds to the corresponding sulfoxides and/or sulfones under mild conditions and (ii) extraction of the oxidized species by the use of polar solvents. The waste-avoiding H_2O_2 is usually the selected oxidant, which must be selectively activated by suitable catalysts, such as polyoxometalates (POMs).[2] The organic-stabilized peroxophosphomolybdate $\{PO_4[MoO(O_2)_2]_4\}^{3-}$, also known as the Venturello anion, has been identified as an active catalytic species for oxygen atom transfer reactions. Despite their known catalytic efficiency, the use of these POMs as catalysts in ODS processes is still scarce.[3]

In the present work, the Venturello complex $TBA_3\{PO_4[MoO(O_2)_2]_4\}$ was applied as an efficient catalyst for ODS of a model and real diesel using a solvent-free system and a low O_{xidant}/S_{ulfur} ratio. This catalyst maintained its catalytic performance and stability for ten consecutive ODS cycles.



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Metal-Organic Frameworks de Cu y Sc modificados para la síntesis verde de heterociclos bioactivos

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Las reacciones multicomponente (RMC) constituyen una de las herramientas más útiles, tanto desde el punto de vista académico como industrial, para la síntesis de sistemas heterocíclicos complejos de forma simple y selectiva. Los 2-amino-4*H*-cromenos son heterociclos bioactivos de gran interés para la industria farmacéutica, ya que son la estructura base de diversos fármacos comerciales. Sin embargo, la obtención de los correspondientes cromenos mediante la RMC entre salicilaldehído **2** y nitrilos con grupos metilenos activos **3** [1], habitualmente requiere prolongados tiempos de reacción y el uso de disolventes, así como metodologías complejas de aislamiento y purificación de los productos de reacción. Es por ello por lo que resulta fundamental el desarrollo de nuevos sistemas catalíticos activos y selectivos en la síntesis sostenible de este tipo de compuestos.

En esta comunicación se presenta el estudio de dos nuevas familias de MOFs de Cu y Sc modificados con aminas de muy distinta naturaleza [2], altamente eficientes en la síntesis de cromenos 1, en ausencia de disolvente y bajo condiciones suaves de reacción (Fig.1). A este respecto, los materiales de cobre, de carácter microporoso, resultaron ser catalizadores más eficientes que sus análogos de escandio, conduciendo a los productos 1 con excelentes rendimientos a tiempos cortos de reacción y temperatura ambiente.

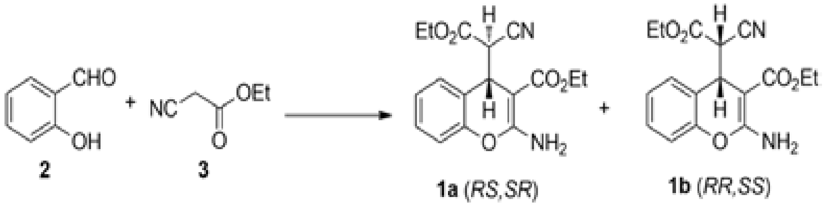

Fig.1. Síntesis de 2-amino-4H-cromenos 1 catalizada por MOFs de Cu (CuBTC) y Sc (Sc-Mil-100) modificados con diversos compuestos nitrogenados, dónde DET=dietilentriamina, TCN=triazaciclononano, EN=etilendiamina y MMEN=N,N'-dimetiletilendiamina.

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Porous coordination polymers isolated in ionic liquids: oxidative catalysis activity

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Metal-Organic Frameworks (MOFs) are crystalline materials that consist of metal centres connected by organic molecules, known as ligands or linkers, usually obtained by conventional hydro/solvothermal methods. This type of materials possesses remarkably interesting applications in gas storage, catalysis and electronic chemistry, among others. Ionic Liquids (ILs) have been applied as reaction media, structural templates or charge-compensating groups, thus contributing greatly to the formation of new materials with unique structural properties. Tuning the structural properties of ILs and then transmitting these effects to the construction of MOFs, is an important strategy for achieving novel functional MOF materials.[1]

In the present work, Cobalt and Zinc MOF materials have been prepared by the reaction of 1,4-benzenedicarboxylic acid (H_2BDC) with respective metal salts in different 1-alkyl-3-methylimidazolium halides (chloride, bromide and iodide), acting as ionic medium instead of the traditional hydro-solvothermal one. The MOFs structures were determined by single-crystal X-ray diffraction as layered metal–organic frameworks and further characterization was performed by Powder X-ray diffraction, FT-IR and TGA techniques. Furthermore, the materials were evaluated as potential sustainable heterogeneous catalysts for the oxidation of olefins.[2]

