XXII Encontro Luso-Galego

Química

9 a 11 novembro 2016

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9 de novembro (quarta-feira)			
9:00 – 11:30	Entrega de Documentação e Afixação de Painéis		
11:30 – 12:00	Sessão de Abertura		
12:00 – 13:00	**Sala Bragança**		
	Lição Plenária 1 - Mario G. Ferruzzi		
Pausa para almoço (livre)			
15:00 – 16:00	**Sala Bragança**		
	Lição Plenária 2 - Francisco Guitián		
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	Sala Bragança	**Sala Porto**	**Sala Vigo**
	QAMA1	BB1	QV1
	QAMA2	QS1	QV2
	QAMA3	BB2	QV3
	QAMA4	QS2	QV4
17:00 – 17:45	Café e Discussão de Painéis S1 (QAMA)		
17:45 – 19:00	Comunicações Orais S2		
	Sala Bragança	**Sala Porto**	**Sala Vigo**
	QAMB1	CAT1	QP1
	QAMB2	CAT2	QP2
	QAMB3	CAT3	QP3
	QAMB4	CAT4	EEQ1
	QAMB5	CAT5	EEQ2
19:30	Receção de São Martinho		

10 de novembro (quinta-feira)

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	Sala Bragança	**Sala Porto**	**Sala Vigo**
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	Lição Plenária 4 - Diego Moldes		
16:15 – 17:15	Comunicações Orais S5		
	Sala Bragança	**Sala Porto**	**Sala Vigo**
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	QV6	QO2	QAMA16
	QV7	QO3	QAMA17
	QA1	QO4	QAMA18
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	CAT7	QA3	QO5
	CAT8	QA4	QO6
	CAT9	QA5	QI2
20:00	Jantar do Encontro		

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	QF6	QAMA20	QV9
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	QAMA26	QAMB13	BB5
Pausa para almoço (livre)			
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	QAMA27	QS8	QF8
	QAMA28	BB6	QIE4
	QAMA29	QS9	QF9
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Química

LIÇÕES PLENÁRIAS

Plant phenolics as a tool to modify glycemic response of foods

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Epidemiological studies have reported a link between consumption of phenolic rich foods and a reduced risk of Type-2 diabetes [1,2]. The apparent link between food phenolics and acute glycemic response has strengthened the notion that these compounds may play a protective role through their ability to (1) inhibit starch digestion and (2) modify rate of intestinal glucose transport. While promising, these effects have been observed largely from studies reliant on purified phenolics and/or extracts [3] with little consideration of the translatability of these findings to whole food matrices or mixed meals containing phenolic rich foods. Additional insights are required to facilitate translation of these promising findings into meaningful recommendations and products for consumers. With this in mind, the objectives of these studies were to determine the extent to which phenolics in foods perceived to be high glycemic value (fruit juice and potatoes) may modulate starch digestion and intestinal glucose transport both from the specific foods and from a model meal.

Initial studies focused on 100% juice from American grape varieties (*V. labrusca*; Niagara and Concord) finding modest inhibitory capacity for grape phenolics toward α-amylase and α-glucosidase (6.2%–11.5% inhibition; $p < 0.05$). However, grape juice (GJ) phenolics (10–100 μM total phenolics) did reduce intestinal trans-epithelial transport of ,2,3,4,5,6,6-d_7 -glucose (d7-glu) and ,2,3,4,5,6,6-d_7 - fructose (d7-fru) by Caco-2 monolayers in a dose-dependent fashion (10%–38% reduction compared to control) [4]. To expand these findings to whole foods, the ability of 100% GJs to modify starch digestion and glucose transport from a model starch-rich meal were assessed using a coupled in vitro digestion/Caco-2 model system. 100% Niagara and Concord GJ samples were combined with a starch rich model meal (1:1 and 1:2 wt:wt) and subjected to a 3-stage in vitro digestion simulating oral, gastric and small intestinal phases of digestion. Digestive release of glucose from the starch model meal was decreased in the presence of 100% GJs (5.9%–15% relative to sugar matched control). Furthermore, transport of d7-glu was reduced 10%–38% by digesta containing bioaccessible phenolics from 100% GJ compared to control. Similarly, phenolics in starch rich snack foods were studied for their ability to modify glycemic response. Chips prepared from phenolic rich potatoes (red and purple) or white potatoes were compared in vitro for starch digestion and glucose transport as before. Following in vitro assessment, a pilot clinical study (n=11) assessed differences in acute glycemic response and gastric emptying between chips from pigmented and white potatoes. While no significant effects were observed on starch digestion in vitro, phenolics from all potatoes were found to significantly ($p<0.05$) decrease the rate of glucose intestinal transport across Caco-2 human intestinal cell monolayers by 4.5-83.9%. Consistent with in vitro results, consumption of purple potato chips by healthy participants resulted in moderate, albeit significant ($p<0.05$), decrease in blood glucose (4.7mM) at 60 min post consumption compared to white chips (5.3 mM) without any significant changes in gastric emptying. These results suggest that these modest changes in glycemic parameters are likely mediated by modification of intestinal glucose transport, consistent with in vitro predictions. Taken together, these data support the notion that phenolics intrinsic to select foods may have the ability to modify glycemic response through alteration of glucose transport and, to a certain extent may alter starch digestion from other foods in a meal. The ability to extend these effects to whole foods and potentially to a co-consumed meal may be leveraged to develop new products or improve dietary guidance for selection of foods to improve glycemic response from a meal.

Acknowledgments
Funding for these studies was provided by the USDA, Welch's Ltd and PepsiCo Global R&D

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Biocerámicas y química: de la ciencia básica a la industria

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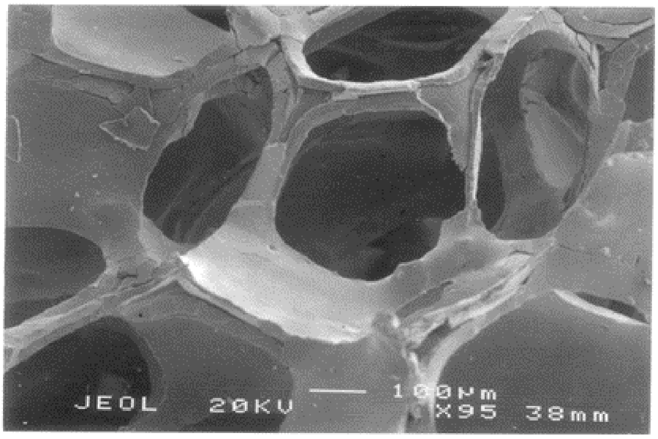
Tras una muy breve presentación del Instituto de Cerámica de Galicia y de sus líneas de trabajo, la conferencia pretende realizar una introducción a las biocerámicas para regeneración ósea y a sus mecanismos de actuación y características principales.

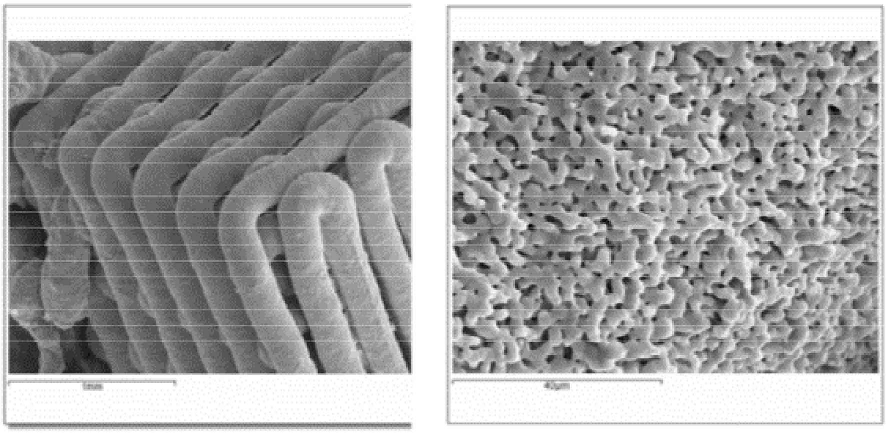
Se revisan en primer lugar los distintos tipos de biocerámicas y sus interacciones con el tejido vivo, para estudiar después las características esenciales de este tipo de materiales: su composición química y su microestructura, y como estas dos características determinan el comportamiento del material una vez implantado.

Una vez establecidas las características "ideales" de la biocerámica: Cómo se obtienen estas características? Qué tipo de procesamientos se utilizan? En la segunda parte de la conferencia, se describen los procesamientos de estas biocerámicas, y su fabricación, revisando los avances actuales en este campo, con la aparición de la ingeniería de tejidos, los materiales con liberación sostenida de medicamentos y el "bioprinting".



Biocerámica porosa de fosfato tricálcico, fabricada en el Instituto de Cerámica

Finalmente se relata la creación de la empresa KERAMAT S. L., fundada por investigadores del Instituto de Cerámica en 1999, y líder española en la fabricación y venta de biocerámicas.



Implante de hidroxiapatito poroso obtenido por 3Dprinting. a) aspecto general de la pieza a bajos aumentos; b) detalle de la microestructura porosa

Designing hydrogels using natural-based polymers for biomedical applications

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The process of aging with good quality of live has been improved with general medicine, but it has facing huge challenges with the increase of the lifespan of the population. The possibility of regenerating organs and tissues would bring new possibilities of improving current treatments or find solutions for untreatable situations. Tissue Engineering has been integrating principles of engineering, materials science, biology and health sciences in order to develop regenerative-based therapeutic strategies combining stem cells and biomaterials.

From the different sources of biomaterials, natural-based macromolecules have been proposed to produce matrices able to interact favourably with cells. Due to their hydrophilic nature and richness in chemically active groups, such polymers can be used to produce a variety of structures fabricated using aqueous-based procedures. Examples of chemically-modified polysaccharides are shown for the development of hydrogels with controlled structures or with functional properties such as adhesion or specific cell recognition. In particular we developed double-network hydrogels just composed by natural-based polymers presenting outstanding mechanical properties. The hydrogels are also engineered to be capable to encapsulate cells or to provide cell attachment onto the surface. Some processing technologies to process hydrogels into different shapes and sizes are also presented.

Biomasa lignocelulósica: una fuente de productos para la Química Verde

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La biomasa es una fuente casi inagotable de productos de interés, desde combustibles a productos de alto valor añadido. La búsqueda de metodologías sencillas, eficientes y económicamente asumibles para procesar la biomasa y obtener estas familias de compuestos, acapara actualmente un gran esfuerzo investigador. De este concepto de aprovechamiento global de la biomasa, nace el término de biorrefinería, como aquella instalación con la capacidad de llevar a cabo estas tareas y que pueda suponer una alternativa a las refinerías convencionales basadas en la utilización de petróleo como materia prima.

Por otra parte, la química verde es aquella disciplina de la química que trata de diseñar, desarrollar e implementar productos y procesos químicos que eliminen o reduzcan la utilización y generación de sustancias nocivas para la salud y el medio ambiente. Por tanto, los conceptos de química verde y biorrefinería están relacionados en su propia definición [1].

Las industrias maderera y papelera forman parte de un sector que comercializan productos de un limitado valor añadido, al mismo tiempo que emplean grandes cantidades de biomasa, lo que, de forma casi inevitable, hace que generen grandes cantidades de residuos. Este es el caldo de cultivo ideal para tratar de aplicar los conceptos previamente comentados.

Uno de los residuos más característicos y cuantiosos de la industria papelera es la lignina Kraft. Es un subproducto del proceso mayoritario de obtención de pasta de papel, que normalmente se utiliza como combustible en las propias plantas de producción de pasta de papel. Sin embargo existen vías alternativas para su valorización. Se presentarán diversas posibilidades como su utilización como sistema adhesivo en el proceso de fabricación de tableros de fibras de madera. Esta aplicación puede estar apoyada por la introducción de enzimas comerciales con capacidad de promover la unión de la lignina con las fibras de madera, de modo que se generarían, gracias a la lignina Kraft, nuevas uniones entre fibras. Por otra parte, la lignina también posee interesantes propiedades que la hacen idónea para utilizar como tratamiento superficial de la madera. Mediante un tratamiento combinado de lignina Kraft y enzimas es posible modificar las propiedades de la madera con el objetivo de mejorar los tratamientos convencionales.

La combinación de enzimas, en concreto lacasas, y determinados compuestos químicos se puede utilizar también como sistema para realizar "grafting" o injerto de estos compuestos a la madera. Este tipo de modificaciones presenta varias ventajas: funcionalización "a la carta" de la madera, durabilidad de los tratamientos y sostenibilidad medioambiental. Este tipo de modificaciones pasan por una etapa previa de activación de los compuestos seleccionados mediante una reacción enzimática. Luego estos compuestos activados se unen a la madera confiriéndole sus propiedades. Como compuestos químicos a unir a la madera se pueden seleccionar multitud de ellos, siempre que sean activables por las lacasas, de tal modo que es posible emplear compuestos comerciales e incluso extractos de materiales lignocelulósicos. Se mostrarán casos en los que se ha modificado la composición química y las propiedades de la madera utilizando estas herramientas, como por ejemplo la cloración estable de la madera [2], su hidrofobización [3] o la mejora de la durabilidad utilizando lignina Kraft y extractos de plantas.

Agradecimientos
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Referencias

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Membrane engineering …… What else?

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This lecture discusses the use of synthetic membranes – porous or dense – in order to organize the transport of specific solutes and their (bio)conversion into target compounds. Due to their permselective properties membranes offer the possibility to create compartments that may communicate between them, allowing to regulate transport of solutes at required rates. Transport regulation may be combined with (bio)catalytic steps.

A number of different potential applications will be presented and discussed during this lecture: biphasic membrane bioreactors for specific enzymatic conversion; combined membrane transport and bioconversion using porous membrane contactors; membrane contactors for selective solute transport and for crystallization processes, such as protein crystals' derivatization. The development of membrane processes for the recovery and fractionation of target biological compounds – small bioactive molecules and proteins – will be also presented and discussed.

A particular emphasis will be given to the use of monitoring techniques able to provide information about membrane transport and conversion at molecular scale, in real-time. On-line process monitoring will be discussed, namely using non-invasive molecular probing techniques, which allow for on-line, real time decision and control of membrane processes.

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Química

COMUNICAÇÕES ORAIS E EM PAINEL

Bioquímica e Biotecnologia

Aqueous biphasic systems composed of mixtures of ionic liquids: platforms of high selectivity for the separation of amino acids

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Aqueous biphasic systems (ABS) are commonly used as more biocompatible liquid-liquid separation strategies – a main result of their high water content. ABS composed of ionic liquids (ILs) were introduced in 2003 [1] as promising replacements of the well-studied polymer-based systems. Due to the wide variety of chemical structures of ILs, IL-based ABS allow to overcome the narrow hydrophilic-hydrophobic range of the more traditional systems. As a result, the potential of IL-based ABS for improved extraction efficiencies and high selectivity in the separation of a wide plethora of bio(molecules) led to a tremendous growth in their applications [2]. Phase diagrams and possible applications of ABS composed of ILs and salts were widely investigated in the past decade [2], and it is now accepted that the polarities of the coexisting phases largely depend on the IL anion hydrogen-bond basicity [3].

In this work, mixtures of two ILs with a common cation and different anions were investigated aiming a more controlled manipulation of the phases' polarities and ABS ability to undergo liquid-liquid demixing. Novel ABS phase diagrams were determined for systems composed of K_2CO_3, water and mixtures of $[C_4C_1im]Cl$ and $[C_4C_1im][CF_3SO_3]$ in different mole fractions. The extraction efficiencies of these systems for tryptophan and tyrosine (two model amino acids widely produced at an industrial scale) were then evaluated. It was found that the selective partitioning of amino acids mainly depends on the IL ratio in each mixture (Fig.1). ABS composed of two ILs allows to obtain separation systems of tailored polarity at the coexisting phases, an essential feature regarding the extraction and purification of value-added compounds obtained from biotechnological processes.

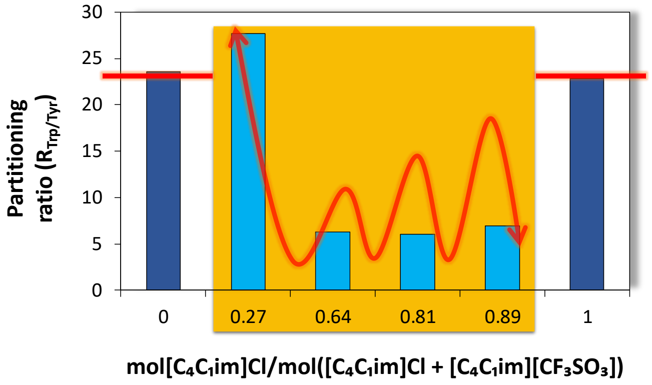

Fig.1. Selective partitioning of Tryptophan (Trp) over Tyrosine (Tyr) in ABS composed of K_2CO_3 and mixtures of ILs

Acknowledgments
This 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 FEDER under the PT2020 Partnership Agreement. H. Passos acknowledges FCT for the grant SFRH/BD/85248/2012. M. G. Freire acknowledges the European Research Council under the European Union's Seventh Framework Programme (FP7/2007-2013) / ERC grant agreement n° 337753.

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The use of mushroom extracts as bioactive ingredients in the development of cosmeceutical formulations

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The cosmetic industry is in a constant search for natural compounds, or extracts, with relevant bioactive properties to act as active ingredients. Among the possibilities, mushrooms can play an important role. They are rich sources of bioactive metabolites, known since long for their nutritional and medicinal properties, but underexploited as cosmeceutical ingredients [1].

In the present work, ethanolic extracts obtained from *Agaricus bisporus* L., *Pleurotus ostreatus* (Jacq. ex Fr.) P.Kumm. and *Lentinula edodes* (Berk.) Pegler, purchased in a local supermarket in the Northeast of Portugal, were analysed for their anti-inflammatory activity by quantification of NO production in RAW 264.7 macrophages cells, tyrosinase inhibition assay using L-DOPA as substrate, antioxidant activity by DPPH radical-scavenging and ferricyanide/Prussian blue reducing power assays, and also for their antibacterial activity by determining the minimum inhibitory concentration (MIC) and minimum bactericidal concentration (MBC) using the microdilution method. The extracts were chemically characterised in terms of phenolic acids and ergosterol content by HPLC-PDA and HPLC-UV, respectively. The extract samples were further incorporated in a base cosmetic cream considering the EC_{50} and MIC values previously determined resulting in a scale of 100 mg of extract per gram of base cream. The final formulation was mixed properly to attain sample homogeneity and then evaluated for the same bioactive purposes.

In terms of chemical composition, ergosterol and cinnamic, *p*-hydroxybenzoic, *p*-coumaric and protocatechuic acids were found in the characterized mushrooms. The mushroom extracts, as well as the final cosmeceutical formulations, were found to display antioxidant, anti-inflammatory, antibacterial and anti-tyrosinase activities. Furthermore, the final cosmeceutical formulations revealed the presence of 85-100% of the phenolic acids and ergosterol levels detected initially in the mushroom extracts.

In conclusion, the results suggest that mushroom extracts can be interesting multifunctional cosmeceutical ingredients for topical application to combat skin aging, inflammation and as preservative and hyperpigmentation correcting ingredients.

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Redução de acidez de gordura de suíno por catálise enzimática

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O crescimento acentuado da população e o aumento do seu nível de vida nas últimas décadas, especialmente nos países em desenvolvimento, resultou em mudanças profundas nos hábitos alimentares. Em particular ocorreu um aumento significativo no consumo de peixe, carne e produtos derivados. Os resíduos gerados devem ser tratados conveniente, de modo a minimizar o impacte ambiental, procurando mesmo valorizá-los economicamente. As gorduras animais são um dos sub-productos/resíduos mais significativos. Estas podem ser utilizadas para diversos fins, como por exemplo para produção de biocombustíveis (biodiesel) e para alimentação animal (Mata et al., 2013). O seu potencial de utilização e valor comercial depende de vários factores, de entre os quais o teor em ácidos gordos livres (AGL) ou índice de acidez é um dos mais relevantes. Este é responsável pelo nível de qualidade do produto, uma vez que provoca alterações indesejáveis de cor, sabor, aroma e consistência. Deste modo, é essencial encontrar métodos que permitam diminuir o índice de acidez de modo a obter a qualidade mínima pretendida para as gorduras e permitir a sua utilização posterior.

Neste trabalho foi estudado experimentalmente a esterificação enzimática com etanol para reduzir o índice de acidez de gorduras residuais de mamífero, em particular de suíno. Em comparação com o processo químico o processo enzimático não utiliza uma base ou ácido forte como catalizador homogéneo, opera a temperaturas mais baixas, e permite a utilização de etanol em vez de metanol como reagente, resultando num processo mais seguro, como menor impacte ambiental e menores custos de operação. As gorduras residuais de mamífero usadas no estudo foram obtidas numa instalação industrial de tratamento de subprodutos animais, em particular mamíferos, aves e peixe.

Numa primeira fase foi feito um estudo exploratório para determinar qual a enzima mais adequada para processar a gordura de suíno, tendo-se concluído que a Lipozyme CALB L [1] era a que permitia maiores reduções do índice de acidez. Numa segunda fase procurou-se determinar experimentalmente quais são as condições ótimas de processo em termos de temperatura, razões mássicas etanol:AGL enzima:gordura e tempo de reação. As condições ótimas correspondem a uma temperatura de 45 °C, razão EtOH:AGL de 3,25 m/m e razão enzima:gordura de 0,0060 m/m e estas permitiram uma redução do índice de acidez inicial de 67 %. A cinética da reação foi também estudada, tendo-se verificado que leis cinéticas de segunda ordem, definidas apenas em função da concentração de AGL ou na combinação das concentrações de AGL e etanol, descrevem adequadamente os resultados experimentais.

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Caracterização de extratos fenólicos de águas de lavagem de cubas de vinho tinto usando dois solventes – efeito dos extratos na inibição do crescimento de leveduras da espécie *Candida albicans*

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A produção de vinho é uma atividade agrícola de elevada relevância a nível mundial e também na região de Trás-os-Montes e Alto Douro. Gera uma grande quantidade de subprodutos, sob as mais variadas formas. A partir destes subprodutos é possível extrair uma grande quantidade de compostos, que graças às suas características podem ser utilizados em inúmeras áreas, tais como as industrias alimentar e farmacêutica. Destacam-se os compostos fenólicos, compostos naturais que derivam do metabolismo secundário das plantas, cujas bioatividade estão já descritas e que incluem efeitos antioxidantes, antimicrobianos, anticancerígenos entre outros [1]. A reportada atividade antimicrobiana destes compostos tem levado a um estudo mais intensivo dos seus constituintes, devido à diminuição da suscetibilidade dos microrganismos patogénicos e/ou oportunistas aos tratamentos atualmente existentes [2]. Um desses organismos é *Candida albicans*, uma levedura comensal/oportunista com capacidade de formar pseudo-hifas e deste modo adquirir maior resistência aos antifúngicos [3].

Nesta investigação foram utilizadas duas amostras provenientes da lavagem de duas cubas de vinho tinto após a trasfega do vinho. A partir destas amostras foi realizada uma extração líquido/líquido a fim de analisar a composição da fração fenólica das amostras por HPLC. A extração foi efetuada usando dois solventes com polaridades diferentes, etanol absoluto e acetato de etilo. Os extratos obtidos foram posteriormente avaliados quanto aos seus efeitos na inibição do crescimento de leveduras da espécie *Candida albicans*. A avaliação foi feita recorrendo ao teste de difusão em agar, e por microscopia eletrónica de transmissão. Os resultados obtidos mostraram que com ambos os solventes, as amostras apresentaram uma fração fenólica semelhante. No entanto, as amostras extraídas com etanol absoluto apresentaram uma maior diversidade de compostos, ainda que a extração com acetato de etilo tenha aparentemente extraído maior quantidade. Este facto é particularmente evidente quando se analisaram as antocianinas. Das oito antocianinas identificadas, a malvidina-3-monoglucosido foi a mais abundante. Identificaram-se ainda vários ácidos fenólicos benzóicos e cinâmicos.

No que se refere aos efeitos destes extratos no crescimento das culturas de *Candida albicans*, não se registou inibição do crescimento em placa. No entanto, a obtenção de microfotografias por microscopia eletrónica de transmissão mostrou que as leveduras sujeitas à ação destes extratos apresentavam alterações da ultra-estrutura celular, particularmente marcantes na membrana plasmática e parece celular. Registou-se também aumento da formação de vesículas densas citoplasmáticas, de conteúdo desconhecido. Esta investigação acrescentou alguma informação sobre os efeitos da aplicação de frações fenólicas no crescimento microbiano. Há um efeito inibidor potencial que se refletiu na alteração da ultra-estrutura das leveduras testadas. É importante aprofundar este estudo para tentar potenciar o efeito dos compostos extraídos, por forma a implementar alterações nas leveduras que impeçam o seu crescimento, e não causem apenas alterações cujos efeitos não se refletem na sua morte.