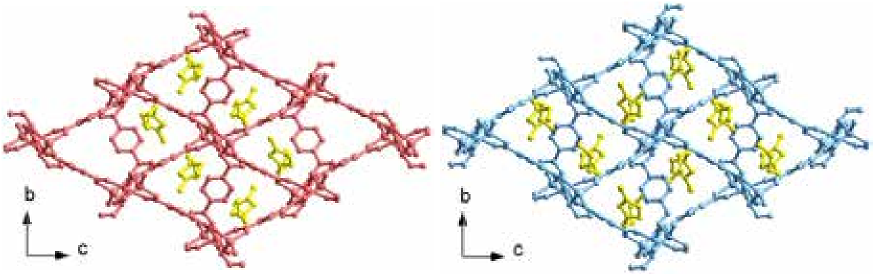

Fig.1. Structural representation of Cobalt layered MOFs obtained in related ILs: 1-propyl-3-methylimidazolium bromide (left) and 1-propyl-3-methylimidazolium bromide (right)

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Reversible aqueous biphasic systems formed by ionic liquids and polymers

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Liquid-liquid separation processes usually apply organic solvents, which exhibit several drawbacks such as high volatility and toxicity [1]. Aqueous biphasic systems (ABS) represent an alternative liquid-liquid extraction technique since they are mainly composed of water and two water soluble non-volatile solvents (two polymers, polymer and salt, or two salts). More recently, ABS formed by ionic liquids and salts or polymers have been reported [2]. Although most reports in the literature focused on aprotic ILs (AILS), protic IL (PILs) are receiving significant attention due to their mobile proton between the composing ions. PILs are synthetized by transfer of a proton from a Brønsted acid to a Brønsted base and have thus at least one proton that is able to participate in extensive hydrogen bonding. That characteristic opens the doors to the possibility of moving from monophasic to biphasic systems by applying different stimuli [3]. In this work, four ethanolamine-based PILs combined with polypropylene glycol 400 $g \cdot mol^{-1}$ were studied for the development of reversible ABS, driven by temperature and/or pH. The determination of the phase diagrams of the corresponding ABS at atmospheric pressure was carried out at different temperatures (25, 35 and 45 ªC) and pH values (4, 7, 10). Based on the gathered results, it was observed that such systems display an upper-critical solution temperature behavior, and their phase diagrams depend on the pH value. Based on their reversible behavior by applying temperature and/or pH, innovative biotechnological processes could be developed by the appropriate choice of temperature and pH of the system.

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Gels for paper artwork preservation: an nmr approach

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Fungal biodeterioration is a global problem that affects both chemical and physical characteristics of paper artworks. Fungal debris constitute a health risk due to their allergenic and toxigenic potential. Currently, fungal stains are removed from paper artefacts either by using bleaching agents, solvents, enzymes or laser ablation. However, all these methods present major drawbacks such as lack of cleaning effectiveness, potential risks to artwork, and the toxicity of the cleaning components. [1,2]

Therefore, there is an urgent need to develop new solutions that are non-toxic, environmentally friendly and easy to apply. [2] Ionic liquids (IL) have several applications from CO_2 capture to catalysis and electrochemistry. [3,4] Lately, they have also been suggested for cleaning artworks. [1] The most frequent paper stains are usually caused by phenol and polyphenol derivatives. [5]

Herein we report a new NMR based methodology for polyphenol extraction that avoids a slow and unsustainable process of trial and error. Taking advantage of the molecular view provided by NMR, nuclear Overhauser effect (NOE) and diffusion experiments allowed us to examine the specific interactions between IL anions and cations and the polyphenol-like compounds. From these experiments, the structural features in ILs which lead to different types of interactions were revealed.

The NMR methodology enabled a rational development of IL based gels, using agarose and polyvinylpyrrolidone matrixes. These gels showed a higher affinity for polyphenol-like stains. The efficacy of these new materials was tested on fungal stained paper samples.

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Ionic Liquids as Functional Materials for Energy

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Ionic Liquids (ILs) showed relevant properties such as high thermal and chemical stability and large electrochemical window for application in electrochemistry as well as energy field.

In this context, our group have developed different ILs as functional materials for several applications in the energy research topic:

a) Capture and Conversion CO2 to fuels: Nowadays, the search of efficient Carbon dioxide (CO_2) Capture and Conversion into fuels is a very relevant topic of research. Recently, we showed the possibility to convert CO_2 in methane using ruthenium nanoparticles prepared in situ in the presence of fluorinated ILs [1].

b) Alternative Electrolytes and Electrochromic devices: The search of alternative and sustainable electrolytes for application in devices is very attractive for academic and industrial point of view. We developed electrolytes based on task-specific ILs and Deep Eutectic Solvents (DES) with very promissory properties [2, 3]. In parallel, we also prepared electrochromic ILs based on viologen cations which can be incorporated in efficient and reversible devices [4].

The type of substituents from viologen cation as well as the anion influences the electrochromic performance and coloration of the devices. This type of materials can be applied as smart windows, in batteries or information displays.

The recent developments using task-specific ionic liquids and DES can be relevant in the context of the discovery of alternative sources of energy as well as to create sustainable processes for application in batteries or production of fuels.

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Understanding the Environmental Toxicity of Deep Eutectic Solvents and their Components: A Multitasking Quantitative Structure-Toxicity Relationship Modelling Approach

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Deep eutectic solvents (DESs) are a novel group of chemicals used in various chemical and biological processes. DESs are prepared by mixing multiple low-cost components with hydrogen bond formation characteristics in different molar ratios to produce a eutectic mixture, the melting point of which is lower than either of their individual components [1]. Some recent studies have highlighted the toxic nature of these solvents as well as of their components towards several environmental species [2]. Quantitative structure toxicity relationship (QSTR) analyses are frequently applied to gain insights into the toxic behaviour of a wide range of chemicals [3]. However, only a limited number of DES toxicity data is currently available that restricts the applications of conventional QSTR. Whereas conventional QSTR resorts to data pertaining to a specific measure of toxicological effects (*i.e.*: derived against a single target and specific assay condition), multitasking-QSTR (mtk-QSTR) allows incorporating multiple assay conditions, biological targets and many additional factors [4]. Therefore, mtk-QSTR modelling is particularly useful for a limited number of data [4]. Here, we report a mtk-QSTR modelling of 453 DESs and their components according to the OECD guidelines. The DES toxicity dataset used contains multiple experimental conditions depending on the effect' measures (me), the biological target (bt) and the presence of water (wt). Since DESs are mixtures of multiple components, the so-called technique 'sum of weighted (by molar fraction) descriptor calculation' was applied for the calculation of modified molecular descriptors [5]. Two *in silico* tools, *i.e.* linear discriminant analysis and support vector machine, were employed separately for setting up the model and validation. The best model developed with eight descriptors, derived from the Box-Jenkins approach [4], displays an accuracy >90% for both training and validation sets. The model discloses the importance of electronegativity, dipole moment, molecular mass and topological properties for inferring the toxic behaviour of DESs. Moreover, using the developed mtk-QSTR model, different DES components were ranked on the basis of their toxic contributions. To the best of our knowledge, this is the first QSTR attempt to model the toxic effects of the DESs and their components. The derived model is proved to be an efficient tool to mine relevant STR information guiding the design of potentially safe DESs.

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Ring-Shaped Donor-Acceptor Nanoarchitectures for the Removal of Cyperquat Pesticide From the Environment

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Weed killers are phytosanitary substances used to control and remove unwanted weed species leaving the desired crop unharmed [1]. Through history, herbicides have played a key role in order to avoid large losses in crops, to obtain sufficient food for the growing world population and also to control the transmission of diseases in human beans. Despite of the great advantages that they bring to agriculture negligent applications together with the excessive dose that is usually added to treat various pests generates serious environmental problems due to contamination of soils and water.
Since the biological activity of cationic quaternary ammonium pesticides (quats) was discovered in the 1950s they have been used widely in the management of crops. Due to the widespread use in different areas in combination with the large half-life in the environment, many of them may be present as persistent residues in soils and surface waters even though some of them have been banned some years ago. It is well known the environmental harmful effects of diquat and paraquat but also their toxic effects because they interfere biological redox reactions generating superoxide radicals that destroy cell membranes. Due to the toxic effects mentioned above, the elimination of this compounds from the environment once they have fulfilled their function as herbicides is of vital importance. In this work we explore the potential use of ring-shaped nanoarchitectures to capture and store quaternary ammonium herbicides. The hosts, chemically known as [*n*]Cycloparaphenylenes, possess a unique rigid architecture composed of n-benzene rings linked at *para* positions to form a fully conjugated cylindrical structure [2,3] that enhances the capture ability of this supramolecular structure for different quat guests. A deep theoretical study about the intermolecular host-guest interactions using Symmetry Adapted Perturbation Theory (SAPT) and various computational quantum chemistry techniques for the study of non-covalent interactions were applied. Based on those results he have designed novel donor-acceptor supramolecular structures with high complexation energies for cyperquat removal from the environment.