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Exploring ionic liquids for the development of a purification platform for therapeutic immunoglobulin Y (IgY) from egg yolk

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Biopharmaceuticals, and in particular antibodies, have greatly improved the treatment of many diseases and sometimes are the only approved therapies available for a particular disorder [1]. Although a large interest has been devoted to passive immunotherapy by the use of mammal antibodies, namely immunoglobulin G (IgG), immunoglobulins from egg yolk (Immunoglobulin Y, IgY) have also been reported as viable alternatives to these antibodies [2]. Furthermore, producing these new antibodies is more effective since more than 100 mg of IgY can be isolated per egg, corresponding to the same amount that is obtained from 200 mL of rabbit serum [2]. However, IgY still is very expensive due to the absence of an effective purification technique able to separate IgY from other contaminant proteins present in egg yolk [3]. Hence, the search of new and more scalable extraction/purification platforms for IgY is of upmost importance. In this context, liquid-liquid extractions using aqueous biphasic systems (ABS) could be a viable option. In particular, ionic-liquid-(IL)-based ABS emerged in recent years as suitable alternatives to traditional polymer-based ABS, and their major advantages are related with the lower viscosity of the coexisting phases and the possibility of tailoring their polarities and affinities so that more effective and selective extractions can be achieved [4]. Therefore, in this work, three types of aqueous biphasic systems (ABS) were studied, namely constituted by a polymer and a salt, a polymer, a salt and an ionic liquid (IL) as adjuvant and by an IL and a salt, as alternative liquid-liquid systems for the selective extraction, and thus purification, of IgY from egg yolk. According to the obtained results, systems composed of imidazolium-based ILs led to protein extraction efficiencies in the range between 88% and 98% in a single-step. Moreover, systems composed of ILs and salts allow the selective extraction of β-livetin (the major contaminant protein) for one phase while retaining IgY in the opposite layer. Based on these promising results, it can be concluded that a cost-effective platform using ABS for the purification of the value-added IgY from egg yolk could be developed, fomenting the adoption of this technique by pharmaceutical industries in the near future.

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PorGal8 mediated photodynamic therapy induces cell death and cytoskeleton protein changes in bladder cancer cells

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Aim: To investigate whether the phototoxicity induced by PorGal8 is correlated with alterations in cytoskeletal structures of cancer cells.

Introduction: Photodynamic Therapy (PDT) is an anticancer therapy, which use a non-toxic light sensitive compound that upon excitation with harmless visible light of appropriate wavelength in the presence of molecular oxygen can generate reactive oxygen species toxic to targeted cells. The ultimate effect of PDT is the induction of cancer cell death. The cell death mechanisms induced after PDT can also instigate changes and reorganization on the main cytoskeletal components (microtubules, microfilaments and intermediate filaments), which play a critical role in the maintenance of cellular morphology, membrane integrity, and are involved in vital cellular processes.

Materials and Methods: UM-UC-3 and HT-1376 human bladder cancer cells, exhibiting different sensitivities to PDT, were used. PorGal8 uptake by bladder cancer cells was determined by fluorescence spectroscopy. PDT was carried out with LEDs array system at 8.4 mW/cm2. The levels and distribution of the cytoskeletal proteins were evaluated by Western Blotting and fluorescence microscopy.

Results and discussion: PorGal8 uptake and PDT-induced cytotoxicity were higher in UM-UC-3 compared to HT-1376 bladder cancer cells. These differences were correlated with cytoskeleton alterations. Thirty minutes after PDT, HT-1376 cells showed loss of cell-cell contacts and reduction of the F-actin. Twenty-four hours after PDT, there was a reorganization in actin filaments distribution similar to control cells. In UM-UC-3, thirty minutes after PDT, cells retraction was observed, with loss of stress fibers and collapse of actin filaments. Twenty-four hours after PDT, the F-actin pattern distribution was distinct, showing a clear increase in F-actin fluorescence in the sites of cell indicating a reduction in cell-cell interaction. In UM-UC-3 bladder cancer cells it was also observed reduction on the expression levels of vimentin and no alteration for α-tubulin.

Conclusions: Rearrangement of the cytoskeleton in bladder cancer cells may play a critical role in cell death triggered by PDT with PorGal8.

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Flow behaviour in microchannels of an innovative blood analogue fluid based on giant unilamellar vesicles

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The development of blood analogue fluids continues to draw much attention from researchers around the world, in order to mimic the physical and rheological characteristics of the real blood [1, 2]. One of the biggest challenges in blood analogues is to incorporate cellular-like components able to perform fundamental functions, such as the transport of gases and nutrients, and the ability to deform under flow when they pass through a narrower capillary.

This work focused on the development of an innovative blood analogue, containing giant unilamellar vesicles (GUVs), to mimic the flow behaviour of red blood cells (RBCs). The GUVs were prepared using soybean lecithin by hydration of a lipid film followed by extrusion through polycarbonate membranes of 8 µm. The rheological characterization of different blood analogue solutions was performed in a stress controlled rheometer (Bohlin CVO, Malvern) and the results have shown a good agreement when compared with a sample containing 5% of RBCs (see Figure 1).

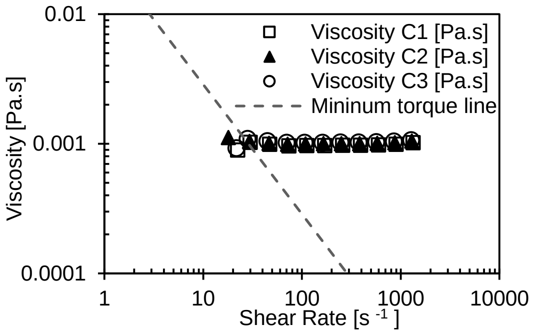

Fig. 1. Viscosity of GUVs solutions with different concentrations of soybean lecithin as a function of shear rate

In addition, flow visualizations were performed in a hyperbolic constriction microchannel, where a cell free layer was formed at the constriction downstream. At this region of the microchannel, the deformation of GUVs was also measured and it was also found that the deformation index increases with the flow rate. Overall, our results show that the proposed blood analogue has a close rheological behaviour to *in vitro* blood samples with low hematocrits.

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Analysis of the effects of Portuguese propolis extracts on DNA damage

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Propolis is a natural resinous product produced by bees from tree buds and exudates and used in the beehives. Among the various biologically active compounds present in propolis, flavonoids are some of the most important ones. Flavonoids have been valued by their antigenotoxic effect, which is a direct consequence of their antioxidant properties, as they are reactive oxygen species (ROS) scavengers. ROS are small molecules/free radicals whose effect is associated with various diseases. Extracts rich in flavonoids have been widely used in the food, drug and cosmetic industries. Although propolis has already been intensively studied worldwide, studies with Portuguese propolis are relatively scarce.

The aim of this study is to elucidate the influence of propolis ethanol extracts from a Portuguese apiary - Pereiro (P.EEs) -, at Beira Alta (district of Guarda), on DNA damage and recovery. Extracts from propolis samples harvested every year from 2010 to 2014 and also mixtures of these extracts revealed different cytotoxicity in *Saccharomyces cerevisiae* depending of the year. As expected, all the tested extracts and mixtures show antioxidant effects assessed by the DPPH radical scavenging activity and the reducing power assays, which correlates with their DNA-preventive activity against Fe^{2+}-induced damage, shown in a DNA topology assay. However, analysis by flow cytometry showed that yeast cells treated with P.EE from 2010 appear to be affected when it comes to cell cycle progression, which is in accordance with the high cytotoxicity shown by this extract. As the tested extracts show antioxidant activity, the mechanism that affects yeast cell viability and cell cycle progression is not related to prooxidant activity.

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Study of the role of ellagitannins in astringency: a molecular approach

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Tannins, a complex group of polyphenols, can be divided into two classes according to their structure, condensed and hydrolysable tannins [1]. The second ones, also known as ellagitannins, are found in fruits such as pomegranate (e.g. punicalagin) and also in red wine due to migration from oak wood during ageing (e.g. vescalagin and castalagin) [2, 3]. Tannins are highly involved in astringency sensation. Astringency, described as dryness, puckering and tightening of the oral cavity, is perceived during the ingestion of tannin-rich food and beverages. Besides being related to a negative perception, some quality beverages required a balanced level in astringency [1]. Thus, it becomes noteworthy to understand how this mechanism occurs and how can it be modulated. It has been generally accepted that astringency is due to the tannin-induced interaction and/or precipitation of salivary proteins (SP) in the mouth [2]. This interaction is highly dependent on the protein size, charge and structure, as well as on its molecular weight [1]. Among salivary proteins, the most important families include acidic, glycosylated and basic proline-rich proteins (PRPs), statherin, P-B peptide, cystatins and mucin. Most of astringency studies are focused on condensed tannins, due to its considerable amount in diet. To our knowledge, there are no studies about the interaction between SP and hydrolysable tannins [3].

The aim of this work was to study the interaction between three ellagitannins (castalagin, vescalagin and punicalagin) and some human SP (statherin, P-B peptide and cystatins) with different structure. P-B peptide is similar to basic PRP [4] and its composition is high in proline residues, contrasting with the other two SP selected. These proteins were purified from human saliva by preparative-HPLC. The referred tannins were isolated from their natural sources [5, 6]. These interactions were addressed by two spectroscopic techniques: fluorescence quenching and Saturation Transference Difference(STD)-NMR.

Both spectroscopic methods revealed that castalagin, vescalagin and punicalagin interact significantly with human statherin, P-B peptide and cystatins. However, this interaction was different according to each SP-tannin complex. From all three ellagitannins, punicalagin showed the higher binding affinity to the three SP approached. Regarding the different SP, it appears that punicalagin interacts better with P-B peptide. According to the STD-NMR analysis (Table 1), this complex has the smallest dissociation constant (KD = 0,127 mM) and thus appears to have the strongest interaction.

Table 1. Dissociation constants (K_D) between SP and ellagitannins

SP	**K_D / mM**		
	Castalagin	Vescalagin	Punicalagin
Sthaterin	0,568	0,632	0,277
P-B Peptide	0,297	1,173	0,127
Cystatins	0,461	1,402	0,380

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Redução de acidez de óleo de peixe por esterificação enzimática

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Cerca de um milhão de toneladas de óleo de peixe é anualmente produzido ao nível mundial, e usado principalmente como ingrediente em rações animais e aquacultura [1]. O óleo de peixe é composto principalmente por triglicéridos, di e mono-glicéridos (normalmente > 95 % em peso), dos quais uma quantidade significativa são ácidos gordos polinsaturados, altamente susceptíveis de oxidação. Os compostos não-triglicerídeos também estão presentes, tais como ácidos gordos livres (AGL), humidade e componentes oxidantes (p.ex., metais vestigiais, pigmentos, tocoferóis e fosfatidos) e compostos contendo azoto, enxofre e halogéneos. O óleo de peixe é produzido em simultâneo com a farinha de peixe num processo de cozimento, onde todo o peixe ou subprodutos de peixe são processados e a massa é prensada para remover a maior parte do óleo (2-10% em peso) e a água [2]. Alguma degradação e impurezas presentes no óleo extraído ocorrem durante o armazenamento e manipulação das matérias-primas de peixe, devido à sua deterioração por ação microbiológica, resultando em elevados níveis de AGL (5-15 % em peso), que prejudicam a sua qualidade e aceitabilidade para alimentação, devido ao sabor e cor que conferem ao óleo e porque reduzem a sua estabilidade ou tempo de vida útil. Assim, é um objectivo da indústria de óleo de peixe obter um produto de qualidade satisfatória e aumentar seu valor comercial, para o qual são necessárias etapas de purificação. Assim, este trabalho teve como objetivo estudar a redução da acidez do óleo de peixe através de esterificação enzimática com etanol, de modo a converter o AGL em ésteres-etílicos. As amostras de óleo de peixe foram obtidas numa empresa Portuguesa de tratamento de subprodutos, as quais eram compostas por mistura de diferentes tipos de óleo de peixe, incluindo sardinha, atum, cavala, salmão, bacalhau, redfish e congro. Estas foram caracterizadas no seu índice de acidez (10-14 mg KOH/g óleo), índice de iodo (109-219 g iodo/100g oil), viscosidade cinemática (32.54-34.78 mm^2/s a 40ºC), densidade (0.932-0.937 g/cm^3 a 15ºC) e teor de água (0.5-1.8 wt%). Para a esterificação foram testadas quatro enzimas como catalisador (Novozym 435, Lipozyme RM IM, Lipozyme CALB L, Palatase 20000 L) e a que conduziu a uma mairo redução do índice de acidez foi seleccionada (Lipozyme® CALB da Novozymes, uma lipase não-específica obtida a partir da Candida antarctica B). Foram estudadas diferentes condições de operatórias: temperatura de reacção (35, 45 e 55 ºC) e tempo (de 0 to 180 min), razão enzima/óleo (0.00225 e 0.0045 wt/wt) e razão etanol/AGL (3.235, 4.879, 4.907 e 6.566 wt/wt). Os resultados mostraram que nas melhores condições de operação (150 min de tempo de reacção, 45ºC de temperatura, razão mássica enzima/óleo de 0.0045 e razão mássica etanol/AGL de 4.879) foram obtidos mais de 70 % de redução de AGL em apenas um passo de reacção. Este resultado pode ainda ser melhorado num segundo passo de esterificação ou num processo de reacção com remoção contínua de água formada durante a reacção (como p.ex. no processo patenteado FAeSTER, numa secagem flash ou outra tecnologia de secagem). Concluiu-se que a esterificação por catálise enzimática é um método eficaz para a redução de AGL, com perdas reduzidas de óleo em comparação com o processo de neutralização alcalina, devido à formação de sabões. Para além disso, a reacção enzimática ocorre a temperaturas baixas (< 60 ºC), deste modo reduzindo o consumo e custos de energia e preservando as propriedades nutricionais do óleo, sendo menos sensível à presença de água no óleo do que a reacção por catálise homogénea com um ácido forte.

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Impressão molecular de polifenóis em partículas de polímero sensíveis a estímulos

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Polifenóis como o *trans*-resveratrol, catequina, ácido elágico, etc, apresentam aplicações importantes na indústria farmacêutica, cosmética ou em medicina devido às suas propriedades antioxidantes. Estes compostos estão presentes em diversas fontes vegetais e existe um elevado interesse no desenvolvimento de técnicas e processos de extracção, purificação e concentração que permitam a sua utilização de forma eficiente. Por outro lado, muitos polifenóis (ex. resveratrol) têm baixa biodisponibilidade por administração oral devido a múltiplos factores como a fraca solubilidade em meio aquoso e a sua elevada taxa de metabolização e excreção pelo organismo. Desta forma, é também vantajoso o desenvolvimento de veículos para a sua retenção e libertação controlada. A técnica de impressão molecular tem como objectivo criar numa rede de polímero cavidades com tamanho molecular que apresentem elevada afinidade e especificidade com uma molécula alvo (T). Idealmente, o material molecularmente impresso deve ser capaz de reconhecer essa molécula em sucessivos ciclos de retenção/libertação. Nos últimos anos assistiu-se a um franco progresso no desenvolvimento de diferentes tipos de polímeros molecularmente impressos (MIPs) e à sua aplicação em diversos domínios, incluindo a biotecnologia e a engenharia biomédica [1,2]. Neste trabalho são apresentados resultados relativos à impressão molecular de polifenóis em micropartículas de polímero considerando monómeros funcionais (FM) como o ácido metacrílico, acrilamida ou 4-vinilpiridina. Através de polimerização por precipitação, são gerados diferentes MIPs para polifenóis considerando em alternativa o mecanismo radicalar clássico (FRP) e a técnica de transferência reversível de cadeia por adição-fragmentação (RAFT) [3,4]. Usando polimerização RAFT, são posteriormente enxertadas cadeias de polímero funcional na superfície das partículas MIP, conferindo-lhes sensibilidade à variação do pH e da temperatura [4]. O desempenho dos diferentes MIPs na retenção/libertação selectiva de polifenóis é avaliado através de adsorção batch, extracção em fase sólida (SPE), análise cromatográfica e análise frontal (Fig. 1). Mostra-se que é possível potenciar o desempenho *in vitro* dos MIPs na retenção/libertação de polifenóis através da selecção de condições particulares de impressão molecular (ex. combinação T/FM). A introdução de sensibilidade nos MIPs revela-se também promissora, nomeadamente para aplicações de libertação estimulada pelo pH e/ou temperatura.

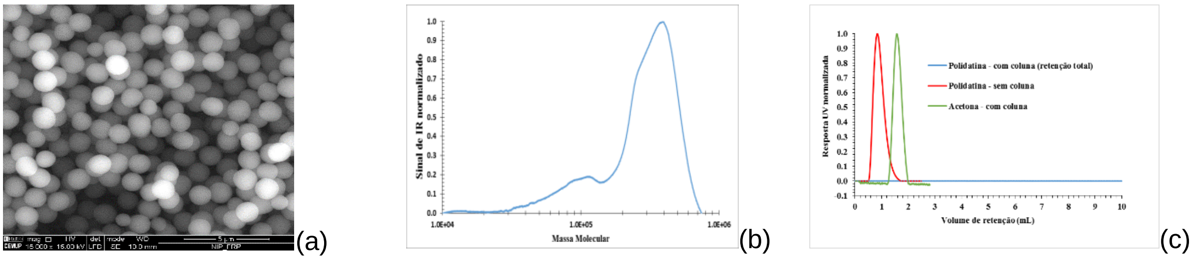

Fig.1. (a) Morfologia das partículas sintetizadas. (b) Tamanho molecular das cadeias primárias dos MIP obtido por SEC. (c) Avaliação do desempenho dos MIP através de análise cromatográfica

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Effect of high pressure and temperature on the physicochemical properties of heather honey

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Honey is natural sweet substance produced by *Apis mellifera*, which is consumed as a high nutritive value food. The physicochemical quality criteria of honey are well specified by the European Legislation (EC Directive 2001/110) [1]. The quality properties of honey can be diminished by the influence of heating in the thermal pasteurization of honey [2]. As an alternative to conventional thermal pasteurization, the non-thermal high pressure processing has potential to produce safety food with similar characteristics to the raw unprocessed foods [3].

Therefore, the purpose of this work was to study the effect of three treatments: 1) high pressure (725 MPa for 10 minutes); 2) high pressure with temperature (725 MPa for 10 minutes at temperature of 50 °C); and 3) thermal treatment (75 °C for 5 minutes) on the physicochemical parameters (moisture, pH, electrical conductivity, free acidity, diastase activity and hydroxymethylfurfural content) of a Portuguese heather honey.

The results obtained for several physicochemical parameters were significantly different among the samples under the different treatments, for instance, the HMF content. This parameter, widely recognized as indicator of honeys' freshness [4], depends on several factors, such as temperature, time of heating and storage conditions [5]. The value of HMF in the raw honey was 5,5 ± 0,5 $mg.kg^{-1}$ of honey (EU limit is 40 $mg \cdot kg^{-1}$), ensuring that it was a fresh product that has not been subjected to heating or inadequate storing conditions. Concerning the treatments, the ANOVA results showed that the amounts of HMF did differ significantly (P-value= 0.0315). The thermal treatment significantly increased the HMF concentration comparing with the raw honey (P-value= 0.0355). The preliminary results did not show significant increase in the HMF content when high pressure processing, with and without temperature, were applied. Further studies should be performed to confirm that high pressure processing has no adverse effect on the honey quality.

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Componente volátil de lúpulo: uma análise comparativa entre clones espontâneos e variedades

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Introdução:
O *Humulus lupulus* L. é uma espécie pertencente à família Cannabaceae. O lúpulo, como é vulgarmente conhecido, é uma planta herbácea perene, dióica e normalmente diplóide (2n=20) [1]. É na produção de cerveja que o lúpulo apresenta o seu maior valor económico a nível internacional. Foi na Flandres que começou verdadeiramente a produção de cerveja, uma vez que desde o início da sua fabricação na Mesopotâmia, até então, a cerveja era uma bebida adocicada, baseada na fermentação de malte, com o nome de Ale sendo a sua conservação um dos maiores problemas. A utilização de lúpulo veio resolver esse problema, visto que produz compostos com acção bactericida, em particular contra bactérias Gram-negativas [2]. A sua produção estendeu-se por toda a Europa e, daí, ao resto do mundo.

Actualmente a procura de novos aromas tem vindo a aumentar, impulsionada pela recente expansão da produção artesanal de cerveja em Portugal. Uma vez que existe lúpulo espontâneo em grande parte do país, a recolha e análise dos aromas desses lúpulos poderá levar-nos ao desenvolvimento de novos e mais aromas. As componentes voláteis extraídas de lúpulos espontâneos recolhidos na zona de Bragança, foram analisadas e comparadas com as de variedades comerciais.

Material e métodos:
O material vegetal foi colhido em diferentes zonas do distrito de Bragança, junto a cursos de água. Os cones femininos foram recolhidos e os voláteis foram extraídos num sistema Likens-Nickerson e posteriormente analisados por CG e CG-EM.

Resultados e conclusão:
Os resultados obtidos evidenciam uma certa semelhança na componente monoterpénica, com o β-mirceno como composto maioritário (75 e 64%, respectivamente na amostra do cultivar e na amostra do espontâneo) e diferenças notórias na componente sesquiterpénica, bem evidente nos casos do α-humulene (12% no cultivar, 0,2% no espontâneo) e do *trans*-β-farnesene (não detectado no cultivar, 9% no espontâneo). É também merecedor de realce a maior riqueza da componente sesquiterpénica do clone espontâneo, em particular nos compostos oxigenados

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Antigenotoxicity of *Ginkgo biloba* extract in colonocytes

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Plants have been used over centuries in traditional medicine for the treatment of human diseases. In the last decades the interest in medicinal plants has increased significantly owing to the antioxidant effect found in their natural extracts which is responsible for many therapeutic effects. The *Ginkgo biloba* leaf extract (GBE), widely used in traditional Chinese medicine, is intensively studied and sold all over the world due to its many health benefits, being used for the treatment of human pathologies such as neurodegenerative and cardiovascular diseases, and also to delay the ageing process. Although the antioxidant properties of GBE are well documented [1-3], studies on the antigenotoxic activity of GBE are still scarce.

The colonic environment is continuously exposed to a large diversity of dietary compounds, some of them potentially carcinogenic, that may affect DNA integrity (e.g.: DNA oxidation and strand breaks) and alter cell genetic information, contributing to the development of colorectal cancer (CRC). Diets that are mainly composed of fruits and vegetables are rich in polyphenols and have been associated with CRC prevention [4]. Medicinal plant extracts may also be rich in polyphenols and can be used to prevent or reduce DNA damage.

The chemical analysis of GBE allowed the identification of some *G. biloba* characteristic compounds, being mainly composed of one type of polyphenols designed as flavonoids, which are known for having strong antioxidant activity. Owing to this property, GBE could be a potential chemopreventive agent against CRC. Thus, GBE was subjected to simulated *in vitro* human digestion of the upper tract, originating a product (DGBE) that represents the extract when it reaches the colon during the digestive process. Both forms of the extract demonstrated *in vitro* antioxidant activity, DPPH and NO scavenging activity for GBE and only NO scavenging activity for DGBE. The extracts were tested in human colorectal adenocarcinoma cell line for their cytotoxicity (MTT assay) and antigenotoxicity (comet assay), where cells were pre-treated with each extract and subsequently challenged with H_2O_2 (75 μM). Both forms of the extract did not affect cell viability and decreased the level of DNA damage induced by oxidative stress. GBE and DGBE seem to be protecting DNA from damage, which could be the result of the stimulation of antioxidant defence mechanisms (such as the induction of antioxidant enzymatic activity or non-enzymatic defences) and DNA repair, or the extracts might be inducing moderate stress in cells, causing cell adaption when exposed to H_2O_2. Therefore, GBE shows a potential antigenotoxic effect, that seems to be retained after the digestive process, and might be the result of the antioxidant properties provided by the flavonoid fraction of the extract and suggested by the results of the *in vitro* antioxidant assays.

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Protection against nitric oxide genotoxicity by *Ginkgo biloba* extract

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For a long time, plants have been used in traditional medicine to treat various health conditions despite the lack of knowledge about their effects and benefits. Over the last years, a considerably good reputation involving the use of the *Ginkgo biloba* plant has been growing within the scientific community and today its potential in terms of beneficial effects is very well sustained in the literature [1]. However, most of those studies only face towards the antioxidant properties and just a little was explored relatively to any antigenotoxic activity.

The excessive production of oxidative species, being ROS or RNS, can reveal to be stressful to the cell to a point where it compromises survival. In between their molecular targets, reactive oxygen species can affect DNA, possibly causing loss of stability and integrity, and becoming a very dangerous threat. SNP is a NO-releasing agent that can be used to simulate an excessive increase in NO production. NO is recognized for its biological roles in the regulation of vasodilation, and nervous system and immune system signaling as well as for its potentially adverse effects [2]. Depending on the molecules it encounters inside the cell, NO may oxidize into peroxynitrite or dinitrogen trioxide (among many others), both molecules being able to interact with and modify DNA [3].