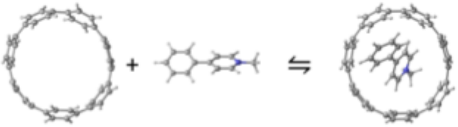

Fig.1. Chemical equilibrium of cyperquat-nanohoop inclusion complex formation

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Computational Evaluation of Vibrational Spectroscopy Techniques as New Candidates for the Rapid, Selective and Univocal Detection of Saxitoxin

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Owing to climate change dinoflagellate blooms are becoming frequent events in coastal regions of the ocean. Out of all of the toxin-related contamination issues, harmful algal blooms, commonly known as red tides, are some of the most important. They are responsible for approximately 60000 human intoxications every year, affecting the coasts of many regions of the world. When one occurs, many species that were previously edible by humans and other predators become poisonous or even lethal, resulting in not only negative impact on the food industry but also in deaths and environmental imbalance. Saxitoxin, the main Paralytic Shellfish Toxin (PSP) [1] is nowadays detected by using the Mouse Bioassay (MBA), a technique that not only causes animal deaths but also it doesn't have a detection limit small enough to determine if a sample contains a harmful quantity of toxin (lower than the DL_{50}) [2]. For these reasons, the development of reliable, robust and accessible detection techniques for toxins is turning into a matter of deep concern. In this work a computational model of the saxitoxin molecule was developed and validated in order to analyze its spectroscopic properties. The applicability of a series of vibrational spectroscopic techniques like Infrared, Raman spectroscopy, Resonance Raman and Surface-Enhanced Raman Spectroscopy have been investigated. The quiral versions of all this vibrational spectroscopy techniques such as Vibrational Circular Dichroism or Raman optical activity among others were also evaluated. All the computational studies done make us able to select an appropriate candidate that could improve the detection methodology.

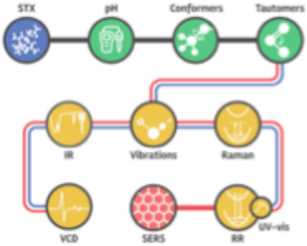

Fig.1. Experimental procedure followed for testing the ability of vibrational spectroscopy to detect STX

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On the Origin of Drug Recognition Changes and P-Glycoprotein Polyspecificity

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Multidrug resistance (MDR) to anticancer drugs is, currently, a major contributor for cancer treatment failures. One of the most significant MDR mechanisms results from the overexpression of P-glycoprotein (P-gp, *ABCB1*), a membrane efflux pump that lowers the intracellular concentration of a wide range of structurally unrelated compounds as anticancer drugs by transporting them towards the extracellular milieu. Thus, modulating drug efflux by P-gp pump in cancer cells is one of the promising approaches to overcome MDR, but the lack of information about the molecular basis underlying drug specificity and efflux-related signal transmission mechanism between the transmembrane domains (TMDs) and the nucleotide binding domains (NBDs), hampers the development of more potent and selective efflux modulators [1]. Starting from three published murine P-gp crystallographic structures in an inward-facing conformation as templates, several homology models of human P-gp were developed, and from the most stable model a comprehensive study on the effect of four P-gp mutations was performed. Thus, G185V, G830V, F978A and ΔF335 mutations that are experimentally related with changes in efflux and drug-stimulated ATPase activity were evaluated regarding its impact on P-gp's architecture.

Overall, our work provides evidences that i) all mutations are responsible for inducing a significant repacking of the TMDs, deeply changing the volume of the internal cavity and drug-binding sites (DBSs) properties such as volume, shape and polarity [2,3], ii) all mutations show differences in drug binding as assessed by molecular docking approaches and ii) some mutations have a distinct impact at the signal transmission interfaces (especially the third transmission interface), suggesting that a perturbation at the TMDs may be transmitted to NBDs through changes in the residue interactions between the intracellular coupling helices (ICHs) and the respective NBD, may affecting ATP binding.

Furthermore, to gain more insights on the molecular basis underlying the drug binding alterations described above, molecules experimentally known to interact in each DBS were docked at the corresponding site and the best top-ranked docking pose were used as starting point for several short 20 ns molecular dynamics runs to assess the free energies of binding through the calculation of polar solvation energies corrected through an implicit membrane approach [3]. The obtained results agreed with the experimentally determined changes in drug efflux for each specific mutation. Thus, while in some cases the increase of drug affinity inside the pocket is the major determinant (G185V), in other cases variations in residue contacts at the TMD-NBD interface were the main reason for changes in drug efflux (ΔF335).

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Discrete-Molecule Enhanced Raman Spectroscopy for the Detection of Pesticides in the Environment. Can Molecular Sulflowers Be Used as Enhancement Substrates?

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Many investigators believe and have pointed on the literature that besides the many aesthetic aspects of chemistry, such as molecular complexity, self-organization, and nonlinear dynamics, the sheer beauty and elegance of molecular structures has always played an important role in the development of chemistry [1,2]. For a long time, great efforts have been done to the synthesis of sulfur-rich polycyclic aromatic hydrocarbons. For example, highly annulated oligothiophenes remained practically unexplored because of the lack of suitable synthetic methodology. Although some significant progress in this area has been made in the last years, there are many structures that nowadays the procurance present a unique challenge due to the lack of effective, simple, and straightforward synthetic procedures. One elegant persulfurated polycyclic chemical structure involving only sulphur and carbon atoms known as sulflower (octathio[8]circulene) have been obtained in 2006 by Nenajdenko and coworkers. This particular organic-inorganic hybrid structure [2,3] contain one eight-membered central ring fused with eight tiophene units, that makes the structure to have a unique redox behavior and promising charge transport properties that can be used in organic photovoltaics and electronics [3].

Every year more properties of thio[n]circulenes family are found. The presence of non-conventional electronic properties together with the absence of hydrogen atoms made us think about the possibility of using this molecule as a sensor. The search for new substrates due to the boom of Surface-Enhanced Raman Spectroscopy motivated the study of this system as an amplification platform. In the present work we perform a computational exploration of these structures as Raman spectroscopy amplifiers for the detection of environmentally important molecules such as pesticides and fungal toxins. Very promising results point to thio[n]circulenes as excellent substrates to perform Discrete-Molecule Enhanced Raman Spectroscopy. The spectroscopic computational study is complemented with a deep analysis of the analyte-substrate interactions, fact that allows proposing structural improvements to make the detection of these toxic substances more selective.

Fig.1. Molecular sulflower structure used in this study for the detection of harmful substances

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¿Pueden emplearse nanoplaquetas de BN como sustrato de SERS para realizar una detección selectiva de micotoxinas?

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La detección y cuantificación de analitos tóxicos es de vital importancia en numerosos ámbitos como la industria alimentaria, la cosm*ética,* la farmacéutica e incluso en otras áreas como la ciencia forense. Los enormes avances científicos en el área de la toxicología permiten cada año conocer nuevas sustancias perjudiciales para los organismos vivos que deben ser detectadas de manera selectiva y unívoca. Las bajas dosis letales de algunos compuestos hacen que cada vez se necesiten técnicas con límites de detección y cuantificación más bajos. De entre todas las técnicas disponibles en el mercado, la espectroscopía Raman está cobrando cada vez más importancia gracias a la posibilidad de detectar vibraciones estructurales características de la mol*écula más allá de* los grupos funcionales que posee. La posibilidad de analizar muestras en agua sin que esta interfiera en la medida, la poca o nula preparación de muestra, la elevada sensibilidad y las características no destructivas hacen de la espectroscopía Raman una técnica muy interesante. Sin embargo, esta técnica suele tener señales de baja intensidad (solamente 1 de cada 10^8 fotones incidentes en la muestra provocan efecto Raman), por lo que se han desarrollado nuevas técnicas amplificadas en las cuales la intensidad se puede incrementar en algunos casos hasta 10^{14} veces [1,2]. La amplificación de las señales se logra gracias a la adsorción de la molécula a detectar sobre una superficie de metal como oro o plata o sustratos nanoestructurados como el grafeno, y diferentes nanopartículas.