So far, the chemical analysis of the ethanolic extract from *Ginkgo biloba* leaves revealed the presence of some characteristic compounds and the properties of the extract were tested *in vitro* with positive results. An effect of protection against SNP was observed in viability assays with the fission yeast *Schizosaccharomyces pombe* wild type strains and DNA repair-affected mutants. The analysis of cell cycling revealed that *Ginkgo biloba* alone causes a quicker advance in cell cycle progression and that treatment with *Ginkgo biloba* extract slightly reduces the delay caused by exposure to SNP. Finally, experiments involving green fluorescent protein fused with oxidative stress response Sty1 and Pap1 proteins pointed to a possible protection mechanism, where the interaction with the extract may be functioning as a mild stress elicitor, preparing cells for the stress induced by NO. Putting all the evidence together, the extract from *Ginkgo biloba* protects cells from the effect of SNP through a DNA-repair independent mechanism, which may involve the scavenging of NO and subsequent decrease in DNA modifications, and/or the signalling of oxidative stress-response proteins preventing the excessive accumulation of oxidant molecules.

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XXII Encontro Luso-Galego
Química

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Catálise

The effect of graphene oxide (GO) on the performance of Au/TiO_2-GO bifunctional catalyst in cellobiose valorisation

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Bifunctional catalysts open a door to inexpensive and environmentally friendly domino/cascade-reactions of biomass valorisaton in a single pot [1]. In this context, direct selective oxidation of cellobiose is an interesting process, because it yields important platform biomass-derived chemicals, such as gluconic acid and its derivatives. This process involves cellobiose hydrolysis to glucose (taking place on the acidic sites of the support), followed by glucose oxidation step (on Au nanoparticles) to the final product.

A unique electronic interaction between Au and TiO_2 leads to excellent results in many oxidation reactions [2]. On the other hand, graphene oxide (GO) sheets demonstrate superior electron mobility and contain oxygen functional groups, which can catalyse many chemical reactions, including hydrolysis of cellobiose [3]. With this in mind, TiO_2-GO composites were employed for the first time as supports for Au and their catalytic activity was evaluated in tandem oxidation of cellobiose to gluconic acid. The pristine TiO_2 and TiO_2-GO supports were additionally tested in hydrolysis of cellobiose to glucose, which is the first step of many biomass valorization processes. The TiO_2-GO composites were prepared using TiO_2 with varied content of anatase and rutile crystalline phases, different surface acidity and particle size. Subsequently, gold was deposited on these supports and their catalytic performance was compared with that of Au supported on corresponding pristine TiO_2, in order to evaluate the influence of the presence of GO on the performance of these bifunctional catalysts.

Increased cellobiose conversion was obtained by Au supported on TiO_2-GO containing rutile whereas in the case of Au supported on TiO_2 containing only anatase, the yield of gluconic acid was always higher in the absence of GO. Concerning the hydrolysis of cellobiose, the conversion was independent of the crystalline phase of TiO_2, but improved results were achieved by addition of GO to TiO_2 with smaller particle size. In general, in both processes, the addition of GO to TiO_2 supports resulted in decreased selectivity to glucose and gluconic acid, which was attributed to the stronger adsorption of the reactants on the composite supports, leading to undesired side reactions as well as to higher Au particle size on TiO_2-GO. Overall, as shown by UV-Vis and XPS analysis, the performance of these catalysts was governed by the amount of oxygen vacancies present in the TiO_2 structure. It was concluded that the addition of GO to TiO_2 supports hindered the formation of these defects, contributing to the worse performance of Au/TiO_2-GO as compared to Au/TiO_2 in this tandem process.

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Surface of carbon nanotubes for wet peroxide oxidation

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Catalytic wet peroxide oxidation (CWPO) is regarded as a potential solution for the treatment of aqueous effluents containing recalcitrant and toxic organic pollutants, difficult to remove by conventional biological processes, mainly if present at high concentrations (1-10 g L^{-1}) [1]. In a recent study, three magnetic carbon nanotube (CNT) samples, named E30 (undoped), A30 (completely N-doped) and E10A20 (partially N-doped), were synthesized by chemical vapor deposition and tested in the CWPO process, finding that N-doped hydrophilic surfaces promoted the fast decomposition of H_2O_2 into non-reactive species (H_2O and O_2), hindering CWPO [2].

For this study, the surfaces of the CNT samples were modified, analyzing the effect of these modifications on their activity during the CWPO of highly concentrated 4-nitrophenol solutions (4-NP, 5 g L^{-1}), using relatively mild operating conditions (atmospheric pressure, T = 50 °C, pH = 3), a catalyst load of 2.5 g L^{-1} and the stoichiometric amount of H_2O_2 needed for the complete mineralization of 4-NP. As shown in Table 1, the removal of surface functionalities by calcining the CNT samples at 800 °C enhances significantly their activity towards CWPO, evaluated in terms of 4-NP removal and total organic carbon (TOC) conversion, due to the increased hydrophobicity of the CNTs after the treatment. In particular, E30-calc and E10A20-calc were able to remove *ca.* 100 % of 4-NP after 8 h of operation, owning to high mineralization levels. On the contrary, the activity of the more hydrophobic surfaces became worse upon increasing the concentration of surface carboxylic acid groups by treating the CNT samples with nitric acid solutions (samples -NA).

Table 1. Catalytic activity during CWPO after 8 and 24 h

	8 h			**24 h**		
	$X_{4\text{-}NP}$ (%)	**$X_{H_2O_2}$ (%)**	**X_{TOC} (%)**	**$X_{4\text{-}NP}$ (%)**	**$X_{H_2O_2}$ (%)**	**X_{TOC} (%)**
E30	92	33	*n.d.*	100	54	59
E30-calc	99	40	45	100	59	59
E30-NA	38	89	18	99	70	54
E10A20	46	43	*n.d.*	88	67	44
E10A20-calc	97	71	38	99	99	48
E10A20-NA	38	31	4	60	42	13
A30	6	93	*n.d.*	9	93	18
A30-calc	31	90	22	35	99	22
A30-NA	22	99	0	48	100	0

n.d.: not determined.

Acknowledgements

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Compósitos óxidos bimetálicos CoMn-Nanotubos de carbono: catalisadores bifuncionais para reações de oxigénio

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A natureza finita dos combustíveis fósseis e os problemas ambientais provenientes do seu uso fomentaram o desenvolvimento de tecnologias mais limpas utilizando fontes de energia renováveis. Neste contexto, as células de combustível regenerativas são uma tecnologia de armazenamento de energia que começa a gerar grande interesse, sendo constituídas por uma célula de eletrólise e uma célula de combustível, ou apenas um equipamento com estas duas células combinadas, sendo assim denominada célula de combustível regenerativa unificada.

Na célula de combustível regenerativa unificada ocorrem quatro reações diferentes: no modo célula de eletrólise as reações de evolução do hidrogénio (HER) e do oxigénio (OER) e durante a operação em modo célula de combustível a reação de redução do oxigénio (ORR) e a reação de oxidação do hidrogénio (HOR). [1] Em qualquer um dos casos, o tipo de catalisador a utilizar é fundamental para garantir a maior eficiência do dispositivo. A HOR e a HER são geralmente eficientes, residindo o maior obstáculo na ORR e OER. Atualmente, estas reações são aceleradas com a introdução de catalisadores derivados de metais nobres [2,3]. Como estas podem apresentar mecanismos diferentes, tem sido um desafio sintetizarem-se catalisadores bifuncionais que possam ser adicionados ao cátodo por forma a catalisar ambas as reações, sem encarecer o dispositivo final.

Neste trabalho pretende-se desenvolver uma classe de novos catalisadores para as reações em questão, de menor custo e igualmente eficientes, podendo assim contribuir para um melhor desenho da camada catalítica das células de combustível regenerativa unificada menos dispendiosa. Para tal, um conjunto de óxidos de cobalto e manganês da família dos *hidróxidos duplos lamelares* (LDH, layered double hydroxides) foram sintetizados e caracterizados físico-química, morfológica e electroquimicamente. Numa fase posterior, também foram sintetizados compósitos com materiais de carbono, nomeadamente, nanotubos de carbono originais e oxidados, onde foi possível aferir a contribuição dos grupos funcionais de oxigénio e do aumento da condutividade no desempenho eletroquímico destes catalisadores em meio alcalino.

Agradecimentos
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Comparison between diferent polyoxometalate@porous materials catalysts in oxidative desulfurization processes

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The desulfurization of petroleum derived fuels has become an important part of refining processes due to environmental concerns with respect to sulfur content in fuels. Hydrodesulfurization (HDS) is the current method to remove sulfur from fuels. To achieve ultra low levels of sulfur content in fuels, HDS requires harsh conditions of high temperature, high pressure and high hydrogen consumption resulting in elevated operation costs Therefore, more sustainable desulfurization methods have been investigated. Oxidative desulfurization (ODS) is one of the most promising and low-costly processes to achieve sulfur-free fuels, which operates in two main steps: oxidation of sulfur compounds in sulfoxides and/or sulfones and its removal by an extraction process. The success of this sustainable process depends on the presence of an efficient and robust catalyst with capability to be recycled.

Polyoxometalates are metal-oxygen clusters that have been extensively used in oxidative catalysis, mainly due to its remarkable properties such as adjustable acidity and redox properties, high thermal stability and intrinsic resistance to oxidative decomposition. The homogeneous catalysts based POMs provide high catalytic activity; however, the catalyst separation and recovery is very difficult. Different approaches have been used to prepare POMs based heterogeneous catalysts, including silica materials and metal organic frameworks (MOFs) [1-3].

In this work, Keggin-type derivative polyoxometalates were used as active catalytic species: the mono-lacunar phosphotungstate (PW_{11}) and the zinc mono-substituted phosphotungstate ($PW_{11}Zn$). Several heterogeneous catalysts based POMs have been investigated mainly using porous material supports (MOFs and sílica) and also hybrid materials. The catalytic performance of this catalysts in oxidative desulfurization of a model diesel containing refractory sulfur compounds usually present in liquid fuels namely dibenzothiophene (DBT), 1-benzothiophene (1-BT) and 4,6- dimethyldibenzothiophene (4,6-DMDBT), was evaluated and compared. Hydrogen peroxide was used as oxidant.

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High catalytic performance of gold nanoparticles immobilized onto L-serine functionalized clay on 4-nitrophenol reduction

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Catalysis by gold nanoparticles (Au NPs) is a fast growing area within the field of metal-based nanocatalysis due to their unique physicochemical properties. One of the most important reactions catalyzed by Au NPs is the reduction of 4-nitrophenol (4-NP), which is among the most common organic pollutants found in industrial and agricultural wastewaters [1]. The reduction of 4-NP leads to the formation of 4-aminophenol (4-AP), which is a valuable compound used as intermediate in the synthesis of numerous pharmaceutical and natural products [2]. Nevertheless, Au NPs show a tendency to form aggregates, which reduces their catalytic performance. Thus, their immobilization onto solid supports is a promising alternative to overcome this disadvantage. Clays are of particular interest since they are cheap, eco-friendly and readily available. However, the direct immobilization of Au NPs onto clays usually leads to an inactive catalyst or to significant leaching during the catalytic reaction [3]. Therefore, the previous functionalization of the clay *via* covalent attachment of organic ligands is the best solution for the efficient attachment of Au NPs. L–serine derivatives are particularly interesting linking agents since they are cheap and have several coordinating functionalities, namely nitrogen groups.

In this work, we report the preparation, characterization and successful application of Au NPs immobilized into two different L-serine functionalized clays (K10-montmorillonite) in the reduction of 4-NP (Fig. 1). Both catalysts led to nearly 100% 4-NP conversion in only 1 minute, presenting pseudo first-order rate constants normalized for Au loading (by ICP) of K = 638 and 408 mmol^{-1} s^{-1}. The catalysts showed outstanding stability upon 10 consecutive catalytic cycles, leading to conversions up to 95% without any Au leaching.

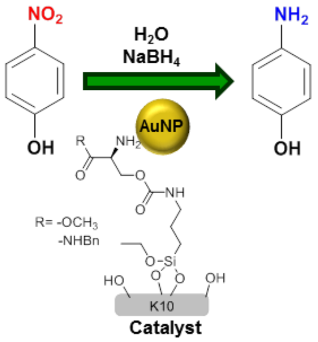

Fig.1. Scheme of 4-NP reduction catalyzed by Au NPs immobilized into L-serine functionalized K10

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Experimental and modelling study of CWPO over P-doped carbon black catalysts

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The catalytic wet peroxide oxidation (CWPO) of 4-nitrophenol (4-NP) with phosphorous doped carbon black catalysts (P-CB) was studied in the present work. The effect of reaction time (0-8 h), temperature (50-80 ºC) and initial pH (2-4) on 4-NP removal and hydrogen peroxide consumption was investigated. Results exhibited the presence of an induction period showing an inverse dependence with the operating temperature and initial pH (pH$_0$). The power law model described well the reaction rates of 4-NP removal and hydrogen peroxide consumption. The slow initial rates were reproduced by taking into account the evolution of pH, expressed in terms of proton concentration in the model. Fitted kinetic equations and estimated parameter values are summarized in Table 1. As can be seen in Figure 1, the kinetic model properly describes the oxidation process.

Table 1. Kinetic model for CWPO of 4-NP upon P-doped carbon black

Kinetic equation	R^2
$-\dfrac{d[4\text{-}NP]}{[W]\cdot dt} = 237\cdot exp\left(\dfrac{-\mathbf{94}\ kJ\ mol^{-1}}{R\cdot T}\right)\cdot[4\text{-}NP]\cdot[H_2O_2]\cdot[H^+]$	0.95
$-\dfrac{d[H_2O_2]}{[W]\cdot dt} = 65.6\cdot exp\left(\dfrac{-\mathbf{89}\ kJ\ mol^{-1}}{R\cdot T}\right)\cdot[H_2O_2]^2\cdot[H^+]$	0.88
$\dfrac{d[H^+]}{[W]\cdot dt} = 1.97\cdot 10^6\cdot[H^+]^{0.77}$	0.98

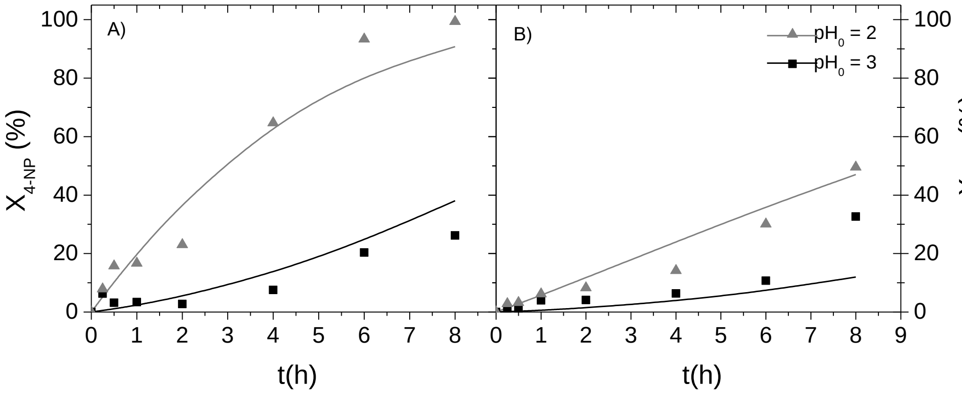

Fig. 1. Experimental data (symbols) and predicted values (curves) of 4-NP (A) and H_2O_2 (B) conversion in CWPO of 4-NP at 50 ºC and 2.5 g$_{cat}$ L^{-1}. $C_{4\text{-NP},0}$ = 5 g L^{-1} and $C_{H2O2,0}$ =17.8 g L^{-1}

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Orange II degradation by wet peroxidation using gold catalysts

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Azo dyes are non-biodegradable compounds under aerobic conditions; therefore their discharge in water bodies can cause several problems to the aquatic ecosystems [1]. The conventional processes only transfer the pollutants to another phase and are inefficient for dyes removal since these compounds are often non-biodegradable and toxic for the microorganisms used in the treatment units. Wet peroxide oxidation (WPO) is one of the advanced oxidation processes that allows removing organic compounds from water through highly oxidative hydroxyl radicals, generated by decomposition of hydrogen peroxide [2], in the presence of a metallic catalyst.

The main goal of this study was to use different types of oxides (Fe_2O_3, TiO_2, ZnO and Al_2O_3) as supports for gold catalysts, in order to evaluate the most suitable for Au deposition. Materials were prepared by the deposition-precipitation method, which yielded nanosized gold particles well dispersed over the supports, with mean particle sizes ranging from 2.2 to 5.5 nm. A commercial catalyst (Au/Fe_2O_3 Type C reference material, supplied by the World Gold Council) was used for comparison purposes.

The experiments were performed in a slurry batch reactor to determine the effect of the oxidant per se, and to compare the adsorption and the oxidation reaction using the supports (without gold) or the catalysts (with gold). Performances reached were compared in terms of dye and total organic carbon (TOC) removals, efficiency of oxidant use and rate of hydroxyl radicals generation.

The efficiency of wet peroxide oxidation depends on the type of oxide used as support, gold loading and diameter of gold nanoparticles. The Au/Al_2O_3 catalyst, which has the highest BET surface area (210 m^2/g), showed the highest turnover frequency (TOF) value, TOC and dye removals – Table 1.

Table 1. Dye and TOC removals after 16 h of reaction and TOF values for each catalyst used

Catalyst	Dye removal (%)	TOC removal (%)	TOF*10^6 (s^{-1})
Au/Fe_2O_3	51.4	36.9	21.8
Au/Fe_2O_3 WGC	40.9	29.6	5.4
Au/TiO_2	68.9	32.4	14.0
Au/ZnO	62.6	31.9	42.4
Au/Al_2O_3	99.4	48.3	75.5

The catalysts were reused for three consecutive cycles, with no Au leaching being detected into the solution, showing their high stability. This was also confirmed by textural and chemical characterization of the fresh and used catalysts.

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Preparação de compósitos de TiO_2 e nanotubos de carbono através do moinho de bolas para a ozonização fotocatalítica

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A ozonização fotocatalítica é um processo de oxidação avançada usada na remoção de poluentes das águas residuais e de consumo humano que combina radiação electromagnética, ozono e um catalisador. A utilização do moinho de bolas tem sido sugerida na literatura como uma técnica eficaz de preparação e modificação de diversos materiais, entre os quais TiO_2 e nanotubos de carbono [1, 2]. Com este trabalho pretendeu-se estudar a eficiência de diferentes compósitos de TiO_2 e nanotubos de carbono (MWCNT) preparados no moinho de bolas na degradação de compostos orgânicos através da ozonização fotocatalítica. Neste estudo foram avaliadas diferentes condições de preparação dos compósitos, entre as quais o tempo e a frequência de moagem, as propriedades do TiO_2 e MWCNT, o efeito da adição de solvente e dopagem com nitrogénio. Utilizaram-se compósitos com 90% de TiO_2 comercial (P25) e 10% de MWCNT, designados P25/MWCNT_x_y, onde x e y correspondem ao tempo (min) e frequência de vibração (vibração/s) de moagem, respetivamente. Os resultados obtidos foram comparados com a atividade catalítica de um compósito com a mesma composição mas preparado pelo método de hidratação-desidratação, amostra P25/MWCNT [3]. Na Fig.1 a) observa-se que o aumento do tempo de moagem conduz a uma melhoria no desempenho dos materiais para a degradação do ácido oxâmico (OMA) através de ozonização fotocatalítica. Por outro lado, a influência da frequência de vibração revelou-se menos evidente.

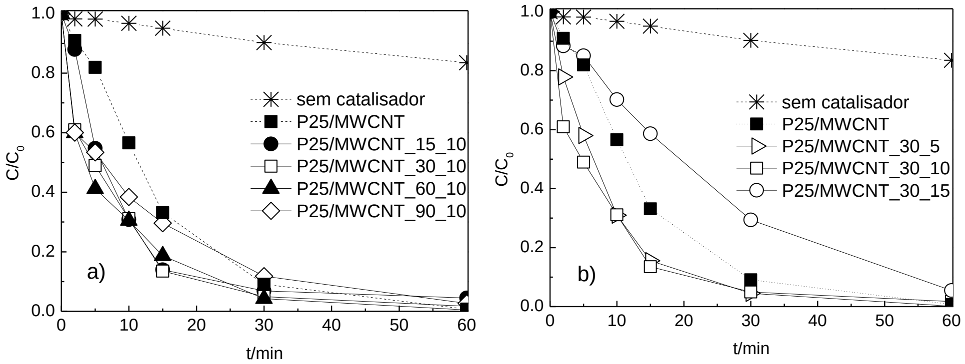

Fig.1. Influência do tempo (a) e frequência (b) de moagem nos compósitos durante a remoção do OMA por ozonização fotocatalítica.

Independentemente do tempo de moagem, todos os catalisadores apresentaram uma remoção de OMA superior à do compósito preparado pelo método convencional. As amostras tratadas durante 15, 30 e 60 min apresentam comportamento semelhante entre si, enquanto que o compósito preparado durante 90 min apresenta uma atividade catalítica ligeiramente inferior. Relativamente à frequência de vibração utilizada, os compósitos sintetizados com 5 e 10 vibração/s apresentam uma remoção de OMA superior à do compósito P25/MWCNT. O aumento da frequência de rotação para 15 vibração/s produz um efeito negativo, diminuindo drasticamente a cinética de degradação do poluente.

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Photodegradation of anthocyanins by UV-A LEDs/TiO_2

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The agri-food industry originates recalcitrant compounds to the conventional biological treatment, in particular phenolic compounds like anthocyanins, strongly coloured compounds that are known to be powerful antioxidant agents. In order to achieve mineralization, advanced oxidation processes, such as heterogeneous photocatalysis, are promising alternatives for water treatment. Mercury vapour lamps have been used as UV irradiation but light emitting diodes (LEDs) appeared as a next generation devices, being safer, non-hazardous, having longer lifetime and better efficiency [1].

In the present work, it was investigated the photodegradation of *p*-hydroxybenzoic (pHB) acid as a model compound and the mineralization of anthocyanins coming from the washing of *Sambucus nigra* berries, using UV-LEDs and Evonik P25 TiO_2. An UV-LED system with 12 InGaN Roithner APG2C1-365E LEDs was constructed, with UV optical power of 85 W/m^2 and used in a reactor with 11x7x1.4 cm^3. Different experimental conditions such as the concentration of compounds, pH, temperature and concentration of TiO_2 were studied.

The effects of pHB acid concentration, keeping [TiO_2] = 500 mg/L, P= 85 W/m^2 and T= 21˚C, was studied by a pseudo-first order kinetics (figure 1 a). The photocatalytic experiments carried on the washing water were only successful with an initial TOC content under 60 mg C/L, with 70% of mineralization in 5 hours. For higher TOC content (TOC_0 = 1860 mg C/L) combined systems like UV-photo-Fenton/TiO_2 were succeeded to obtain mineralization. For the different processes it was used: [TiO_2]= 1000 mg/L; [H_2O_2]= 1%; [$FeSO_4{\cdot}7H_2O$]= 25 g/L; P= 85 W/m^2; T= 21°C, and the results were analysed by pseudo-first order kinetics (figure 1 b).

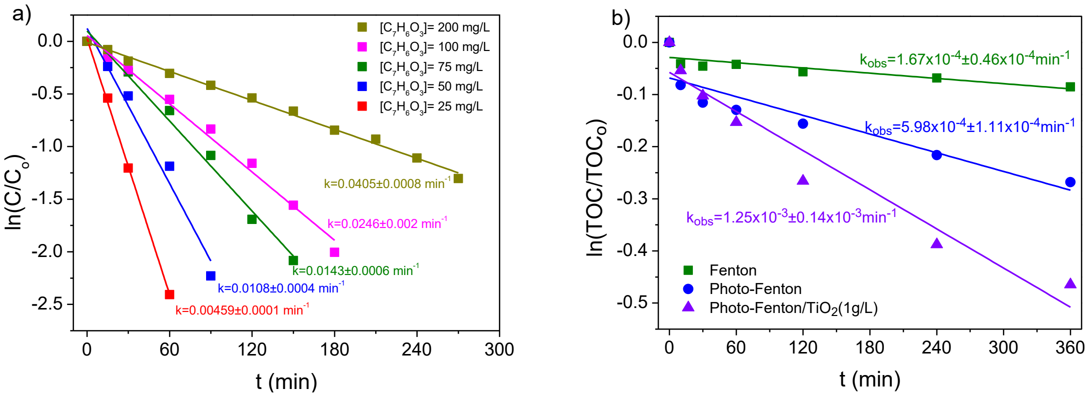

Fig.1. Determination of the pseudo-first order kinetics constants: a) *p*HB acid; b) washing water

Acknowledgements

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Lime catalysts for biodiesel production from food wastes

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The Biodiesel production by alcoholysis of vegetable oils, particularly, used frying oils (UFO) is indicated as a feasible renewable fuel for diesel engines. Several solids can be used to catalyse the transesterification/esterification of vegetable oils [1]. Lime catalysts have been extensively studied for the methanolysis of vegetable oils [2].

There are numerous natural calcium sources from food wastes such eggs shells, molluscs and crustacean shells available to be used as cheap raw materials to produce CaO [3]. Many researchers used eggs shells to prepare CaO catalysts for biodiesel production. The molluscs shells are also reported as a resource for lime catalysts [4, 5]. Liquid wastes like oils and animal fats can be used too as raw-materials to produce biodiesel.

In the present study the solid and liquid wastes from food industry in Portugal were selected for biodiesel production. The food wastes with High Ca content (eggs and molluscs shells) are used to produced lime catalysts by a simple calcination step, this minimize not only the solid wastes costs but also the biodiesel production costs. Additionally UFO are used in the transesterification process.

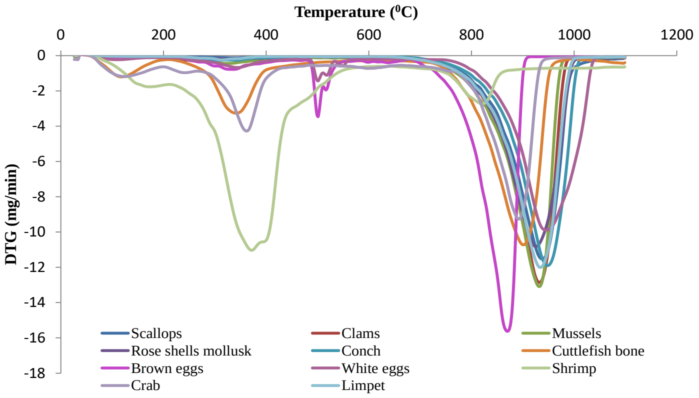

Fig.1. Thermal degradation differential profiles (DTG) of the raw Ca wastes (under air; 30 ºC/min).

Acknowledgments
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Optimization of biodiesel production through esterification catalysed by an acidic ionic liquid

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Recently, there is an increasing interest in the development of alternative technologies to the oil economy, based on renewable energy sources. A possible solution is a biofuel for compression-ignition or diesel engines, obtained from fat-rich biomass. Therefore, a wide variety of raw materials can be used for the production of biodiesel, ranging from waste oils to edible commercial oils.

Biodiesel is chemically composed by a mix of fatty acid methyl esters (FAME's), and it is usually produced by transesterification of triglycerides, from vegetable oils and animal fats, in the presence of homogeneous or heterogeneous catalysts. However, alkali catalysts which provide high yields for the production of biodiesel in relatively mild conditions require previous neutralization of the oils. In fact, the use of high acidic raw materials may introduce operational problems, especially when resorting to second generation triglyceride sources. This type of raw materials, like waste cooking oils, do not compete with the food market, but usually feature high levels of free fatty acids (FFA's), which may introduce complications in the classic production process of biodiesel, through alkaline transesterification. Thus, these problems can be partially prevented by the use of alternative acidic or basic catalysts, such as ionic liquids (IL's) that also mediate esterification reactions of FFA's to FAME's.

An increased interest in the application of IL's in multiple fields has been observed lately, mainly as solvents [1] and catalysts [2-4] to a wide variety of reaction and/or separation systems. In this work, it is presented a study of the performance of the acidic IL, 1-butyl-3-methylimidazolium hydrogen sulfate ($[BMIM]HSO_4$), as a catalyst for the esterification of a mix of fatty acids (mostly oleic acid) to the respective FAME's, using methanol.

Multiple reaction batches were designed varying several operational parameters: temperature, reaction time, oleic acid/methanol mole ratio and mass of catalyst, in order to optimize the reaction yield. The prediction of the reaction yield was done using two indirect methods: measuring the final product acidic value through volumetric titration and assessing the total FAME content of the biodiesel product by Gas Chromatography (GC-FID). The GC-FID analysis made possible the identification and quantification of the several FAME's present in the produced biodiesel.

Using the conditions described above the reaction yields reach values as high as 90%, and the total weight content of identified FAME's in the biodiesel product is 95-98%. The optimized process conditions which allow the obtaining of higher reaction yields are summarized in Table 1. Thus, it is concluded that the ionic liquid $[BMIM]HSO_4$ proves to be a promising catalyst for esterification reactions, and a potential alternative for biodiesel production.

Table 1. Optimized reaction conditions for esterification

Parameter	Selected value
Reaction time	4 h
Reaction temperature	90 ºC
Mole ratio (OA/Met)[a]	1:10
weight % catalyst[b]	10%

[a] OA – oleic acid; Met – methanol
[b] relating to oleic acid weight

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Epoxidation of alkenes catalysed by V-(amino acid) complexes using the O_2/THF system as oxidant

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The aerobic oxidation of ethers is a well-known reaction due to the potential formation of explosive ether peroxides. This, in turn, presents a considerable hazard when handling solvents such as diethyl ether or tetrahydrofuran (THF) in a large scale. Nevertheless, this reactivity can be harnessed to an advantage: the ether peroxides may be used as terminal oxidants in catalytic oxidations such as epoxidations.[1]

In line with our previous research efforts,[2,3] we developed a series of L-phenylalanine derived vanadium complexes which were used as catalysts in the aerobic epoxidation of alkenes, such as *trans*-anethole (Figure 1). This particular system was developed with the intent of taking advantage of the aerobic oxidation of THF, which generates the terminal oxidant (THF peroxide) *in situ*.

Preliminary testing of the V-(amino acid) catalysts shows that, in the case of the epoxidation of *trans*-anethole, the epoxide product is formed along with the respective aldehyde. The reaction only occurs to a significant extent with temperatures above 30ºC. There is only vestigial oxidation of the substrate in the absence of metal catalyst. The presence of an organic base such as triethylamine may suppress the oxidative cleavage of the epoxide product to some extent, thus minimizing the amount of aldehyde formed. The present catalytic system will be optimized for maximum epoxide yield and enantioselectivity under the mildest conditions possible. Optimization will also entail the reduction of the amount of THF used.

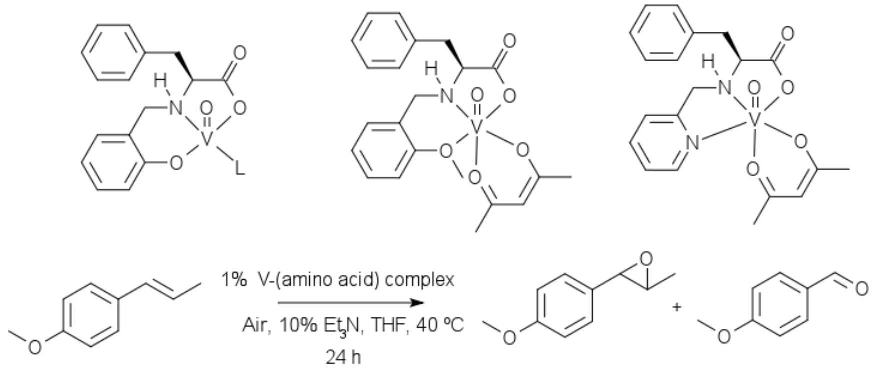

Fig.1. Structural formulas of the V-(amino acid) complexes and the epoxidation reaction scheme

Acknowledgements
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Chiral diamines derived from (1*R*,3*S*)-camphoric acid in the enantioselective alkylation of aldehydes

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The enantioselective alkylation of aldehydes is a valuable tool in obtaining chiral secondary alcohols [1,2]. These alcohols are important building blocks in the synthesis of many biologically active compounds. They are structural units of several drugs, agrochemicals, perfumes, precursors of various functional groups and liquid crystal components.

In this study various chiral diamines derived from (1*R*,3*S*)-camphoric acid **1** were synthesized (**Fig.1**). For the synthesis of the diamines, the corresponding diiminas were first prepared from **2** and various aldehydes, using microwave irradiation in the presence of *p*-toluenesulfonic acid, in just 15 minutes with a small amount of ethanol as a solvent. The diimines **3** were subsequently reduced to the corresponding diamines **4** using $NaBH_4$ in (1:1) $MeOH/CHCl_3$ [3].

The synthesized diamines **4** were tested as ligands in the enantioselective alkylation reaction of aldehydes with diethylzinc (**Fig.2**). The best result using the model substrate benzaldehyde was complete conversion and an enantiomeric excess of 72%, in the presence of (1*R*,3*S*)-*N,N'*-bis[1-(2-methoxyphenyl)methyl]-1,3-diamino-1,2,2-trimethylcyclopentane, at room temperature, in cyclohexane. The scope of this ligand was further tested using other aromatic aldehydes as substrates. With these, complete conversions were achieved, giving preferentially the (*S*) enantiomer of the product alcohol with enantiomeric excesses up to 86%.

In this communication details on the synthesis of the chiral diamines, as well as their use in the enantioselective alkylation of aldehydes with $ZnEt_2$ will be disclosed.

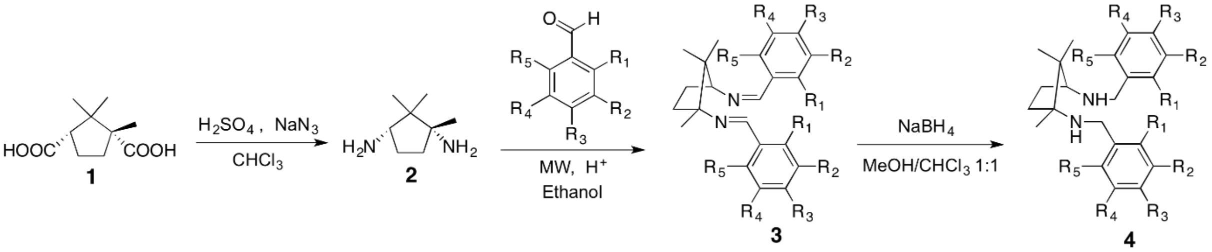

Fig.1. Synthesis of chiral diamines derived from (1*R*,3*S*)-camphoric acid

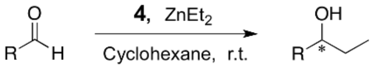

Fig.2. Enantioselective alkylation of aldehydes using diamines **4** as ligands

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Reacciones de formación de enlaces C-C y C-heteroátomo en cascada promovidas por aerogeles de carbón dopados con nanopartículas de Cu (0)

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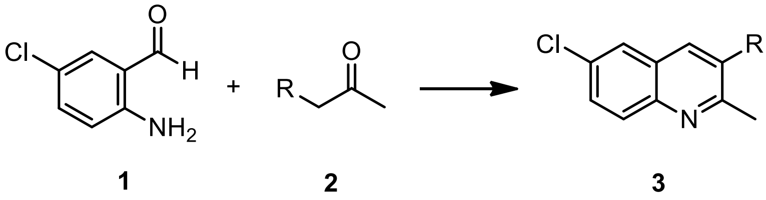
Los materiales carbonosos pueden considerarse catalizadores alternativos de menor impacto ambiental útiles en procesos de Química Fina. Entre sus propiedades destacan su alta porosidad y química superficial modulable y los bajos coste de producción, entre otras. En este contexto, los aerogeles de carbón son materiales que presentan una alta pureza y buena homogeneidad y porosidad controlable, mostrando altas actividades catalíticas [1].

Nuestro interés se centra en el desarrollo de nuevos aerogeles de carbón, dopados con nanopartículas de Cu(0), capaces de catalizar eficiente y selectivamente la síntesis de heterociclos biológicamente activos que tengan aplicación en el campo de la medicina y la farmacia. En este sentido, en esta comunicación se presenta, por primera vez, la síntesis de quinolinas **3**, *via* condensación de Friedländer [2], entre 2-amino-5-clorobenzaldehído **1** y compuestos 1,3-dicarbonílicos **2**, bajo condiciones suaves de reacción y ausencia de disolvente (**Esquema 1)**.



Esquema 1. Condensación de Friedländer entre 2-amino-5-clorobenzaldehído **1** y un compuesto carbonílico **2**

Los resultados obtenidos demuestran como la porosidad de los aerogeles de carbón se ve afectada por la presencia, o no, de metales de transición, la temperatura de carbonización y los tratamientos de activación. Esta variación en las propiedades texturales del catalizador influencian notablemente su actividad catalítica, siendo los aerogeles más activos aquellos que contienen nanopartículas de Cu(0).

Finalmente, y con el fin de racionalizar los resultados obtenidos, estamos realizando un estudio computacional, mediante cálculos teóricos, empleando la metodología DFT, que nos permita proponer el mecanismo por el que transcurre la reacción.

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Solid-acid catalysis: from furfuryl alcohol to alkyl levulinates

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The development of cost-effective and energy-efficient processes for the valorisation of biomass to secure energy, fuel and chemical supplies for future needs is one of the challenges of XXI century. Therefore, catalytic processes that transform biomass into valuable products under competitive and sustainable conditions have become a mandatory target in recent years [1].

Acid catalysis plays an important role in carbohydrate conversion for production of valuable furanic platform chemicals such as 5-hydroxymethyl-2-furfural (Hmf), furfural (Fur) and levulinic acid, which are excellent precursors for biofuels and fuel additives [2].

In the recent years, there has been a growing interest in the synthesis of alkyl levulinates such as ethyl levulinate, which is a versatile compound widely applied in different sectors of the chemical industry: as flavouring agent, as precursor to other valuable-products (e.g.;γ-valerolactone), as solvents and plasticizing agents; also, it has been used as additive for transportation fuels with an excellent performance [3]. Alkyl levulinates can be synthesized directly from levulinic acid, furfuryl alcohol (FAlc) or Hmf [4,5].

Here in we present the work, developed in collaboration with INNOVCAT company (www.innovcat.pt), on solid-acid-catalyzed conversion of FAlc into alkyl levulinates, including methyl, ethyl, and n-butyl levulinate. Catalytic reactions were performed using INNOVCAT catalyst, FAlc and different aliphatic alcohols, temperatures and reaction times, in order to reach the maximum substrate conversion and selectivity. The reusability of the best catalytic systems was also evaluated. To benchmark the catalytic performance obtained with INNOVCAT catalysts, the reactions were also carried out using commercial catalysts. The results showed that 100 % conversion and 80 % selectivity for ethyl levulinate was achieved using INNOVCAT catalyst, 80 ºC, ethanol, after 5 hours. The conversion and selectivity was obtained by gas chromatography and ^{1}H NMR analysis.

Acknowledgements
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Iron-(amino acid) complexes in oxidative coupling reactions

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Carbon-carbon bond forming reactions represent one of the major group of reactions in Organic Chemistry. From these type of transformations, coupling reactions have demonstrated a crescent role, from the last 1970's until nowadays, in the synthesis of many relevant fine chemicals such as polymers, active pharmaceutical ingredients, natural products, dyes, pesticides, among others. Notwithstanding the great influence and importance of palladium- and nickel-mediated coupling methodologies, the preparation and application of more sustainable and efficient transition-metal catalysts has gained relevance in the last years, in order to reduce negative environmental impact and chemical waste treatment expenditures of many processes in the chemical industry.

The subject of our study is the synthesis and application of iron amino-acid-based complexes as catalysts for C-C coupling reactions, using environmentally-friendly conditions. Herein we describe the synthesis of novel iron (III) complexes derived from chiral amino acid-based ligands and their application as homogeneous catalysts for the asymmetric oxidative coupling of 2-naphthol [1, 2] (**Figure 1**). The results obtained indicate that these structurally simple iron complexes can be used as catalysts in the development of mild and environmentally-friendly procedures for the oxidative coupling of 2-naphthol.

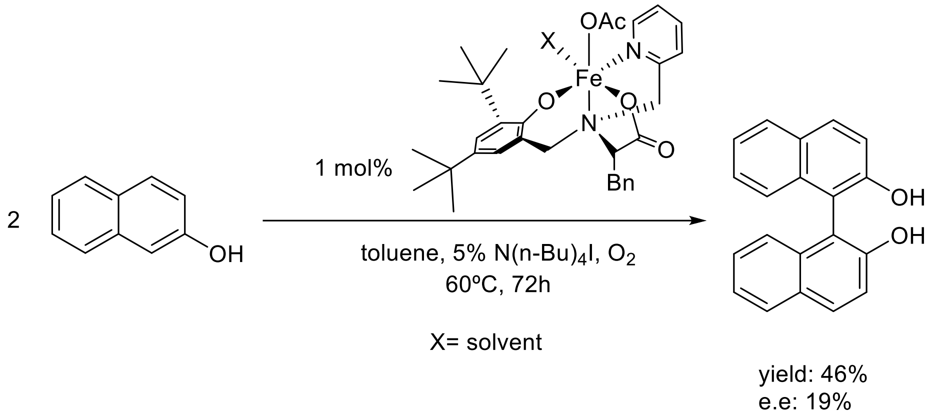

Fig. 1. General procedure for the oxidative coupling of 2-naphthol mediated by Fe-(amino acid) complexes

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Production of 5-hydroxymethylfurfural from wheat straw using ionic liquid

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The processing of lignocellulosic materials in media made from ionic liquids is an interesting method for a number of purposes, including raw material fractionation or making part of reaction media, for example, for derivatization or hydrolysis-dehydration reactions of polysaccharides. The concept of lignocellulose biorefinery is an important approach for the current needs of energy and chemical building blocks (for example, 5-hydroxymethylfurfural (HMF) and furfural), that gradually may replace current dependence on fossil-fuel resources [1, 2].

This work provides an experimental assessment on the production of HMF from wheat straw. The autohydrolysis stage plays the role of a preliminary fractionation treatment, obtained a solid phase (enriched in cellulose and lignin) which be used for obtaining of HMF [3]. Different severities of autohydrolysis treatment were studied (in the range 170-230 °C) in non-isothermal conditions and operating with 8 kg water/100 kg oven dry substrate.

The wheat straw without pretreatment as well as the cellulosic fraction (obtained at 230 and 215 °C) were treated in media containing the ionic liquid (1-butyl-3-methylimidazolium chloride) and different amount of catalyst ($CrCl_3 \cdot 6H_2O$), operating at fixed loadings of substrate (10 g/100 g ionic liquid) [4]. The effects of temperature (130-160 °C) and reaction time (5-360 minutes) on the concentrations of HMF were determined.

The experimental results enabled the identification of operational conditions leading to conversions in HMF around 45% at 150 and 160 °C, using the solid phase of autohydrolysis treatment at 215 °C.

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Furfural production from xylooligosaccharides of wheat straw using an acidic ionic liquid such as catalyst-solvent

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Biomass derived furans (5-hydroxymethylfurfural and furfural) have emerged as an important platform chemical for the production of value added chemicals and liquid fuels that are currently obtained from petroleum. Particularly, furfural (OC_4H_3CHO) is a bio-based platform chemical that contains a heteroaromatic furan ring and an aldehyde functional group. Owing to its interesting properties, a bright future is expected for this compound, which has been included among the top 30 added-value chemicals from biomass [1].

According to the concept of biorefinery, the processing of xylooligosaccharides from wheat straw in catalyzed ionic liquids (as 1-butyl-3-methylimidazolium hydrogen sulfate) is an interesting method for converting of hemicellulosic fraction into furfural, as it opens an alternative way for a sustainable and environmentally friendly production.

This work provides an experimental assessment on the production of furfural from a substrate enriched in oligosaccharides (mainly xylooligosaccharides, corresponding to 90.6% of total pentoses) resulting from autohydrolysis treatment under optimal conditions, 215 °C (see Table 1).

The substrate was treated with the acidic ionic liquid in a biphasic system using the organic solvent methyl isobutyl ketone (MIBK) in the absence of externally added catalysts, where the acidic ionic liquid:substrate:MIBK ratio was established based on preliminary works [2,3]. The effects of temperature and reaction time on the concentrations and conversions of furfural were determined.

Table 1. Composition of autohydrolysis liquor

Compound	g/L
Hexoses (glucose)	2.9
Pentoses (xylose and arabinose)	21.5
Acetyl groups	2.2

Acknowledgements
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Hybrid monovacant polyoxometalate as effective catalyst for desulfurization

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One of concerns worldwide is the emission of SOx resulting from combustion of sulfur-containing fuels which are responsible for several undesired issues, such as acid rain, air pollution, respiratory disorders as well as irreversible catalyst poisoning [1, 2.]. As a consequence, the production of ultra-clean fuels has become of the most challenging subjects for petroleum refining industry and it has been attracting researchers' attention [3]. In particular, the oxidation desulfurization (ODS) process offers very promising advantages due to its cost-effectiveness and mild operational conditions while being able to efficiently remove the most refractory sulfur-compounds from fuels [4].

In this work, we prepared quaternary ammonium catalysts based on the monovacant polyoxotungstate ($[PW_{11}O_{39}]^{7-}$, abbreviated as PW_{11}). The desulfurization performances of the organic-inorganic hybrids ($TBAPW_{11}$ and $ODAPW_{11}$) were evaluated and optimized in the ODS of a multicomponent model diesel. The ODS studies were performed using aqueous H_2O_2 as oxidant and acetonitrile or an ionic liquid ($[BMIM][PF_6]$) as the extraction solvent. The ionic liquid-based systems have shown faster desulfurization achieving complete desulfurization after only 40 min of reaction. In particular, the $ODAPW_{11}/[BMIM][PF_6]$ system revealed a remarkable desulfurization performance with 97.1% of sulfur compounds removed in the first 20 min. The recyclability of both catalysts has been assessed through their reuse in consecutive ODS cycles.

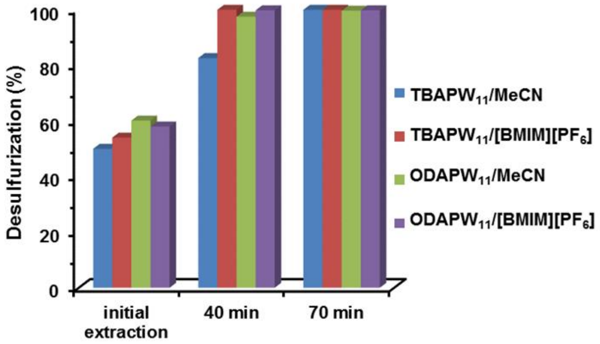

Fig.1. % Desulfurization of $TBAPW_{11}$ and $ODAPW_{11}$ in both extract solvent, acetonitrile (MeCN) and ionic liquid ($[BMIM][PF_6]$)

Acknowledgments
This work was partly funded through the national projects REQUIMTE-LAQV [FCT (Fundação para a Ciência e a Tecnologia) Ref. UID/QUI/50006/2013], and by FEDER (Fundo Europeu de Desenvolvimento Regional) under the PT2020 Partnership Agreement. The FCT and the European Union are acknowledged for the PhD grant to D.J. (SFRH/BD/102783/2014) and the European Social Fund through the program POPH of QREN.

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Photocatalytic reforming of biomass-derived compounds for hydrogen production using g-C_3N_4 catalysts

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Hydrogen (H_2) has been seen as the fuel of the future due to its bountiful abundance all over the planet and its non-polluting energetic conversion. The sustainable production of such non-polluting fuel by the conversion of natural renewable resources like solar energy into chemical energy constitutes an enormous challenge in the present. Photocatalytic water splitting and photocatalytic reforming of biomass are two promising methods for the sustainable production of H_2. The second process, in particular, combines simultaneous H_2 production and biomass oxidation. The major advantage is that H_2 can be efficiently produced by photocatalytic degradation of organic compounds present in aqueous media at mild conditions, with simultaneous treatment/valorization of industrial wastes or by-products [1]. Graphitic carbon nitride (g-C_3N_4) is a polymeric semiconductor with a 2.7 eV, with the conductive band (CB) and valence band (VB) positions, respectively, at ca. -1.1 eV and +1.6 eV vs. normal hydrogen electrodes (NHE). The suitable electronic band structure makes this a suitable photocatalyst for hydrogen production [2].

In the present work, g-C_3N_4 obtained by thermal decomposition of dicyandiamide and loaded with different noble metal co-catalysts (Pt, Au and Pd) were used for the photocatalytic production of H_2 from aqueous solutions containing saccharides (L- or D-arabinose), under UV(385 nm)-LED irradiation. The results show that the yield of H_2 production depend on both the biomass molecule and the nature of the co-catalyst (Fig. 1).