Una de las aplicaciones que posee la espectroscopía Raman amplificada por superficie (SERS) es la detección y cuantificación de tóxicos en diferentes matrices, y dentro de todas las posibilidades existentes estamos interesados en las micotoxinas, en especial en la orellanina. Este metabolito secundario proveniente de la ruta del ácido shikímico interfiere en las reacciones metabólicas a nivel corporal puesto que compite con el NAD^+ como aceptor de electrones impidiendo que las reacciones bioquímicas corporales fundamentales puedan llevarse a cabo. La baja dosis letal de la orellanina (12-20 mg/Kg de peso) hace que sean necesarias técnicas ultrasensibles para identificar este t*óxico como SERS* [3].

En este trabajo exploramos computacionalmente la viabilidad de usar nanoplaquetas hexagonales de nitruro de boro como nuevo sustrato de SERS para la detección selectiva de micotoxinas como la orellanina. Puesto que para emplear esta técnica es necesario adsorber sobre la superficie la molécula a detectar, previamente al estudio espectroscópico se realiza un análisis detallado del proceso de adsorción de los dos tautómeros tóxicos que posee la orellanina. Posteriormente, el estudio espectroscópico completo permite seleccionar las longitudes de onda de láseres incidentes óptimas para producir una amplificación selectiva de los modos vibracionales deseados. Empleando las longitudes de onda óptimas para este sistema es posible realizar una identificación selectiva de ambos tautómeros.

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Evaluación de la Exposición a Contaminantes Químicos en el Tratamiento de Residuos Vegetales

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La proliferación de la agricultura intensiva, debido a la creciente demanda de sus productos, no ha llevado aparejada una adecuada gestión de sus residuos sólidos y en consecuencia una determinación de los riegos ambientales y laborales potenciales que pueden generarse en esta actividad. Estos residuos se tipifican como biomasa y como tal y en orden a lo establecido en la jerarquía de residuos deberían reutilizarse en procesos de generación de energía [1].

La tecnología empleada en el tratamiento de estos residuos vegetales obliga a disponer de una adecuada evaluación de riesgos [2] para obtener las correspondientes autorizaciones de actividad. Los riesgos potenciales suelen incluirse como alteraciones no deseadas de las condiciones de operación, fallos de unidades o equipos, derrames o fugas incontroladas, etc.

La peligrosidad de los productos químicos emitidos al tratar los residuos vegetales, dependen de múltiples factores tanto de composición como de tipo estructural, que suelen conocerse por su toxicidad, inflamabilidad, explosividad, carcinogenia, o su peligrosidad para el medio ambiente, entre otros. En el presente trabajo se analizan los riesgos derivados de los efluentes de la planta de gasificación [4] por tratamiento de los residuos vegetales empleados.

Previamente se analizan los riesgos existentes en la planta de tratamiento en sí, esto es, en el diseño de equipos, procedimientos de operación y mantenimiento, paradas o picos de producción. Unidades como la de almacenamiento de residuos (combustible), gasificador o enfriador y depuradores de gases permiten un abatimiento de las emisiones con la consiguiente reducción de riesgos ambientales pero con el correspondiente aumento de otros riesgos laborales en las unidades mencionadas.

Identificados y caracterizados los riesgos se proponen las medidas para su minoración de cara a conseguir la adecuada protección individual y colectiva de los trabajadores de la planta.

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Correlación entre accidentabilidad y economía en el sector de la construcción y sus efectos en plantas químicas

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Esta comunicación tiene como objetivo estudiar la relación entre la situación económica de un sector de actividad y la cantidad registrada de accidentes laborales [1].
Existen ya trabajos en cuales se ha estudiado la evolución de la siniestralidad laboral y se ha relacionado con los ciclos económicos, concluyéndose en ellos que en la expansión económica, para aumentar la producción en cualquier industria, se debe intensificar el trabajo. Esto lleva consigo un aumento en la exposición a factores de riesgo y una menor formación en seguridad de los trabajadores empleados, lo que hace aumentar el índice de incidencias.
Por el contrario, en los procesos de recesión económica, al producirse numerosos despidos y reducirse la carga de trabajo, se mejoran los procesos de selección y formación a la vez que se incrementa la gestión de la seguridad con lo que se reduce la siniestralidad [3]
Con esta comunicación se pretende analizar la evolución que ha tenido el sector de la construcción en España en los últimos diez años y su incidencia en el sector químico, dado que los fallos de construcción suelen ser el desencadenante de otros de operación que entrañan un riesgo potencial muy superior [2].
El análisis estadístico de los datos aportados nos permite asegurar la relación clara entre economía y accidentabilidad en los sectores estudiados.

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