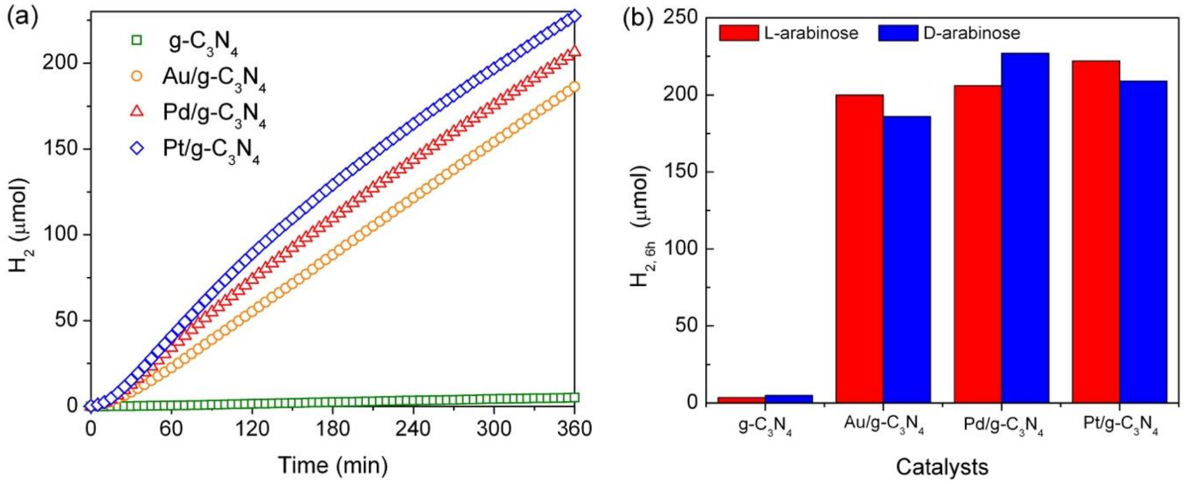

Fig.1. H_2 production profiles for the reactions with D-arabinose (a) and H_2 obtained at 6h of UV-LED irradiation using bare and metal-loaded g-C_3N_4 photocatalysts (b)

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XXII Encontro Luso-Galego
Química

COMUNICAÇÕES ORAIS E EM PAINEL

Educação e Ensino da Química

¿Qué saben los alumnos de Educación Secundaria sobre las reacciones químicas?

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El objetivo de esta investigación es averiguar las ideas previas que manifiestan los alumnos de Educación Secundaria sobre las reacciones químicas. Las reacciones químicas están presentes en todos los aspectos de nuestra vida cotidiana, así como fenómenos basados en cambios físicos y químicos.

Las ideas alternativas en química son la resultante del intento y esfuerzo de los alumnos por comprender el mundo que les rodea. Es por ello, que en el proceso de Enseñanza/Aprendizaje deben considerarse con el fin de promover un aprendizaje significativo.

Así, la Teoría del Constructivismo pone de manifiesto que el aprendizaje es un proceso basado en la construcción activa de significados, a partir de los conocimientos previos que los alumnos poseen (Driver, 1986 [1]; Gil, Carrascosa y Martínez, 2000 [2]; Wanderse, Mintze y Novak, 1994 [3]). Además, en las investigaciones llevadas a cabo por Domingos-Grilo, Mellado y Ruíz (2004) [4], determinan que el profesor debe partir de las ideas previas de los alumnos y diseñar estrategias para que se produzca el choque cognitivo y que el alumno construya un conocimiento científicamente correcto acorde con las orientaciones curriculares.

Por todo ello, es necesario averiguar lo que los alumnos ya saben sobre un tema concreto, con el fin de establecer estrategias de enseñanza que faciliten y mejoren el aprendizaje significativo de los alumnos, para así construir los conocimientos científicamente correctos.

La muestra está constituida por un total de 27 alumnos del tercer curso de Educación Secundaria Obligatoria de un centro concertado de la ciudad de Badajoz (España). El 46.4% de la muestras son chicos y el 53.6% son chicas.

El instrumento utilizado en esta investigación educativa para la recogida de datos ha sido un cuestionario de elaboración propia sobre el conocimiento de los alumnos. El cuestionario estaba constituido por 9 ítems cerrados de opción múltiple con una única respuesta correcta. Cada ítem se centraba en cuestiones sobre fenómenos cotidianos en los que están presentes los cambios físicos y las reacciones químicas.

Los resultados muestran que existen ideas alternativas relacionadas con los cambios físicos y químicos, así como en conceptos de las reacciones químicas.

Agradecimientos
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Concepciones alternativas sobre la clasificación de la materia en un grupo de estudiantes universitarios del Grado de Maestro en Educación Infantil

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La enseñanza y el aprendizaje de la química es a veces considerada una tarea complicada, debido mayormente a la naturaleza conceptual de la disciplina, con una gran cantidad de conceptos abstractos interrelacionados. Consecuentemente, bastante a menudo, la química es considerada como una materia difícil para los estudiantes e incluso difícil de enseñar, por parte de los profesores.

En el proceso de enseñanza-aprendizaje, los estudiantes construyen su propio aprendizaje siguiendo un proceso iterativo, en el cual los nuevos conceptos o ideas, necesitan de alguna manera encajar con las ideas que los estudiantes ya poseen. Las ideas que los estudiantes poseen acerca de un determinado tema antes de recibir la instrucción del profesor, reciben el nombre de ideas alternativas, y tienen la característica de que no siempre coinciden con el conocimiento científico y académico. Estas ideas alternativas normalmente tienen su origen en el intento de los estudiantes de entender sus propias experiencias, especialmente cuando estos han tenido una educación pobre en ciencias durante la etapa escolar.

Así, la detección de las ideas alternativas de los estudiantes antes de llevar a cabo la impartición de nuevo contenido, se presenta como una etapa clave, ya que supondrá el nexo de unión entre el nuevo y el viejo conocimiento, o dicho entras palabras, entre las ideas alternativas y el conocimiento científico. Una vez conocidas las ideas alternativas, el profesor diseñará su intervención teniendo en cuenta las mismas, con el objeto de impulsar la evolución de las ideas alternativas hacia conocimiento científico, transformación denominada “cambio conceptual” [1].

En esta comunicación se presentan los principales resultados de una investigación en la que se estudió la evolución de las ideas alternativas sobre la composición de la materia de un grupo de estudiantes universitarios del tercer curso del Grado de Maestro en Educación Infantil. Específicamente, el tema escogido fue la diferenciación entre sustancias puras y mezclas. Para detectar las ideas previas se elaboró un cuestionario con una serie de preguntas de respuesta cerrada o semi-cerrada. El análisis de los resultados permitió identificar importantes ideas alternativas, y a continuación se diseñó una intervención de carácter teórico práctico, teniendo en cuenta las ideas alternativas detectadas y con el objetivo de promover su evolución hacia el conocimiento científico. El éxito de la intervención se mide pasando a los estudiantes el mismo cuestionario tras la intervención.

Agradecimientos

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Evolución de las concepciones alternativas sobre la composición de la materia y sus cambios en maestros de Educación Primaria en formación

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En este trabajo se estudia la evolución de las concepciones alternativas que poseen maestros de Educación Primaria en formación sobre los conceptos relacionados con la composición de la materia y sus cambios. Conocer la presencia de concepciones alternativas en relación con los contenidos científicos ha demostrado ser de gran utilidad a la hora de abordar el aprendizaje de la ciencia [1]. A través de la actuación docente se debe propiciar la transformación de estas concepciones hacia las científicamente correctas. Esta transformación se denominada cambio conceptual, entendiéndose como un proceso en el que se produce una modificación gradual y parcial de los modelos mentales que presentan los estudiantes, durante el cual pueden coexistir las concepciones de los alumnos con los propios modelos establecidos por la ciencia [2].

En el estudio han participado 207 alumnos de segundo curso del Grado en Educación Primaria de la Universidad de Extremadura (España) y 4 profesores de la asignatura Didáctica de la materia y la energía (DME). La metodología seguida se ha desarrollado en varias fases. En un primer lugar se han detectado las concepciones alternativas que presentaban los alumnos, para ello se ha empleado un cuestionario de preguntas abiertas y cerradas. En una segunda fase se ha llevado a cabo una intervención didáctica que ha tenido lugar durante los seminarios prácticos de la asignatura DME. Para el diseño de esta intervención se ha partido de las concepciones alternativas detectadas en los alumnos a través del cuestionario. Se ha intentado diseñar actividades que ayudaran a superar la idea equivocada para lograr un cambio conceptual hacia la idea científicamente correcta. La intervención consistió en la realización de diferentes trabajos experimentales relacionados con los cambios de la materia. Una vez concluida la intervención, los alumnos completaron un segundo cuestionario encaminado a determinar si la intervención didáctica había promovido un cambio conceptual en los participantes del estudio, incorporando en sus estructuras cognitivas, de este modo, modelos mentales más próximos al conocimiento científico.

Los resultados obtenidos en la primera fase mostraron la existencia de ciertas concepciones alternativas en relación a la composición de la materia. De forma genérica clasificaban como sustancias puras aquellos materiales extraídos de la naturaleza, confundiendo el concepto de sustancia pura con natural. En relación a los cambios que experimenta la materia, los alumnos mostraron dificultad a la hora de diferenciar cambios químicos de cambios físicos. Finalmente, en los resultados del cuestionario realizado tras la intervención didáctica se observa que un mayor porcentaje de alumnos proporcionan respuestas científicamente correctas, tanto en las relativas a la composición de la materia como a las referentes a los cambios que eta sufre.

De este modo podemos decir que la identificación de las concepciones alternativas que presentaban los alumnos de este estudio, ha resultado una estrategia adecuada para el diseño de una intervención didáctica apropiada para propiciar el cambio conceptual, y así aproximar los modelos mentales de los alumnos a modelos científicamente correctos.

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Conocimientos previos de química de alumnos de magisterio

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A la hora de determinar el nivel de alfabetización científica, uno de los aspectos considerados es el "conocimiento" entendiendo este como "conocimiento de los principales hechos, conceptos y teorías que conforman la base del conocimiento científico". Este conocimiento incluye el conocimiento del mundo natural y de los dispositivos tecnológicos (conocimiento del contenido), conocimiento de cómo se producen estas ideas (conocimiento procedimental) y la comprensión del porqué de estos procedimientos y la justificación de su uso [1].

En esta comunicación presentamos los resultados de un estudio exploratorio sobre las ideas alternativas de química con las que llegan a la universidad los alumnos de magisterio de la Facultad de Educación y de la Facultad de Formación del Profesorado.

La muestra está compuesta por 338 alumnos de los grados de Educación Primaria e Infantil. El instrumento utilizado para la recogida de datos fue un cuestionario verdadero/falso con 8 items (Tabla 1) y una pregunta abierta.

Los resultados obtenidos ponen de manifiesto la existencia de distintas ideas alternativas en los alumnos encuestados. Por ejemplo, las ideas referentes a la conservación de la masa en las reacciones químicas, la diferenciación de sustancias puras y mezclas o las relacionadas con los cambios de estado de agregación. La prueba de U de Mann-Whitney revela que existen diferencias significativas entre los alumnos pertenecientes al Grado de Educación Infantil y Primaria en cuanto a los conocimientos de química con que llegan a la Universidad.

Tabla 1. Porcentajes de respuestas verdadero, falso y sin contestar

Item[a]	**Respuestas %**		
	V	**F**	**NS/NC**
1.- Cuando el butano arde se desprende vapor de agua. (V)	28,40	68,34	3,25
2.- La masa no cambia durante una reacción química. (V)	29,88	65,98	4,14
3.- El granito es una sustancia pura. (F)	49,70	47,04	3,25
4.- El calcio de la leche es de color gris. (V)	39,94	53,85	6,21
5.- El H_2O del mar es igual que el H_2O del grifo. (V)	24,85	73,08	2,07
6.- Si miramos con un microscopio muy potente una muestra de aire veríamos que en el espacio entre moléculas hay vacío. (V)	61,24	33,43	5,33
7.- En una reacción de combustión se cumple siempre que la masa de los productos es menor que la masa de los reactivos. (F)	37,28	52,07	10,65
8.- Un cambio del estado de agregación de una sustancia es una transformación química. (F)	61,54	31,95	6,51
[b]El agua está formada por oxigeno e hidrogeno. Al hacer reaccionar 2 g. de hidrógeno con 16 g. de oxígeno, la reacción es completa y se forma agua. ¿Qué cantidad de agua se forma?	16,68[c]	44,08[d]	40,24[e]

[a]Entre paréntesis se indica la opción correcta. [b]Pregunta abierta. [c]Respuestas correctas. [d]Respuestas incorrectas. [e]Respuestas en blanco

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“A Nossa Molécula”: uma estratégia de motivação para a aprendizagem de Química Orgânica em cursos de Ciências Farmacêuticas

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Adquirir competências em Química Orgânica é uma tarefa árdua e os resultados obtidos estão frequentemente longe do desejado. Uma das causas de insucesso no ensino de Química Orgânica para cursos na área da saúde é a falta de motivação dos estudantes devida à dificuldade de integração dos conceitos discutidos nas aulas na profissão farmacêutica. Descobrir a melhor forma de ensinar e motivar os estudantes continua a ser um desafio para os docentes.

Nesta comunicação mostra-se a implementação de uma estratégia pedagógica, que denominámos de “A Nossa Molécula”, na Unidade Curricular “Química Orgânica II”, do 2º semestre do 1º ano do Mestrado Integrado em Ciências Farmacêuticas, da Faculdade de Farmácia da Universidade do Porto.

“A Nossa Molécula” permite transformar a informação fornecida durante as aulas em conhecimento aplicado. Assim, a cada grupo de 2 estudantes é atribuído, no início do semestre, um fármaco utilizado na terapêutica. Ao longo do semestre, os estudantes vão incorporando e aplicando os conteúdos discutidos nas aulas na molécula do seu fármaco. No final, cada grupo de estudantes entrega o resultado do seu trabalho, o qual é discutido pelos docentes e colegas. Os resultados obtidos ao fim de dois anos desta estratégia pedagógica mostram um aumento do sucesso escolar e um aumento claro do interesse dos estudantes pela aprendizagem de Química Orgânica, bem como uma maior perceção da integração da Química Orgânica num curso de Ciências Farmacêuticas.

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Utilización de mapas conceptuales para el análisis comparativo de libros de texto sobre el tema de la Materia en 4º de Educación Primaria

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Los libros de texto siguen constituyendo en la actualidad uno de los recursos didácticos más utilizados en los centro escolares [1,2]. Algunos autores [3] indican que en la mayoría de los casos, constituyen la base de los contenidos y actividades que se llevan a cabo en el aula. Por este motivo, es necesario analizar y reflexionar sobre el desarrollo y presentación de los contenidos de un tema específico en la Educación Primaria.

El trabajo que se presenta está centrado en el bloque de contenidos de La Materia, unidad correspondiente al área de Conocimiento del Medio, en el 4º curso de Educación primaria. La muestra ha estado constituida por 5 libros de texto de diferentes editoriales, con el objetivo de realizar un análisis comparativo de todas las secciones y apartados que contienen sobre el tema seleccionado.

Para llevar a cabo la comparación se ha seleccionado como herramienta didáctica el mapa conceptual [4], con la finalidad de facilitar visualmente las diferencias respecto a la estructura, organización, introducción, conceptos, contenidos y actividades desarrollados en cada uno de los libros de texto analizados. Concretamente se han realizado con el software Cmaptools un total de 25 mapas conceptuales. Los resultados muestran la existencia de diferencias relevantes en el tratamiento del tema elegido en las diferentes variables de estudio.

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XXII Encontro Luso-Galego
Química

COMUNICAÇÕES ORAIS E EM PAINEL

Nanoquímica e Nanotecnologia

Preparation, characterization and catalytic application of amine-functionalized graphene *via* Diels-Alder reaction

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Graphene is probably the most intensively studied material at the moment [1]. It is a 2-D carbon nanomaterial that exhibits higher surface area than other carbon allotropic forms such as fullerenes (0-D), nanotubes (1-D) or graphite (3-D). Thus, graphene nanosheets may be an excellent supports for grafting active molecules with the final goal to be used as heterogeneous catalyst. However, due to the high chemical stability of graphene, its efficient functionalization with organic molecules, as well as the chemical modification of its surface, is still a challenge.

In this work we describe the functionalization of a commercial graphene with amine groups through Diels-Alder reaction between graphene nanosheets and the prepared 2-maleimidoethylamine. The resulting nanomaterials were characterized by FTIR, XPS and Raman spectroscopy. Additionally, the amine-functionalized graphene was tested as catalyst in the Knoevenagel condensation between active methylene compounds and several aldehydes/ketones. In the absence of catalyst (or in the presence of non-functionalized graphene) there is no reaction; however, in the presence of the prepared functionalized graphene materials high products yields were obtained. Amine-functionalized graphenes showed high catalytic activity, reusability and stability, with more than 96% yield after 5 reuses. The application of the prepared nanomaterials in the catalysis of other reactions will be also discussed.

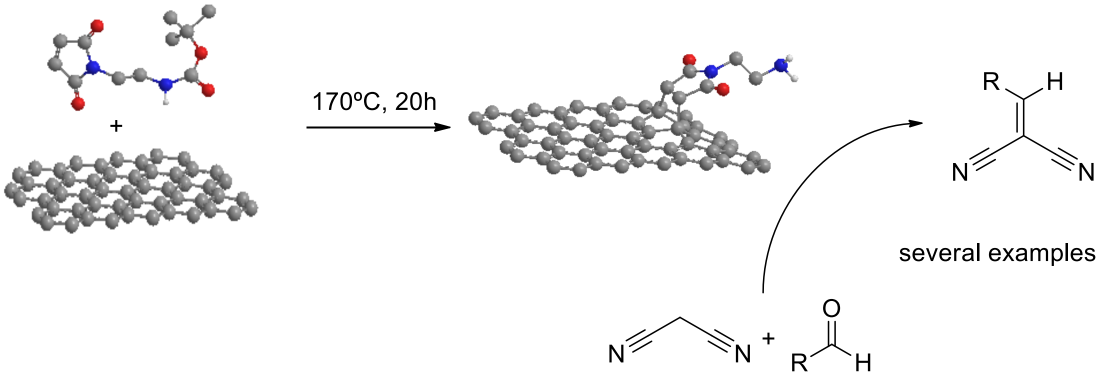

Fig.1. Graphene functionalization with 2-maleimidoethylamine and its application as catalyst on Knoevenagel reactions

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Effect of the incorporation of WO_3 and TiO_2 nanoparticles in the electrochromic properties of a poly[Ni(*salen*)] film

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Conducting polymers (CPs) are a widely studied class of electrochromic (EC) materials [1] that, in addition to the good mechanical properties and potential low cost, show interesting optical properties due to its multiple redox states, with rich color changes and ease of color tuning via structural modifications of the monomers. Unfortunately, their rate of interconversion between redox states is limited by the slow transport of counter ions into the polymer layer and typically show modest electrochemical stabilities [1]. These drawbacks can be overcome by the synergetic combination of CPs with organized metal oxides nanostructures, in order to take advantage of the high surface-to-volume ration and short diffusion distances for ion/electron transport of the metal oxide [2]. The new nanohybrids generally show improved EC performance, with the coloration change being induced by the CPs redox reactions and the metal oxide having an important role in the electronic transport [3]. Among the several metal oxides, tungsten trioxide (WO_3) and titanium dioxide (TiO_2) are among the most investigated n-type semiconductors [3] and are very attractive to be combined with CPs due to their ability to form electron donor-acceptor pairs.

The poly[M(*salen*)]-type films (M ≡ transition metal) are a particular class of conducting (metallo)polymers, derived from metal *salen* complexes, whose interesting EC behavior was recently explored by Freire's group [4]. In this work, two novel nanocomposites were prepared through the incorporation of WO_3 [5] and TiO_2 [6] nanoparticles (NPs) in a poly[Ni(*salen*)] film; the influence of the NPs incorporation in the composition, morphology, electrochemical response and spectroelectrochemical properties of the pristine film was evaluated, with the ultimate goal of to inquire the effect of each nanomaterial in the EC properties of the nanocomposites obtained. Both nanomaterials lead to an enhancement into some EC properties: while WO_3 NPs allowed faster response times, higher optical contrast (+ 40 %) and greater coloration efficiency (+ 13.1-21.7 %) than the pristine poly[Ni(*salen*)] film, the incorporation of TiO_2 NPs resulted in a nanocomposite with an improvement of 16.7 % in the optical density change and with an excellent electrochemical stability (46.7 % improvement).

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Development of stimuli-responsive graphene-based yolk-shell magnetic nanoparticles for controlled release of anticancer drugs

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Magnetic drug delivery systems have attracted much attention in the last decades due to the possibility to improve the therapeutic efficacy of anticancer drugs, by enabling instable and poorly soluble drug agents to reach tumour cells after being guided by low magnetic fields and monitored by magnetic resonance imaging (MRI) [1]. Hence, a lower amount of anticancer drug is needed and the typical side effects of chemotherapy are minimized [2]. Commonly, these nanoparticles are designed with a magnetic core coated with a metal or a non-metal structure, such as gold or silica. However, these approaches present some drawbacks, such as low drug loading capacity and lack of stimuli-responsive release. Alternatively, carbon-coated magnetic nanoparticles offer higher chemical and thermal stability, larger surface area, biocompatibility and easier functionalization due to the high capacity of adsorption. Moreover, these materials have shown great ability to be used as pH stimuli-responsive controlled release platforms, due to the disruption of supramolecular π–π interaction at acidic pH [3]. In this context, graphene-coated yolk-shell magnetic nanoparticles – hybrid materials comprising a superparamagnetic core coated by a graphene-based shell that covers a hollow region (i.e., Fe_3O_4@void@C), – were developed as super-drug nanocarriers systems, exhibiting high loading contents of the anticancer drug Doxorubicin due to the large cavity volume between the shell and the magnetic core, and a stimuli-responsive controlled release in response to acidic environments (pH 5), such as those found in tumour tissues. These results shed light on the development of new hybrid nanomaterials with high potential to be applied in biomedical applications.

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Deposition of thin films of the Lu-Fe-O system using MOCVD and *RF*-Magnetron Sputtering

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Ceramic oxides shown amazing properties making them suitable materials for applications on the electronic field. The Lu-Fe-O system possesses a very rich phase diagram: a stable orthorrombic *Pnma* perovskite (*o*-$LuFeO_3$), the metastable hexagonal P*63cm* noncentrosymetric polar (*h*-$LuFeO_3$), the $LuFe_2O_4$ and the garnet $Lu_3Fe_5O_{12}$. These phases can present multiferroic behaviour, magnetodielectric effect at room temperature (RT) or magneto-optical properties.
The *o*-$LuFeO_3$ reveals a large magnetoelectric coupling at RT where the remanent polarization (P_r) is dependent on the applied magnetic field [1]. The *h*-$LuFeO_3$ is also a multiferroic material where the magnetic order appears below RT [2]. In thin films, it presents antiferromagnetism order below T_N= 440K, followed by a spin reorientation below T_R= 130K [3]. In these phases, the magnetization and electric polarization arise from the iron sites with strong iron-iron correlations.
$LuFe_2O_4$ exhibits hexagonal R-*3m* structure with mixed valence state of iron (Fe^{2+}/Fe^{3+}) called W-layer. It presents extreme sensivity of the dielectric permittivity to applied *dc* bias electric field and frustration in electric and magnetic interactions [4]. $Lu_3Fe_5O_{12}$ garnet presents cubic I*a-3d* structure with mixed valence of iron. Lu^{3+} ions are not magnetic due to the absence of unpaired electrons ($4f^{14}$). Oxygen ions mediate exchange interaction between iron ions in octahedral and tetrahedral sites aligned parallel to each other causing a ferrimagnetic ordering with T_C~539K [5].
High quality films can be obtained using chemical (MOCVD) and physical deposition techniques (*RF*-Magnetron Sputtering). Monocrystalline substrates (Si, $SrTiO_3$, Al_2O_3, and $Gd_3Ga_5O_{12}$) have been used taking advantages of the epitaxy and strain, improving materials properties. Nevertheless, for optical applications it is highly advantageous the deposition on silica glass substrates and also on optical fiber.
In this work we have deposited thin films of the Lu-Fe-O system on silica glass substrates using MOCVD and *RF*- Magnetron Sputtering. The work has started by producing a 5 cm $Lu_3Fe_5O_{12}$ target for using in the *RF*- Magnetron Sputtering deposition system. Several films were deposited on silica glass substrates changing the deposition conditions. In addition we carried out deposition on optical fibers at RT. We have also produced volatile organometallic precursors of $Lu(tmhd)_3$ and $Fe(tmhd)_3$ (tmhd=2,2,6,6-tetramethyl-3,5-heptanodione). These precursors were used on the deposition of thin films by MOCVD on silica glass substrates at 700°C. The films were characterized by XRD that indicates an amorphous structure. They were recrystallized by *ex*-situ thermal treatment at 850°C during 1 hour. The obtained films are being characterized by SEM/EDS, XRD, HR-TEM, AFM, magnetic, electrical, dielectric and optical properties.

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Development and optimization of amoxicillin-loaded lipid nanoparticles as a therapeutic approach for *Helicobacter pylori* infections

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Helicobacter pylori affect around 50% of the world population and are the main cause of peptic ulcers and gastric cancer, being classified as a human carcinogenic by the World Health Organization [1, 2]. Unfortunately, the efficacy of the standard triple therapy against this infection has been declined, mainly due to the increasing number of emergent antibiotic resistant bacterial strains [2]. However, other factors are associated with the lack of efficacy, namely the degradation of antibiotics under acidic conditions, their low diffusion across the mucus layer, their insufficient residence time in the stomach, among others [2]. Therefore, lipid nanoparticles emerged as a promising biocompatible drug delivery strategy. They can improve drugs pharmacokinetic properties, leading to an improvement of the efficacy and a decrease in the incidence of side effects [2].

In this work, amoxicillin-loaded solid lipid nanoparticles (SLNs) were developed to protect amoxicillin against acidic degradation and to enhance its absorption and, consequently, its bioavailability. The SLNs were prepared by double emulsion technique and optimized by a three-factor, three-level Box-Behnken design. The optimized nanoparticles revealed a low polydispersity index around 0.137 with a mean size diameter around 200 nm and a zeta potential superior to |30| mV. Additionally, the loading capacity was satisfactory high, being around 7%. The optimal formulation was stable in suspension at 4ºC during at least 4 months. *In vitro* release studies revealed an initial burst release followed by an increased release at the simulated mucosa medium (pH 5). Then, a sustained and controlled phase was observed at physiologic pH 7.4. Methylthiazolydiphenyl- tetratozium bromide (MTT) assay revealed that the optimal SLNs suspension does not have cytotoxic effects in both L929 fibroblasts and MKN28 gastric cell lines.

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Targeted nanostructured lipid carriers based epigallocatechin gallate delivery system to cancer cells

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Cancer is one of the leading causes of morbidity and mortality all over the world [1]. Conventional treatments, such as chemotherapy, are generally expensive, highly toxic and lack efficiency [2]. (−)-Epigallocatechin-3-gallate (EGCG) is the major bioactive constituent in green tea and has been reported to effectively inhibit the formation and development of tumors [3]. Besides its potential for chemoprevention, EGCG has also been shown to synergize with common anti-cancer agents, which makes it a suitable adjuvant in chemotherapy [4]. However, limitations in terms of stability and bioavailability have hampered its application in clinical settings. Nanotechnology may have an important role in improving the pharmacokinetic and pharmacodynamics of EGCG and specifically target cancer cells.

In this work, EGCG-loaded nanostructured lipid carriers (NLCs) functionalized with folic acid targeting ligand were developed to increase EGCG stability and bioavailability and promote an active cancer cell targeting. The produced nanoparticles (NPs) were characterized in terms of size, zeta potential and encapsulation efficiency (EE), revealing a size of approximately 320 nm, suitable for an oral administration route, a highly negative zeta potential around -30 mV, suggesting physical stability and an EE higher than 80%. Nanoformulations revealed high storage stability, without substantial alterations of their physicochemical characteristics up to 8 weeks of storage at 4ºC. An *in vitro* release assay in simulated gastric and intestinal fluids demonstrated a controlled release of EGCG from the NPs, with only 50% release of the total EGCG after 26 hours. Viability and cytotoxicity assays performed in Caco-2 cell line, showed that concentrations up to 25 μM of EGCG were non-toxic to these cells. The anti-cancer efficiency of the nanoformulations tested in breast cancer cell line MDA-MB-231 revealed a significant decrease in cell viability after treatment with 25 μM of each EGCG-loaded nanoformulation, suggesting an increase in the uptake of EGCG by these cells. After combining the nanoformulations with the cytostatic drug tamoxifen, a demarked reduction in cell viability was observed, which suggests an enhancement of the synergistic effect between EGCG and tamoxifen.

These results demonstrate that the produced NLCs are suitable carriers for oral administration of EGCG protecting it from the gastrointestinal hash conditions and simultaneously, potentiate an active cancer cell targeting. These NPs hold great promise for a future clinical application as innovative supplements for cancer prevention and as adjuvant chemotherapeutic agents when combined with conventional cytostatic drugs, such as tamoxifen.

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Optimization and characterization of chitosan/fucoidan pH sensitive nanoparticles for delivery of methotrexate

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Methotrexate is an antimetabolite immunosuppressive drug widely used in cancer therapy, especially in leukemia, lymphoma and some solid tumors. It has potent anti-inflammatory activity against psoriasis [1] and also has immunomodulatory activity against inflammatory arthritis, so it has been used in rheumatoid arthritis as well [2]. Methotrexate interferes on synthesis of DNA, RNA and proteins because it is a folic acid analogue with ability to inhibit dihydrofolate reductase that is involved in purine synthesis. Despite its efficacy, methotrexate has associated side effects: liver toxicity, gastrointestinal upset, fatigue and in some cases bone marrow suppression, hair loss and idiosyncratic interstitial pneumonitis [3].

As a solution to overcome these significant side effects, it was thought to create nanoparticles to reduce the drug non-specific interactions and take advantage of the lower pH in the tumor microenvironment as a strategy to successfully deliver methotrexate in that area.

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 as nanoparticles for drug delivery.

The first task was to optimize a method to prepare chitosan/fucoidan nanoparticles to achieve an average particle size ranging from 200-300 nm. [4] The marine polysaccharides chitosan and fucoidan were mixed in ratios of 1:1, 1:3 and 1:5, respectively, to evaluate the stability to different values of pH. The chitosan/fucoidan nanoparticles were characterized in terms of size, zeta potential, polydispersity index, morphology and *in vitro* drug release.

The obtained results show that chitosan/fucoidan nanoparticles may present a solution to reduce drug side effects and to achieve successfully oral delivery of methotrexate to target cancer cells where pH is lower than in normal cells.

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N,N´-diaryl-perylene-3,9-diamine derivatives: synthesis, characterization and electroluminescence properties

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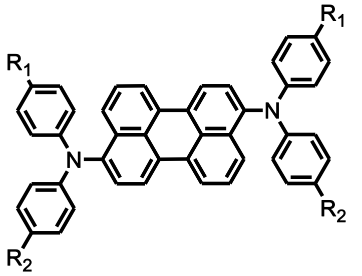
New *N*-*N´*-diaryl-perylene-3,9-diamine derivatives (PDA) with different alkoxyl substituents (methoxyl or hexyloxyl) at *para* position of *N*-aryl rings were synthesized in order to increase the donor strength of DPA group. With this chemical modification we expected not only to have an emission at longer wavelength than previously reported for DPA-substituted perylenes, [1-2] but also improve the compounds solubility in common organic solvents and hence their processability from solution. Their physical properties were studied with various experimental techniques including UV-vis absorption, fluorescence, differential scanning calorimetry, photoelectron emission spectroscopies and cyclic voltammetry [3]. Using the newly synthesized compounds as emissive materials, solution processed organic light-emitting diodes (OLED-A, OLED-B and OLED-C) were fabricated with the emission pattern covering the visible region from 500 to 800 nm. Despite the same functional perylene core of **6a**, **6b** and **6c**, the superior performance of OLED-B and OLED-C over OLED-A may be attributed to the longer alkyl chains present in alkoxyl group which enhance the molecular order and improve charge carrier transport.



6a: $R_1 = R_2 = OCH_3$
6b: $R_1 = OCH_3$, $R_2 = OC_6H_{13}$
6c: $R_1 = R_2 = OC_6H_{13}$

Fig.1. *N*-*N´*-diaryl-perylene-3,9-diamine structures

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Facile solvent-free synthesis of S-doped graphene by ball milling

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Graphene, recently characterized as “the thinnest material in our universe” [1], owing to its single-atom-thick sheet of hexagonally arrayed sp2-bonded carbon atoms, is a promising material for a diverse range of applications. However, similarly to other newly discovered allotropes of carbon (fullerenes and single-walled nanotubes), material availability and processing issues will be the rate limiting steps in the evaluation of the potentialities of graphene. Thus, there is a need for facile, scalable and efficient methods for graphene synthesis and heteroatom doping. Moreover, doped graphene can improve the immobilization of catalytic active phases, metallic nanoparticles, metal oxides and sulphides, [2] resulting in promising candidates for emerging pollutants treatment. [3] Herein, graphene flakes (GFs) were produced by liquid-phase exfoliation of graphite in organic solvents.

Subsequently they were doped with sulphur by solvent-free ball milling using sulphur powder as precursor. The effect of ball milling time and initial amount of doped agent on the doping efficiency and amount of incorporated sulfur-based groups was investigated.The parent graphite, GF and S-doped GF were characterized by Fourier Transform Infrared Spectroscopy (FTIR), X-ray Photoelectron Spectroscopy (XPS), Transmission Electron Microscopy (TEM) and X-ray diffraction (XRD). Fig. 1 shows XPS spectrum of S doped GF in S2p region.

The results confirmed the fabrication of few-layered graphene and successful incorporation of sulphur heteroatoms.

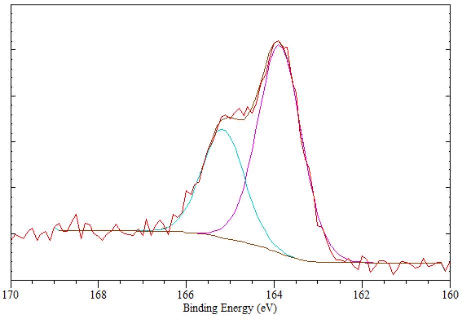

Fig.1. High-resolution S2p XPS spectrum of S-doped graphene

Acknowledgements
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Desenvolvimento de método para avaliação da toxicidade de nanopartículas de prata utilizando testes *in vitro*

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Atualmente, é de suma importância a pesquisa e desenvolvimento de novas alternativas aos antimicrobianos convencionais, devido principalmente ao surgimento de doenças em decorrência de microrganismos resistentes. Com os avanços da nanotecnologia, vêm aumentando o uso de nanomateriais, tais como as nanopartículas de prata (NP) que são alternativas aos antimicrobianos convencionais, principalmente no uso em superfícies inertes, visto seu potencial antifúngico, antibacteriano e antiviral a um amplo espectro de microorganismos.[1,2] O efeito bactericida e a estabilidade da NP são dependentes da sua forma e tamanho e, por esta razão, a sua caracterização é de extrema importância.[3] Entretanto, as mesmas propriedades que fazem a NP tão atraente como antimicrobiano podem torná-la tóxica quando em contato com células humanas.[4] Para observar o potencial tóxico de NP pode ser utilizado o ensaio OECD TG 439, que utiliza linhagens celulares frente a diferentes concentrações da substância a ser testada juntamente com o sal MTT que irá ser metabolizado apenas pelas mitocôndrias de células vivas, produzindo uma coloração.

O objetivo deste trabalho foi realizar a caracterização da NP sintetizada e desenvolver um método adequado para avaliar a toxicidade *in vitro* de NP em células THP-1 pelo ensaio de MTT, juntamente com a verificação da viabilidade celular por azul de trypan.

A caracterização das amostras de NP, sintetizadas utilizando os estabilizantes carboximetilcelulose (CMC) e álcool polivinílico (PVA), quanto à forma foi realizada utilizando absorção molecular UV-VIS, sendo realizadas leituras na faixa de 200 a 600nm. Foi observada uma banda de absorção em torno de 400nm na amostra de NP, o que evidencia a sua forma esférica. Em seguida, foi observado o comportamento da NP no meio de cultivo RPMI utilizado nos testes. No meio RPMI, as amostras de NP apresentaram absorção na região de 400nm, além disso, foi verificado que houve um deslocamento do comprimento de onda de absorção da NP. Adicionalmente, verificou-se que tanto o PBS não apresentou absorção plasmônica na região espectral estudada, assim como, os estabilizantes utilizados na síntese da NP (CMC e PVA). Para a aplicação dos testes *in vitro* foi realizado o cultivo das células THP-1 e estas foram submetidas ao ensaio do MTT com diferentes concentrações de NP por 48 horas. A leitura da reação colorimétrica foi realizada por espectrofotômetro em 570nm. Os resultados demostraram que a amostra de NP apresentou baixa toxicidade quanto ao número de células viáveis e o mesmo resultado foi evidenciado no ensaio do MTT.

De acordo com os resultados obtidos, foi possível avaliar que as amostras de NP esféricas presentes no meio de cultivo influenciam nos resultados obtidos, sendo necessários novos ensaios utilizando o meio de cultura sem a presença do corante. O teste de MTT que quantifica citotoxicidade de forma indireta é equiparado ao método de azul de trypan, sugerindo que o ensaio de MTT pode ser utilizado para estimar a toxicidade da NP. Estudos futuros com outras linhagens celulares são necessários, assim como outros métodos de estimativa de toxicidade deverão ser realizados.

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XXII Encontro Luso-Galego
Química

COMUNICAÇÕES ORAIS E EM PAINEL

Química Agro-Mar-Alimentar

Observação microscópica de emulsões alimentares inversas (água-em-óleo) em escoamentos: caracterização reológica e microstrutural

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As emulsões inversas água/óleo são sistemas multifásicos complexos, constituídos por uma fase líquida aquosa dispersa numa fase lipídica (contínua), e cristais de gordura para estabilizar a fase dispersa [1]. A quantidade de estudos publicados sobre este tipo de emulsões é muito escassa, sobretudo quando comparada com o caso das emulsões directas óleo/água [2].

Neste trabalho apresentam-se os resultados da caracterização reológica e microstrutural de dez emulsões alimentares inversas água/óleo com diferentes formulações, e preparadas à escala industrial. Pela primeira vez, a caracterização reológica em escoamento torcional (pratos paralelos) de emulsões inversas foi complementada com a observação em tempo real das alterações de textura ocorridas durante os ensaios, através da utilização de uma célula óptica de torção acoplada a uma câmara digital [2].

Em todas as emulsões foi possível identificar uma matriz densa de gotas de água envoltas em cristais lipídicos. A baixas velocidades de deformação (< 0,1 s^{-1}) o movimento das gotas é uniforme e regular. Para velocidades de deformação superiores a 0,1 s^{-1}, observa-se um aumento da excentricidade das gotas e coalescência das gotas, fenómeno mais evidenciado em certas composições. A coalescência das gotas provocou perda de nitidez nas imagens, sendo irreversível. Verificou-se também que a assinatura textural de cada emulsão possibilita a identificação do tipo de emulsão a um observador experimentado. As modificações de textura provocadas pelo escoamento (ou por deformações, no caso das experiências de relaxação de tensões) têm correspondência com alterações das funções materiais reológicas características dos ensaios reológicos considerados.

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Phenolic compounds and furanic derivatives as chemical markers of the ageing technology used in wine brandy production

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The freshly distilled wine brandy is characterised by a high concentration of ethanol and richness of volatile compounds, but is devoid of phenolic compounds other than volatile phenols [1]. Therefore, the ageing in wood is a crucial step of wine brandy production. During this process, the beverage undergoes important modifications and becomes a complex mixture with hundreds of compounds in an ethanol-water matrix, leading to sensory fullness and improving its quality [2]. These changes are closely related to the ageing technology, which traditionally involves the wooden barrel characteristics such as the wood botanical species, the cooperage technology and the barrel size [3], or the features of alternative systems [4].

This work presents an overview of our research on compounds that allow discrimination of ageing technology and/or assessment of wine brandy authenticity. For this purpose, several aged brandies from successive trials were analysed by HPLC as described by Canas et al. [5], using a Lachrom Merck Hitachi system with a 250 mm × 4 mm i.d. Lichrospher RP 18 (5 µm) column. ANOVA and multivariate analysis were used to the statistical treatment of the data. The results obtained showed that phenolic compounds released from the wood play a decisive role on the characteristics acquired by the brandy. They also highlighted the role of some phenolic compounds as chemical markers of the ageing technology used. Indeed, the results of many of the trials performed, in different oenological conditions (barrels with different toasting levels; barrels with different sizes; alternative ageing systems), lead to conclude that some phenolic acids (gallic acid and ellagic acid), coumarins (scopoletin) and phenyl ketones (acetovanillone) are closely related to the wood botanical species used - chestnut *versus* oak - and can be used to differentiate the corresponding aged wine brandies [3,4,6,7]. Besides, the analysis of different kinds of aged wine brandies (brandies from the ageing trials, Portuguese commercial brandies, Armagnacs, Cognacs and prepared brandies) revealed that some phenolic aldehydes (vanillin and syringaldehyde) and furanic aldehydes (furfural and 5-hydroxymethylfurfural) are of great interest to assess their authenticity.

Acknowledgments

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Profiling minerals and vitamin B_9 in wild plants: retention dynamics in a membrane dialysis process after a simulated-gastrointestinal model

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Traditionally used wild plants have sparked a growing interest as they are considered a valuable source of natural compounds with recognized health effects on consumer's health. Among these compounds are vitamins and mineral elements with a well-known role in maintaining human health [1]. Vitamin B_9 (folic acid) is an important cofactor of many reactions that occurs on human cells [2], while macro and micro elements play a fundamental role on energy production and maintaining the structural integrity of the cell membrane [3]. Macroelements also function as modulators of metabolism and acid-base equilibrium [4,5]. The analysis of these elements in wild plants and, mainly, in bioavailability related aspects, is still very scarce.

Herein, a membrane dialysis process was performed with the main goal of simulating gastrointestinal conditions to evaluate the bioavailability of the mineral elements present in different formulations (dry plant and infusion) of *Achillea millefollium* L. (yarrow), *Laurus nobilis* L. (laurel) and *Taraxacum* sec. Ruderalia (dandelion). The retention/passage dynamics was evaluated using a cellulose membrane with 34 mm of porosity. The vitamin B_9 contents were also analysed by high-performance liquid chromatography coupled to a fluorescence detector in the different preparations of each sample.

Dandelion showed the highest levels of mineral elements (except for zinc) regardless of the formulation used (dry plant or infusion). On the other hand, yarrow showed the highest content of vitamin B_9. Dry plants, as expected, presented higher quantities of the studied elements, in relation to the corresponding infusions; however, the extraction yield of mineral elements vary considerably, being higher for macroelements; Mg>Ca>K>>Fe>Cu>Zn>Mn. Vitamin B_9 levels were also very low for infusions, possible due to the degradation induced by the boiling water at the time of preparation. Regarding the bioavailability, calcium and potassium showed higher capacity to cross the dialysis membrane.

The studied plant species, especially if used directly in dry form, can be considered for the development of new formulations that act as sources of vitamin B_9 and minerals.

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Recovering starch, oils and waxes from potato chip industry byproducts: an alternative route for packaging production

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Nowadays, a huge amount of plastic and organic wastes resulted from human activity has a significant impact on the environment. For instance, the agrofood industry and its extensive trade are targets of major concern. Herein, an introduction to a circular economy by adding value to non-reused agrofood industrial wastes viz. potato chips industry byproducts as biopolymers' sources for the development of renewable packaging is an opportunity. Potatoes have a high carbohydrates content, in which starch is a predominant polysaccharide. Due to its various functional properties, such as gelling and thickening abilities, starch has a high potential for the development of biodegradable materials. Moreover, frying residues and potato peels contain large fractions of triacylglycerols and other constituents, such as long chain polyesters (waxes), respectively, that are able to promote important mechanical and hydrophobic profiles, thus reducing the often water sensibility of starch-based materials.

In this work, various potato industry byproducts (washing waters, potato peels, and frying residues) were used on packaging production. Potato starch, waxes, and oils were extracted from washing waters, potato peel and frying residues, respectively. Mechanical and wettability properties of different component ratios were tested to investigate the biopolymers influence on potato starch-based films characteristics. Also, a homogenization process using a Miccra D-9 Homogenizer disperser was tested after the gelatinization step aiming reducing oil/water phases separation.

Recovered potato starch revealed to be proper for the development of packaging materials. An increasing of the potato starch-based films tensile strength and deformation ability was achieved by using the homogenization system. Contrary to the expected [1], frying oils incorporation increased not only the Young's modulus and elongation properties of starch based films, but also improved their tensile strength. According to GC-FID analysis, frying residue contains fatty acids with various chain length (C10 – C18) that can lead to both plasticizing effect and ordered molecular arrangement at the starch-lipid interface. On the other hand, low amounts of waxes were able to improve the films tensile strength and deformation ability while higher portions increased their elongation properties. Water contact angle measurements revealed that both lipidic extracts efficiently enhanced the films hydrophobicity, although a highest waxes amount is required to evidence this effect.

Therefore, potato industry byproducts revealed to be a suitable biopolymers' source for designing alternative renewable packaging materials.

Acknowledgments
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Tecnologia vinagreira: compotas agridoces em glaze de vinagre e pickles de abóbora, pêra, pequenos frutos e gin

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O vinagre é um alimento hipocalórico e funcional, que tem vindo a ganhar em prestígio e diferenciação. A abóbora é um hortícola com expressiva produção mundial (25 Mton in INE 2013); Portugal é um pequeno produtor, mas as condições edafoclimáticas, aliadas a tradições da gastronomia mediterrânica e preocupações com a alimentação na saúde, apontam para um tendencial crescimento [1]. A tamareira (*Phoenix dactylifera* L.) é uma planta primitiva cultivada pelo seu fruto comestível nos oásis de zonas desérticas do mundo árabe. Ao contrário de outros frutos, as tâmaras são utilizadas para consumo humano em todas as fases de desenvolvimento do fruto [2].No âmbito do projeto UIIPS-ESAS Tecnologia Vinagreira (2009-), que propõe o aproveitando de matérias-primas e processos incomuns nesta indústria, pretendeu-se contribuir para a sustentabilidade e inovação na oferta, aproveitando a aptidão tecnológica do vinagre, de um fruto nobre e exótico e de um volume de abóbora desperdiçado (calibre/maturação/defeitos) com potencial de aplicação, criando nobreza e valor [1].

Com vinagres simples e abóbora manteiga (*Cucurbita moschata*), adaptou-se a picklagem *fresh pack* de hortícolas a frutos doces. Articulando ensaios tecnológicos, analíticos (físico-químicos, microbiológicos) e sensoriais, otimizou-se ainda as formulações de duas compotas, cuja originalidade tecnológica face ao receituário tradicional, reside no desenvolvimento intencional de duas fases distintas: *glaze* -uma redução de vinagre balsâmico enriquecido com mel de flor de laranjeira ou mel de rosmaninho- e compota, um gel cuja coesão resulta da harmonização de acidez/açúcares/pectina [3], conferida nestes protótipos pela polpa de abóbora ou tâmara e adições de raspa e sumo de laranja ou de limão, gin cítrico (na compota de abóbora) e frutose, em proporções definidas. A imiscibilidade das duas fases permite um uso versátil e liberdade em criar a proporção *glaze*/compota e a tónica (agridoce), mais agradáveis à degustação. Para os pickles, concebidos para dupla utilização -consumo dos frutos e da infusão, como condimento- formularam-se combinações de vinagre de tipo/acidez diferentes (vínicos, de arroz, fruta, sidra, álcool), com abóbora (cubos), ensaiando *blends*, frutos (pêra, mirtilo, groselha), especiarias e plantas aromatizantes (mostarda, pimentas, canela, baunilha, cravinho, hortelã-pimenta). O painel de provadores destacou três protótipos desenvolvidos numa matriz mista de vinagres (de álcool e de fruta) aromatizadas e com adição de gin. Da tecnologia de picklagem, operações de pré-salga, edulcoração (frutose), tratamento térmico e aditivação (E300/E330/E509) revelam-se essenciais [1]. Concebidos para o mercado *gourmet* e posicionados como produtos *diet* e *vegan*, os protótipos cumprem, à data, os requisitos de estabilidade química e microbiológica e possuem, em comum, inovação, versatilidade e conveniência. No presente, decorrem estudos de vida útil [1].

Agradecimentos
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Fluoroquinolones in Portuguese poultry meat

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Antibiotics, especially fluoroquinolones (FQs), have become an integral part of the livestock production industry and can be used therapeutically or prophylactically [1]. The most prominent human health risk associated with intensive animal farming and antibiotic use is antimicrobial resistance and the possible failure of human antibiotic therapy [1].Therefore, this study aimed to compare the results from two different surveillance programs conducted in 2013 and 2015, by our research group, that have identified and quantified FQs, namely norfloxacin (NOR), ciprofloxacin (CIP) and enrofloxacin (ENR), in 182 poultry muscle samples, through an analytical methodology encompassing solid phase extraction and liquid chromatography coupled with fluorescence detection.

The analytical methodology complied with all the validation parameters and the limits of detection ranged between 0.69 and 4.23 μg kg^{-1}. Regarding occurrence, frequencies of 78% and 62% were found for 2013 and 2015, respectively. Four poultry samples were contaminated at levels higher than the maximum residue limit for ENR (100 μg kg^{-1} for the sum of CIP and ENR). Higher frequencies and concentrations were found in 2013, with the exception for CIP average concentration, however, no statistical differences were observed (Fig.1). The results obtained corroborate the findings in the report published by European Food Safety Authority, which refers that since 2010, Portugal is the only European country with over 80% of Salmonella Enteritidis in chickens resistant to CIP and nalidixic acid (precursor of quinolones) [2].

This study demonstrates that there is a widespread contamination of FQs in poultry meat, and although these concentrations are not able to promote acute toxicity in humans, it appears that they are administrated indiscriminately to poultry. With the systematic use of FQs, producers are promoting the emergence of resistant bacterial strains, thus leading to a possible decrease in effectiveness of this important group of antibiotics in human medicine.

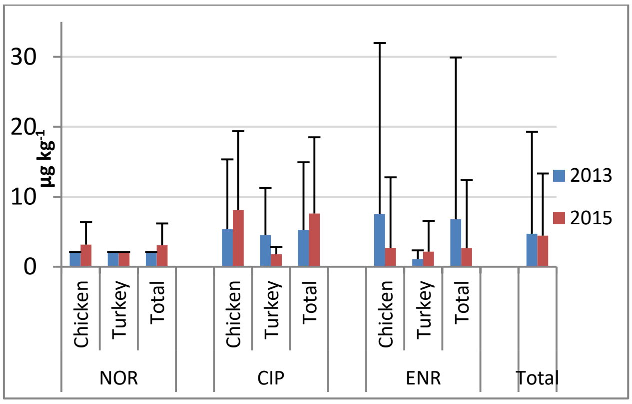

Fig.1. Average concentrations of the studied FQs

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Effect of drying on the physical, chemical and sensorial properties of kiwi

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Kiwi fruit is a highly nutritional fruit due to the high level of vitamin C and its strong antioxidant capacity due to a wide number of phytonutrients including carotenoids, lutein, phenolics, flavonoids and chlorophyll [1]. Drying consists of a complex process in which simultaneous heat and mass transfer occur. Several alterations occur during the drying of foods at many levels (physical, chemical, nutritional or sensorial) which are influenced by a number of factors, including processing conditions [2]. Temperature is particularly important because of the effects it produces at the chemical and also at the physical level, particularly colour and texture [3]. In the present work were evaluated the changes in sliced kiwi when exposed to air drying at different temperatures (50, 60, 70, 80 ºC), namely in terms of some chemical properties like ascorbic acid or phenolic compounds, physical characteristics like colour and texture and also at the sensorial level. All experiments followed standard established procedures and several replicates were done to assess each property.

The results obtained indicated that moisture was reduced with drying by 74 to 87%, depending on the temperature. Also ascorbic acid decreased with drying, being 7% for 50 ºC and increasing up to 28% for the highest temperature (80 ºC). The phenolic compounds and antioxidant activity were also very much affected by the drying temperature. The water activity of the dried samples varied from 0.658 to 0.753, being compatible with a good preservation. Regarding colour, the total colour difference between the dried samples and the fresh sample was found to vary in the range 9.45 – 17.17. The textural parameters were also much affected by drying, namely hardness which decreased by 45 to 72 %, and all other parameters increased: cohesiveness (approximately doubled), springiness (increased 2 to 3 times) and chewiness which increased up to 2.5 times that off the fresh sample. Adhesiveness, which was observed for the fresh samples (-4.02 N.s) disappeared in all the dried samples. The sensorial analysis made to the dried samples allowed establishing the sensorial profiles as shown in Figure 1.

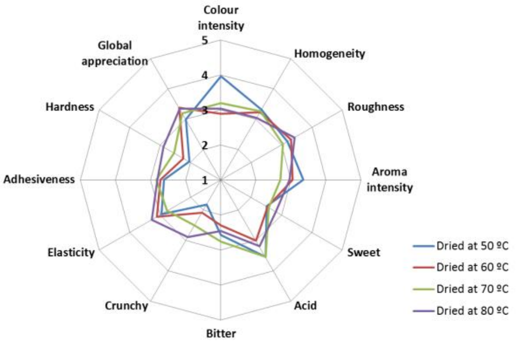

Fig.1. Sensorial profile of the dried samples of kiwi

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Effect of bottle seal on virgin olive oil quality

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Several studies have been published about the negative impact that oxygen has on virgin olive oil quality, namely in promoting the formation and degradation of hydroperoxides, originating volatile compounds of low molecular weight responsible for off-flavours, sensory described as rancidity. These studies on oxidation have focused mainly on the type of conditioning rather than on the most efficient type of bottle seal to be used.

The aim of this study was to assess the effect of natural cork bottle seals as the closing system of glass bottles, in virgin olive oil quality over storage time, making a link between two important Iberian clusters, olive oil and cork.

A comparative analysis between three types of bottle seals: metallic capsule, natural cork, and cork stopper with capsule was performed. The bottle neck from the ones with natural cork stopper was covered with bee wax. The olive oil studied was a blend of extra virgin olive oil “Beira Interior” POD from ‘Galega Vulgar’ and ‘Cobrançosa’ cultivars. The olive oil was bottled in dark glass bottles (500 cm^3), sealed by the previously stated methods and stored in absence of light and at a constant temperature of 22 ºC. Three evaluation periods (beginning, 5 months and 10 months of storage) were performed.

The methods established by the European Regulation (REG (CEE) Nº 2568/91 and subsequent amendments) were used to measure the olive oil's qualitative changes, namely regarding oxidation (peroxide value and UV absorbances) as well as the characteristics related to both nutritional and sensorial characteristics of virgin olive oil (fatty acids composition, phenols and tocopherols).

The preliminary data evaluation performed by principal components analysis showed that the two types of bottle seals with cork act in a different way than the metallic capsule, for the studied oxidation parameters. There's still an ongoing discussion about some results studied for discrimination of sensorial components.

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Distillation process characterization for honey spirit production

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Honey presents a higher amount of carbohydrates (60-82%) [1] mainly fructose and glucose and other minor compounds (proteins, enzymes free amino acids, essential minerals, vitamins and polyphenols). Given their higher amount of sugar, yeast could be convert them into alcohol through the process of fermentation. The more usual alcoholic beverage produced from the honey is mead, however, some spirits are also produced, but no scientific research is known in order to characterize this beverage. The aim of this work is to characterize the distillation process of honey spirit resulting from distillation of mead obtained from different honey raw material: *Lavandula* honey; *Castanea* honey and a mixture of waxes and honey resulting from the bee-keeper uncaps process.

In the distillation process different fraction were collected during the time. The alcohol strength was determined by distillation and electronic densimetry. The volatile compounds of the samples (acetaldehyde; ethyl acetate; methanol; 1–propanol; 2-methyl-1-propanol; 1–butanol and isoamyl alcohols) were analysed by gas chromatography-flame ionization detection (GC-FID) [2].

The honey spirit does not present methanol in the majority of the analysed fractions or it is present in a very low quantity (<0.062 g/L) what is an advantage of this beverage in comparison with other distillates. The raw-material used in the production of the beverage as well as the distillation time has a significant effect in the composition of the fractions collected during the distillation process (Table 1).

The different volatile profile suggests a different quality given the botanical origin of honey used as raw material. The production of honey spirit from waxes and honey resulting from the uncap process has a good quality.

Table 1. ANOVA results. Effect of raw material and distillation time on the honey spirit

Determination	Raw-material		Distillation time		Interaction		Residual
	Sig.	Var(%)	Sig.	Var(%)	Sig.	Var(%)	Var(%)
Alcoholic strength (%v/v)	0.0000***	5.3	0.0000*	93.2	0.0064**	1.0	0.5
Acetaldehyde (g/L)	0.0000***	5.8	0.0000***	76.8	0.0000***	16.0	1.4
Ethyl acetate (g/L)	0.0191*	0.3	0.0000***	91.8	0.0000***	7.3	0.5
1-Propanol (g/L)	0.0000***	4.2	0.0000***	92.2	0.0240*	0.5	3.1
2-Methyl-1-propanol (g/L)	0.0000***	7.6	0.0000***	89.4	0.0000***	2.7	0.4
1-Butanol (g/L)	0.0006***	14.5	0.0000***	64.1	0.0198*	12.8	8.6
Isoamyl alcohols (g/L)	0.0000***	5.9	0.0000***	92.0	0.0003***	1.8	0.4

Sig. – significance level; Var(%) – Variance percentage; n.s. – not significant, $p > 0,05$; * Significant, $0.01 < p < 0.05$; ** very significant, $0.001 < p < 0.01$; *** highly significant, $p < 0.001$

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Activated carbons with different physicochemical properties: efficiency in removing 4-ethylphenol and 4-ethylguaiacol in red wine and their impact on wine phenolic and aroma compounds

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The yeast *Dekkera/Brettanomyces* is considered the main cause of wine spoilage of premium red wines matured in wood barrels, leading to serious economic losses all around the world [1]. The negative aroma impact is mainly due to the formation of 4-ethylphenol (4-EP) and 4-ethylguaiacol (4-EG) by these yeasts through decarboxylation of the corresponding hydroxycinnamic acids to vinylphenols, and subsequent reduction to ethylphenols [2]. Although there are available some preventive strategies and oenological practices that can decrease wine contamination, none of them has an efficiency of 100%. The activated carbon (AC) is a fining agent used in winemaking for many years in juice and white wine (Reg. EU 606/2009) as decolorant and deodorant, and has been also tested in red wines to remove ocratoxin A [3]. Previous works have shown that the AC can be a solution for removing these unpleasant small volatile phenols from red wine [4]. However the efficiency removing and their impact on red wine quality are not well understood.

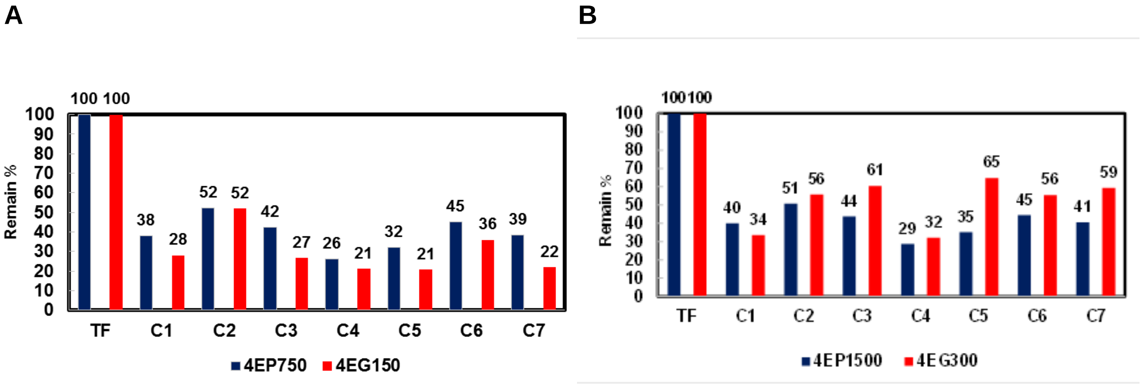

Fig 1. Reduction (%) of 4-EP and 4-EG by ACs (C1-C7) in two level of contaminations (TF) (μg/L)

Thus, the main purpose of this work is to compare different activated carbons and verifying those efficiency in remove the 4-ethylphenol and 4-ethylguaicol and confirm their impact on phenolic and aroma compounds. The results showed that some activated carbons reduced significantly the level of 4-EP and 4-EG, reducing, generally, the level of phenolic and aroma compounds, however, with the better ACs there is an important recover of the red wine quality.

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Performance analysis of Australian vineyard's soils with different infrared instruments: a comparative study

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Soil management has been a major concern in human history ever since agriculture became the most important means of subsistence on the planet. Nowadays, soil organic management and sustainable agriculture focus on the growth of high-quality food and products, while preserving and trying to improve the fertility and quality of the soil. In light of this, the characterization and evaluation of the environmental status of the soil (discriminating between soil types, assessment, management, degradation, etc.) is essential. The information gathered could help to improve future objectives such as proper management planning and sustainable land use as well as play an important role in a more sustainable and precision agriculture. The use of rapid techniques that provide complete information in a fast way is therefore of paramount importance. Current strategies for analysing soils (pedology) are based on wet chemistry methods, which are often laborious, expensive, time-consuming and may be of limited use, particularly over short periods of time such as harvesting campaigns. With this in mind, an efficient, high-throughput analytical method for soil characterization would surely constitute a leap forward in soil management practices.

Infrared spectroscopy (IR's) is a rapid, non-destructive, cost-effective and reliable technique. Its use, combined with chemometric tools, as a method for discriminating soil types and also for determining different soil constituents is rapidly increasing. A comparison of the performance of five different IR instruments – three Fourier Transform Infrared (FT-IR) and two Visible and Near Infrared (Vis-NIR) – analysing the same soil samples was undertaken. Samples were collected from several vineyards in the MacLaren Vale wine region in South Australia. Different parameters were analysed for those samples, including: Organic Carbon, Conductivity, pH, Exchangeable Sodium Percentage (ESP) (%), among others. Spectral analysis was performed using chemometric methods: principal components analysis (PCA) and partial least squares (PLS). The objective was to assess which of the different NIR instruments would yield better results analysing these different soil constituents and determine which instrument would prove a better investment from a practical point of view.

Preliminary results indicate that some of these parameters are easily and accurately analysed using NIRS whereas others not quite so. The performance of the different instruments for a specific parameter also varied somewhat.

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White wine tartrate stability: comparative study of ion exchange resins versus oenological additives

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The precipitation of tartrate crystals is a natural phenomenon in wine evolution, which occurs mainly during wine conservation. Preventative solutions to this phenomenon can be chemical or physical treatments. Within these, ion exchange resins is an accepted stabilization process by the OIV to prevent tartrate instability of wines, according to the Resolution 43/2000 [1].

Tartaric acid is the most important organic acid in the wine. It is easily ionized, leading to the formation of precipitates like potassium hydrogen tartrate (KHT) and calcium tartrate (CaT). These precipitates, although not being harmful to health of the consumer, leads to a decrease in the commercial acceptance and, consequently, to the decrease of the wine commercial value [2]. Thus, the aim of this work was to compare ion exchange resins with oenological additives, such as CMC's with different structural features and metatartaric acid, in a white wine from the Douro Valley, on tartaric stability. It was also studied their impact on wine phenolic compounds, mineral composition, chromatic characteristics and sensorial profile.

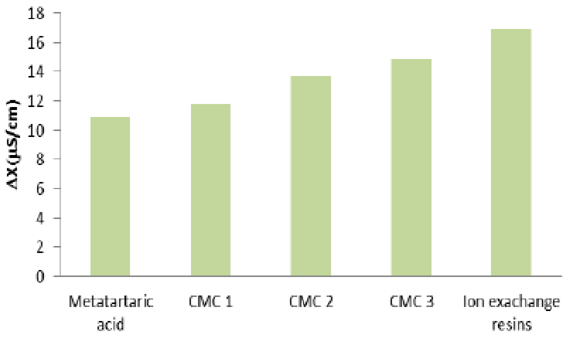

Fig. 1. Effect of stabilization treatments on white wine tartaric stability

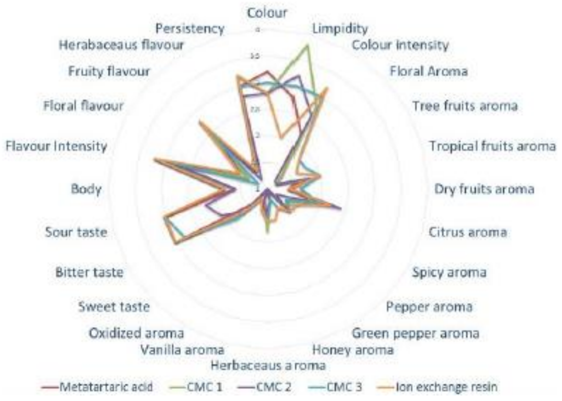

Fig. 2. Sensorial profile of treated white wines

After addition of metatartaric acid, CMC 1, CMC 2, CMC 3 and treatment with ion exchange resins in the acid cycle, all white wines achieved tartaric stability (Fig.1). The application of these treatments for white wine tartaric stabilization showed no significant effect on the wine sensorial profile (Fig.2), yet some descriptors were highlighted in wine treated with ion exchange resins, namely colour intensity, flavour intensity and persistency.

Acknowledgements
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Effectiveness of carboxymethylcellulose in comparison with other oenological additives in red wine tartaric stabilization

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The precipitation of tartrate crystals like potassium hydrogen tartrate and calcium tartrate is the main cause for the formation of sediment in bottled wines [1]. Traditionally, cold stabilization is the technological action carried out for preventing this problem. Electrodialysis is also used to that purpose, removing ions like potassium, bitartrate and calcium from the wine [2]. Metatartaric acid, a polymer obtained by esterification of tartaric acid, is the most used oenological additive for tartaric stabilization [3]. Yeast mannoproteins have also been suggested in order to prevent tartrate precipitation, inhibiting the crystallization of tartrate salts by lowering the crystallization temperature [1]. More recently, carboxymethylcellulose (CMC) was authorized to prevent tartaric instability [4]. CMC is a cellulose derivative obtained by etherification of the free alcohol groups of the glucopyranose units and inhibits tartaric precipitation through a "protective colloid" effect [3]. The aim of this work was to compare the effectiveness of CMC's with different structural features (added at two concentrations levels) and other oenological products like metatartaric acid and mannoproteins, added to a red wine from Douro Valley, on tartaric stability and evaluate their influence in wine characteristics such as phenolic compounds, mineral composition, chromatic characteristics and sensorial profile. In general, mini-contact test showed that CMC's and metatartaric acid stabilized the wine but mannoproteins don't. The use of CMC's on wine tartaric stabilization had no significant effect on the wine potassium and calcium concentration as well as on the wine sensorial profile.

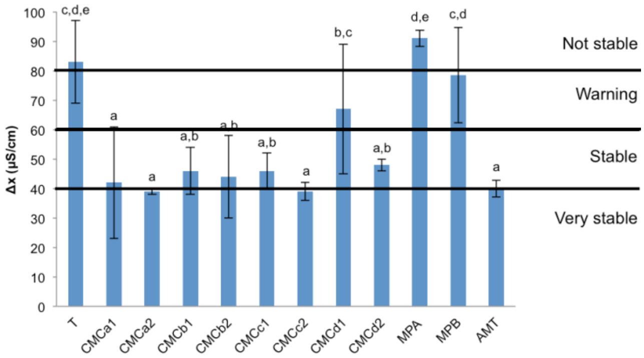

Fig. 1. Effect of oenological additives on red wine tartaric stability
CMCa - MW 441 kDa, DS 1.12; CMCb - MW 441 kDa, DS 0.96; CMCc - MW 344 kDa, DS 0.74; MW 512 kDa, DS 0.63; 1- Medium dosage; 2- High dosage; MPA – mannoprotein; MPB – mannoprotein; AMT – metatartaric acid

Acknowledgment
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Perfil sensorial e cromático de vinhos monovarietais da casta Jean da Região do Dão e da casta Mencia da Região do Bierzo

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A casta Mencia é uma variedade de *Vitis vinifera*, tinta, cultivada na Região do Bierzo em Espanha. Em Portugal, na Região do Dão, tem como casta sinonímia a casta Jaen. Tradicionalmente, a casta tinta Mencia, é utilizada para a elaboração de vinhos leves, com boa acidez, taninos suaves e aromas a framboesa [1]. Em Portugal os vinhos da casta tinta Jaen são caracterizados como elegantes, intensos de cor e muito macios, dada a sua baixa acidez. O seu aroma é intenso e delicado, lembrando amoras a mirtilo, o que torna os seus vinhos muito apreciados [2].

Assim, foi objetivo deste trabalho caracterizar o perfil sensorial dos vinhos monovarietais da casta tinta Mencia/Jaen e correlacionar os dados analíticos (intensidade e tonalidade corante, antocianinas totais e características cromáticas) com os dados sensoriais de modo a perceber se estes influenciam a discriminação dos vinhos recorrendo à análise em componentes principais (ACP).

O perfil sensorial de cada vinho (4 vinhos monovarietais Jaen e 14 vinhos monovarietais Mencia) foi obtido através de uma análise descritiva quantitativa (ADQ) (Fig.1) e os dados foram submetidos a uma análise de variância (ANOVA) que permitiu determinar as similaridades em termos de perfil sensorial. No entanto, pelas análises das antocianinas totais, intensidade e tonalidade corante, verificamos que os vinhos são significativamente diferentes quanto a estes parâmetros.

Após *corr*-ACP (Fig.2) dos dados analíticos e sensoriais podemos verificar que há uma aparente distribuição uniforme dos vinhos da casta Mencia/Jaen.

Fig. 1. Avaliação sensorial dos vinhos pelo painel de provadores

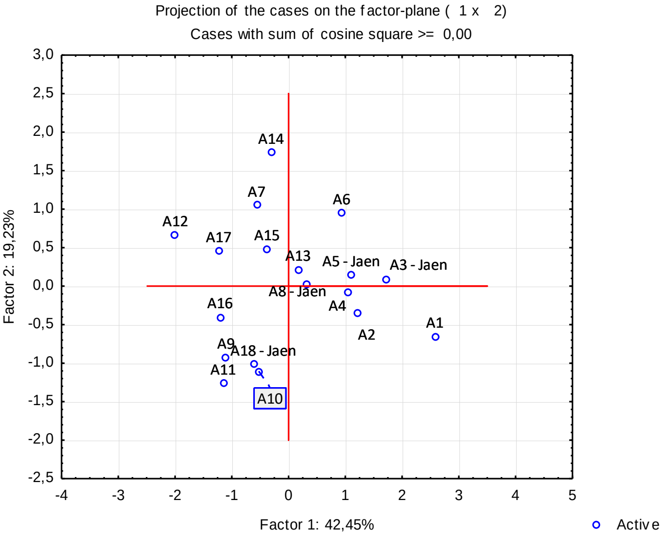

Fig. 2. Projeção da *corr*-ACP das amostras de vinhos monovarietais avaliados química e sensorialmente

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Antioxidant capacity of the extracts from nettle leaves (*Urtica dioica* L.) obtained with Microwave Hydrodiffusion and Gravity (MHG) and distillation techniques

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Urtica dioica L. is a perennial plant distributed all over the world. For centuries, it has been used as food, fertilizer, paint and fiber resource. Its leaves are stinging but they have phytochemicals and bioactive compounds with some pharmacological activities. For this reason, this vegetal is employed in pesticides industry for plant protection and in pharmaceutical and cosmetic industries to treat different pathologies [1,2,3].

In the present work, aqueous extracts of *U. dioca* leaves have been obtained by two techniques and their antioxidant capacities were compared. All extraction experiments were carried out in duplicate and all determinations of the obtained extracts were carried out in triplicate.

With Microwave Hydrodiffusion and Gravity (MHG), one hundred grams of raw material were positioned in the Milestone NEOS-GR MA126 equipment using different irradiation powers (50, 75, 100 and 125 W). This innovate technique extracts the active compounds presents in the sample with the naturally water in the leaves because it does not add any solvent. MHG is also environmentally friendly as it reduces the energy, time and resources needed [4,5]. For the traditional steam distillation without cohobation, fifty grams of leaves with 250 mL of deionized water were used.

Antioxidant capacity of the extracts obtained by both techniques was analyzed by 2,2-diphenyl-1-picrylhydrazyl (DPPH) free radical method, Trolox equivalent antioxidant capacity (TEAC) assay and Ferric Reducing Antioxidant Power (FRAP) method. Total phenols content was also analyzed by the Folin-Ciocalteu assay.

The optimum irradiation power of extraction was 100 W for the microwave hydrogravity because the obtained extracts presented the highest total phenols content. When 125 W was applied, the antioxidant capacity was slightly higher than the other irradiation powers, but it was rejected because the solid fraction after the MHG extraction was burned and it cannot be used for other purposes, for example for animal feeding. The extract derived from the traditional distillation had a lower total phenol content and antioxidant capacity than the obtained from the MHG optimum irradiation power.

The results show that MHG is a technique viable to add value to nettle leaves and get aqueous extracts that can be used in different industries for your antioxidant capacity.

Acknowledgments

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Study of extraction conditions for phenolic compounds from Strawberry fruits

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Strawberries are an important source of phytochemicals, namely vitamins and phenolic compounds such as anthocyanins and tannins with antioxidant properties [1]. The yield and phenolic content of natural extracts are dependent on the conditions used for extraction [2].

In the present work three different types of extracting solutions (methanol, ethanol:water and acetone:water), two times of extraction (15 and 60 min) and three ratios of solid/solvent (5/25, 5/50 and 5/100 g/mL) were tested in order to evaluate the efficiency of the extraction of phenolic compounds. Phenolic compounds were determined by Folin-Ciocalteu method [3]. Each assay was performed in triplicate.

Regarding the extraction solution, it was possible to observe a slight tendency towards a higher efficiency of acetone:water (AcO:H2O, 60:40), but the differences might not be statistically significant. A longer time of contact, 60 min as opposed to 15 min, did not show advantages in the yield of extraction. Considering the factors under study, the results obtained showed that volume of extraction solution was the parameter that most influenced the values obtained. Using a higher volume lead to an increase in the amount of phenolic compounds extracted, in a more pronounced way for 15 min of extraction. For a volume of 25 mL the amount of phenolic compounds quantified ranged from 2.13-2.41 mg GAE/g, and increased 30-68% when it was used 50 mL of solution. Using 100 mL of solution, it was extracted twice as double of phenolic compounds. In case of 60 min, the amount of phenolic compounds quantified in samples obtained with 25 mL of solution ranged from 2.32-2.97 mg GAE/g, and increased for 2.43-4.27 mg GAE/g and 3.98-4.68 mg GAE/g when was used 50 and 100 mL, respectively.

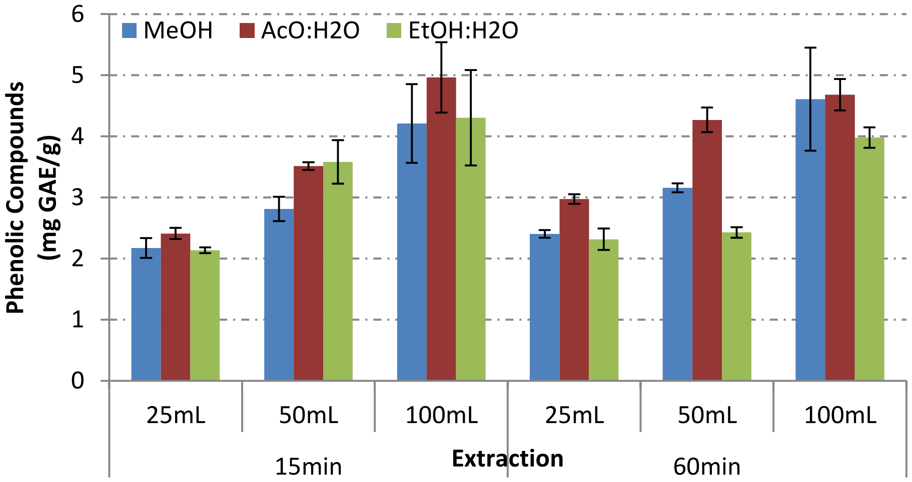

Fig. 1. Phenolic compounds quantified with the different extraction conditions.

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Identification and structural characterization of a new family of ellagitannin-derived compounds extracted from cork

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Cork is a suberized cellular tissue that is continuously produced by the phellogen of the cork oak tree native species (*Quercus suber L.*) in the Mediterranean region. The unique properties of this material allowed its use in a wide range of applications being wine cork stoppers the most common and valuable use [1, 2].

Different polyphenols have been found to migrate from different cork stoppers into bottled wine model solutions [3], being ellagitannins the most relevant ones. In 1978, Puech showed that ellagitannins exposed to alcohols (as beverages e.g.) incorporated ethoxy moieties into their structures (Fig.1) [4]. Bearing this, the aim of this study was to identify and characterize new ellagitannin-derived compounds in corks and to evaluate the reactivity of these compounds in model solutions with a major wine component, (+)-catechin. This yields the formation and identification of several ellagitannin-catechin-derived compounds with a more complex structure that can have impact on the wine sensorial properties.

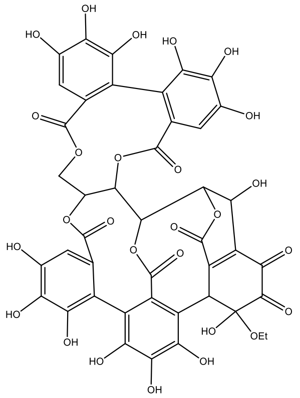

Fig.1. New compound derived from the ellagitannin Vescalagin

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Study of essential oil of *Rosmarinus officinalis* L. in different maturation stages by mass spectrometry (GC-MS)

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The purpose of this work was to characterize the essential oil (EO) of flowers and leaves of *Rosmarinus officinalis* L. in different maturation stages using gas chromatography-mass spectrometry (GC-MS) [1]. Gas chromatography can be applied to non-polar compounds due to its excellent resolution and separation [2], especially when coupled to mass spectometry. It has been widely used to determine the compositions of foods and contaminants, among others. This technique was used in this work to quantify the chemical composition of samples.

Samples of fresh flowers and leaves of *Rosmarinus officinalis* L. growing at Trás-os-Montes, were submitted to hydrodistillation in a Clevenger-type apparatus [3]. The biomass was placed in a round-bottomed flask with distilled water and subjected to hydro-distillation for a period of 3 h at 95ºC. The distillate was collected and submitted to physical separation, after which the EO was kept on sealed vials at 4ºC for further analysis.

The EO of the flowers of the second crop showed higher percentage of antimicrobial compounds than the EO of the first harvest. Thus, it can be concluded that, in principle, the former possesses greater inhibitory properties against microorganisms. The EO of the flowers didn’t showed a percentage of antimicrobial compounds as high as the EO of the leaves but, nevertheless, it has potential to be used as a natural preservative owing to several compounds that exhibit antimicrobial characteristics, such as 1,8-cineol , α-pinene , L-verbenone, borneol and camphor. Therefore, it was possible to characterize the EO of *Rosmarinus officinalis* L. at different stages of development by GC-MS.

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Modifications of yeast cell wall polysaccharides induced by brewing and reutilization generates differentiated by-products to be exploited in diversified formulations and materials

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Brewery industry uses different species of *Saccharomyces* yeasts, which are reused in several fermentative cycles. *Saccharomyces pastorianus* and *S. cerevisiae* are reused 1-7 times depending on yeast performance and/or production requirements before being discarded as brewer's spent yeast (BSY). Recently, it was shown that the brewing process using *S. pastorianus* inoculum yeast (IY), after 3-7 fermentative cycles, originated a BSY with much more insoluble polysaccharides, not solubilized even 8 M KOH conditions [1]. This was due to the presence in higher amounts of (β1→4)-glucans, together with (β1→3)-glucans, glycogen, and mannoproteins [2]. Also, BSY mannoproteins, after several fermentation cycles, became more branched and 3 times more phosphorylated than IY [2].

Microwave water extraction (MWE) were used to recover polysaccharides from *S. pastorianus* BSY, recovering polysaccharides with different extractabilities, which were consecutively removed under different temperature conditions. During the successive MWE extractions the yeast cell wall also preserved the yeast three-dimensional structure. The first two extracts performed at 180ºC for 2 min were composed of mannoproteins and the extracts performed at 200ºC for 2 min one were composed mainly by glycogen, the another extract contained 28% glycogen mixed with 32% of (β1→3)-glucans. The final residue was rich in proteins and poor in polysaccharides, from these 45% were (1→3)-glucans and 14% (1→4)-glucans.

In order to better understand the changes induced by the brewing process, in this work, different BSY obtained from *S. cerevisiae* (Weiss and Ale) and *S. pastorianus* (Carlsberg and Lager) were studied. MWE from the different BSY were performed at 180º for 2 min. *S. cerevisiae* strains were richer in glucans than *S. pastorianus*. Glucans were the main polysaccharides solubilized from *S. cerevisiae* whereas mannoproteins were the main polysaccharides solubilized from *S. pastorianus.* The glucans obtained from *S. cerevisiae* Weiss, which were not reused, contained 24% of (1→3) and 27% of (1→4) glucans while *S. cerevisiae* Ale (2 reuses) contained 2% (1→3) and 51% (1→4) glucans.

The reutilization of *S. cerevisiae* yeasts also induced modification in cell walls polysaccharides as was already observed in *S. pastorianus.* Depending on the species used and the number of times it is reused, it is possible to obtain different polysaccharide extracts from BSY by-products. These can be targeted for different applications, depending on the required functionalities, such as emulsifiers (mannoproteins), dietary fiber with biological activities (β-glucans), and glycogen for new food packaging materials.

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Binding of procyanidins to mucin protein: a molecular approach of astringency

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Astringency is a complex group of sensations involving dryness, tightening and puckering of the oral mucosa [2] closely related to the interaction between food tannins (namely procyanidins) and salivary proteins (SP). These interactions result in SP/tannins aggregation and/or precipitation and loss of SP lubricating properties [2]. Hydrophobic interactions and hydrogen bonds have been described as the main driving forces involved in this interaction [1]. SP can be divided into different families, namely proline-rich proteins, cystatins, statherin, peptide P-B and mucins [3].

Salivary mucins are high molecular weight glycoproteins responsible, among other functions, by hydration and lubrication of the oral cavity [4]. Since mucins are responsible for lubrication of the oral cavity, the aim of this work was to study its possible contribution to astringency sensation. So herein it was studied the interaction between mucin with grape seed procyanidins at a molecular level by fluorescence quenching and Saturation Transfer Difference (STD)-NMR. For this purpose, two procyanidins with different degrees of polymerization (dimer B4 and tetramer) and a mucin model protein (mucin from porcine stomach) were chosen. Furthermore, the influence of the presence/absence of ethanol (EtOH) or dimethylsulfoxide (DMSO)) on this interaction was also studied.

It was expected that mucin-procyanidin interaction increases with the increase of procyanidins' degree of polymerization. However, it seems to exist an exception for procyanidin tetramer, probably due to conformational constraints imposed by its complex structure. Furthermore, the lowest values of binding constants (K_{SV}) pointed out that EtOH and DMSO can disrupt the main driving forces of this interaction, hydrophobic interactions and hydrogen bonds, respectively (Table 1).

Table 1. Stern–Volmer quenching constants (K_{SV}) and Apparent Static Quenching Constant (K_{app})* for the interaction between mucin and procyanidin dimer B4 and procyanidin tetramer)

	K_{SV} (M^{-1})		
Procyanidin	**0.1 M, pH=5.0**	**0.1 M, 10% EtOH, pH=5.0**	**0.1 M, 10% DMSO, pH=5.0**
Dimer B4	38500±404.4*	32460±562.4*	7187±437.1
Tetramer	29130±1256	21540±978.7	21450±908.8

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Batatas fritas no micro-ondas ou forno convencional: serão alternativas saudáveis à fritura tradicional?

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A fritura é caracterizada por um processo de confeção e desidratação de alimentos, com base em mecanismos de transferência de calor e de massa com o meio de fritura, sendo a incorporação de óleo nos alimentos uma preocupação constante do ponto de vista nutricional e de saúde.

O micro-ondas é já usado para cozinhar e secar alimentos, usualmente com tempos de processamento mais curtos e temperaturas inferiores, sendo a formação da crosta e cor típica conseguida por recurso à função de grill acoplada em muitos equipamentos. O processamento no forno combina convecção de ar quente e tempos de processamento mais elevados, sendo mais frequentemente utilizado para “assar” alimentos, quase sempre com adição de gordura. Estas tecnologias podem constituir alternativas de fritura mais saudável, recorrendo a menores quantidades de gordura.

Neste trabalho, foi realizado um estudo comparativo da qualidade nutricional e sensorial de batatas fritas tradicionais, no micro-ondas e forno, utilizando condições otimizadas para se conseguir obter produtos com características sensoriais semelhantes às da fritura. Contrariamente à fritura de imersão, que serviu de controlo, nos dois processos testados utilizou-se gordura adicionada apenas para cobrir a superfície da batata. Utilizaram-se dois dos óleos vegetais mais comuns em Portugal – girassol e azeite. Os parâmetros analisados nas batatas “fritas” incluíram a composição lipídica e indicadores de degradação dos lípidos, teor em vitamina E e C, e acrilamida, tendo sido complementados com análise sensorial.

Em geral, as batatas fritas no micro-ondas e no forno apresentaram menos 74 % e 81 % de incorporação de gordura do que as batatas fritas tradicionais, respetivamente. Independentemente do processamento, os principais ácidos gordos da batata frita refletem o óleo vegetal em que foram confecionadas. No que respeita à extensão da degradação dos lípidos incorporados, esta foi claramente superior nas batatas fritas tradicionais, sem diferenças significativas entre as batatas fritas no micro-ondas e forno. A vitamina E aumentou após o processamento das batatas em proporção direta ao teor inicial dos óleos vegetais e teor de gordura incorporada, enquanto a vitamina C diminuiu em todos os casos. Em termos de escolha de óleo, observou-se menor degradação lipídica com azeite, em todos os processamentos. Em relação à acrilamida verificou-se maior formação na batata frita tradicional, seguida de micro-ondas com grill, sendo inferior no forno. A aceitabilidade sensorial foi menor nas batatas fritas no formo em comparação com batatas fritas tradicionais, ficando as processadas em micro-ondas com aceitabilidade intermédia. Assim, as batatas fritas no micro-ondas e no forno demonstraram benefícios nutritivos para os consumidores, pela menor incorporação de gordura e menor degradação desta, podendo uma correta otimização dos parâmetros de processamento em micro-ondas com grill originar alternativas com aceitação por parte dos consumidores.

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Irradiation as nutrient's preservation technique: comparative effects of gamma and electron beam in *Arenaria montana* L.

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Plants are widely recognized as a source of several bioactive compounds. Nevertheless, effective decontamination techniques are required to be used by the industry in order to guarantee safety issues. Irradiation is being progressively acknowledged as a feasible conservation methodology, in relation to its high decontamination effectiveness [1,2].

In this work, the effects of irradiation (gamma and electron beam) in nutritional and chemical profiles of *Arenaria montana* L. (mountain sandwort), a widely used medicinal species in the Caryophyllaceae family, native from the mountainous areas of Southwestern Europe, were evaluated.

The nutritional value was determined by official methodologies for food analysis; free sugars were analysed by HPLC-RI, fatty acids by GC-FID, organic acids by UFLC-PDA and tocopherols by HPLC-fluorescence.

The effects of gamma irradiation and electron beam in the nutritional parameters were similar, except in fat and protein contents. However, regarding the organic acids, while e-beam irradiation did not cause statistically significant changes in any case, gamma irradiation presented significant changes, with a clear tendency to be higher in the irradiated samples. The same occurred in tocopherols content, especially in samples irradiated with 10 kGy. In respect to fatty acids, it was clear that e-beam irradiated samples showed higher relative percentages of SFA and MUFA, while lower values of PUFA.

In general, the obtained results might be a good guidance to choose irradiation type or dose according to the need of maintaining a specific chemical or bioactive profile.

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Porphyridium cruentum microalgae as a source of sulfated polysaccharides with potential bioactivity

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Marine microalgae are unicellular photosynthetic microorganisms that have gained commercial interest since they are easily grown and contain bioactive compounds, including proteins, lipids, polysaccharides, and vitamins. Thus, microalgae are considered one of the most promising sources of new products for different applications, such as cosmetics, foods, and nutraceuticals [1]. *Porphyridium cruentum* is a marine microalga with a great interest due to the production of high quantity of extracellular sulfated polysaccharides, which have several biological properties, such as immunomodulating, anti-inflammatory, and antioxidant [2]. These properties have been associated to the existence of characteristic structural features, including the presence of sulfate esters [2,3]. As the polysaccharides content and composition may change according to the environmental conditions of growth, the aim of this study was to evaluate the polysaccharides produced by *P. cruentum* grown in different salinities, namely 18, 32, 50 g NaCl/L.

The extracellular media of the microalgae grown in 18 and 32 g NaCl/L showed higher content of polymeric material (116-154 mg/L) and, accordingly, also extracellular polysaccharides (60-70 %). The overall sugars composition of *P. cruentum* was similar in all samples, being the main sugars Xyl, Gal, uronic acids, and Glc. Also, the content of sulfate esters was identical in the three samples (11-15%, w/w). The analysis of the glycosidic substitution revealed the presence of (1→3) e (1→4)-Xyl, (1→3,4)-Gal, (1→2,3,4)-Gal, (1→3)Glc, and (1→3,6)-Glc, the typical linkages described for the exopolysaccharides from *P. cruentum* [3].

The scale-up of the *P. cruentum* production revealed a similar content and composition in sulfated polysaccharides. Then, this study showed the potentiality of *P. cruentum* as a source of these bioactive compounds, which is independent of the main variations of the medium salinity.

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Estudo do efeito da radiação ionizante na cinética de extração de elagitaninos de *Tuberaria lignosa* utilizando a metodologia de superfície de resposta

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A radiação ionizante tem sido utilizada como uma alternativa segura, eficaz e amiga do ambiente em relação aos agentes químicos vulgarmente utilizados para descontaminar alimentos e plantas medicinais [1,2]. De facto, os fumigantes químicos, como o brometo de metilo, encontram-se proibidos na União Europeia devido à potencial formação de resíduos tóxicos, enquanto os tratamentos térmicos podem levar à destruição de um grande número de compostos bioativos [3,4]. Além disso, os tratamentos com radiação ultravioleta possuem uma baixa capacidade de penetração, o que os torna incapazes de descontaminar grandes volumes de material vegetal [4]. A irradiação com raios gama é um tratamento não térmico que pode aumentar a extratabilidade de certos fitoquímicos [2] mas, se aplicada inadequadamente, pode causar a sua degradação. A alcária (*Tuberaria lignosa* (Sweet) Samp.) é uma planta medicinal altamente cotada no Nordeste de Portugal pelas suas propriedades medicinais. Esta planta é fonte de elagitaninos [1], polifenóis de elevado interesse farmacológico [5]. Estes compostos destacam-se pela sua capacidade antioxidante, anti-inflamatória, anti-tumoral, anti-aterosclerótica, hepatoprotetora, anti-bacteriana e anti-HIV [1,5]. No entanto, pouco se sabe acerca do impacto do tratamento por radiação ionizante sobre a integridade e extratabilidade destes compostos de valor comercial.

Este trabalho teve como objetivo investigar os efeitos do tratamento com radiação gama na cinética de extração e/ou degradação de derivados de elagitaninos em partes aéreas de *T. lignosa* utilizando a metodologia de superfície de resposta. O material vegetal foi submetido a doses de irradiação até 10 kGy numa câmara experimental de cobalto-60. Em seguida, o material vegetal não irradiado e irradiado foi submetido a diferentes tempos de extração sólido-liquido, de acordo com um desenho fatorial completo de Box-Behnken com três níveis, utilizando água em ebulição como solvente de extração. Os elagitaninos foram analisados num sistema de cromatografia líquida de alta eficiência (HPLC), ligado a um detetor de arranjo de díodos (DAD) e a um espetrómetro de massa (MS). Os compostos mais abundantes foram punicalina, isómeros de punicalagina e isómeros de galato de punicalagina. Em geral, o tratamento por irradiação e tempos de extração mais longos aumentaram a extratabilidade destes compostos bioativos. Os efeitos em cada composto individual serão discutidos nesta comunicação. Em conclusão, este estudo demonstrou a adequação do tratamento com radiação gama para melhorar a extratabilidade de derivados de elagitaninos de *T. lignosa*.

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Otimização do processo de extração de compostos corantes tendo como fonte alternativa *Gomphrena globosa* L.

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Os corantes são utilizados há muito pela indústria alimentar, sendo utilizados por diversas razões: compensar a perda de cor devido às condições de manufatura e armazenamento; realçar a sua cor natural; dar cor a um alimento sem cor; mas também permitir aos consumidores identificar produtos visualmente. Hoje em dia muitos dos consumidores preferem alimentos com aditivos naturais em detrimento dos sintéticos, que têm sido associados com alguns efeitos tóxicos.

Existem vários corantes naturais utilizados pela indústria alimentar, em particular carotenoides, antocianinas e betalaínas. As betalaínas contêm compostos que possuem cores que vão do vermelho-violeta (betacianinas) ao amarelo-laranja (betaxantinas) [1]. De entre as várias fontes de betalaínas, a fonte mais explorada é a beterraba, devido a sua elevada concentração nestes pigmentos [2]. No entanto, fontes alternativas menos exploradas, como as flores de *Gomphrena globosa* L., uma amaranthaceae, nativa da américa latina e comumente designada por perpétua roxa, possuindo na sua composição uma variedade de compostos com atividade biológica, sendo as betacianidinas um deles, tornando esta planta uma ótima candidata como alternativa na obtenção destes pigmentos [3].

Desta modo e de forma a obter um maior rendimento destes compostos, o objetivo deste estudo foi a otimização do sistema de extração (maceração, uma metodologia tradicional), levada a cabo com o auxílio de uma metodologia de resposta de superfície, na qual várias variáveis foram tidas em conta (tempo (t), temperatura (T), relação sólido-liquido (S/L) e relação água/etanol (Et)). As respostas de extração foram avaliadas tendo em conta o rendimento de extração (peso seco), monitorização das betacianinas por HPLC acoplado a diferentes detetores (DAD e MS) e a sua capacidade corante medida por espectroscopia UV/Vis e colorimetria (Spectra Magic Nx). Estes resultados permitiram estimar as condições ótimas de trabalho, maximizando o potencial corante, diminuindo custos, tempos de produção e aumentando a sua eficiência. Após análise dos resultados concluímos que os valores ótimos de extração para as diferentes variáveis são, t=165 min, T=25°C, Et=0 % e S/L=5 g/L obtendo assim uma concentração ótima de compostos corantes de betacianidinas de 45.1±1.3 mg/g de *Gomphrena globosa* seca com um rendimento de extração de 27.3±1.3 %.

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Avaliação de parâmetros histológicos, químicos e sensoriais da película da uva de mesa var. *Thompson Seedless*

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Devido à expansão do cultivo de uvas de mesa sem sementes, a variedade *Thompson Seedless* tornou-se na principal variedade, sem semente, cultivada no mundo [1]. Com este trabalho pretendeu-se avaliar o perfil sensorial da variedade de uva de mesa *Thompson Seedless*, bem como, através de técnicas histológicas e determinações biométricas, caracterizar a sua película. Após a análise dos cortes histológicos (Figura 1) e avaliações biométricas (Tabela1), foi possível concluir que os bagos apresentaram diferenças significativas entre si, relativamente à espessura total da película. Este resultado sugere que dentro do mesmo cacho, os bagos não atingem o mesmo grau de desenvolvimento em simultâneo, devido, provavelmente, a diferenças de exposição e temperatura.

Tabela 1 - Valores médios e desvios-padrões das avaliações da cutícula, epiderme e hipoderme, por bago, na variedade *Thompson Seedless*

	Cutícula(µm)	**Epiderme**(µm)	**Hipoderme** (µm)	**Esp. total** (µm)
Bago 1	3,06 ± 0,58 **a**	14,88 ± 2,05 **a**	29,19 ± 2,55 **a**	47,12 ± 5,01 **a, b**
Bago 2	3,85 ± 0,52 **a**	19,00 ± 3,03 **a**	37,86 ± 2,19 **b**	60,71 ±15,82 **b**
Bago 3	3,46 ± 0,37 **a**	14,68 ± 2,08 **a**	31,00 ± 3,99 **a, b**	49,13 ±6,37 **a, b**

Pelo teste de Tukey, médias com letras comuns não são significativamente diferentes ($p \leq 0,05$).

A variedade de uva estudada apresentou valores de acidez total de 9,30 (g/L ácido tartárico) e 16,2 ºBrix, um valor considerado ideal para consumo de uva de mesa. Sensorialmente, os descritores *tonalidade* e *uniformidade da cor*, *firmeza do bago*, *crocância* e *suculência* foram os mais pontuados (Figura 2). Uma uva mais crocante terá uma película mais resistente e elástica, logo, mais resistente ao transporte e armazenamento, chegando ao consumidor com melhor aspeto e palatibilidade.

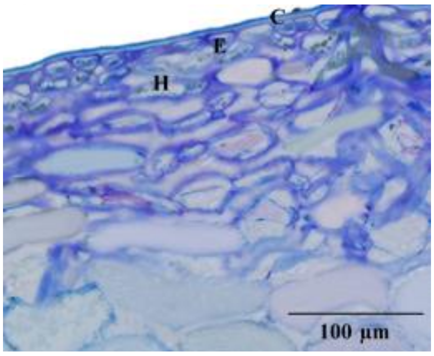

Fig. 1 – Secção transversal de um bago de uva: (C) cutícula, (E) epiderme, e (H) hipoderme

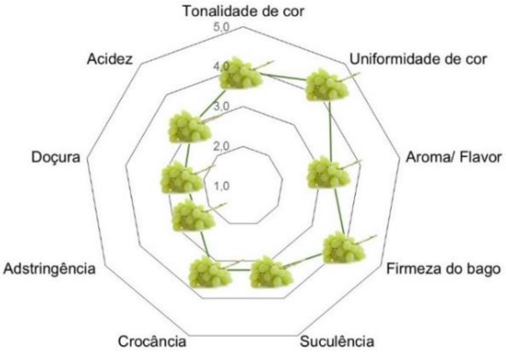

Fig. 2 - Perfil sensorial da uva *Thompson Seedless*

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Impact of recovered agroindustry by-products on dough and bread characteristics

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According to Food and Agriculture Organization of the United Nations, approximately one-third of the edible parts of food produced for human consumption gets lost or wasted globally. These by-products (BP) are a cost-effective source of valuable bioactive compounds, namely dietary fiber.

In order to obtain value-added breads, four types of agroindustry BP were tested: Orange peel; Pomegranate peel and interior membranes; Elderberry skin, pulp and seeds, and Spent yeast. Resulting extracts (Elderberry extract (EE); Orange extract (OE); Pomegranate extract (PE); and Yeast extract (YE)) were characterized for their content in dietary fiber fractions. Seven bread formulations with different extract replacements (g extract/100g flour mixture) were tested. For control bread (C) no extract was incorporated. Optimum water absorption and kneading time were determined for each bread formulation. Dough characteristics were evaluated through dynamic mechanical thermal analysis with oscillatory measurements, protein microstructure, and gaseous release and dough development. Bread characteristics were evaluated through bread volume, crumb texture and structure analyses.

Significant differences ($p<0.05$) were found between extracts for dietary fiber fractions. An increase in optimum water absorption and reduction development time was observed as the extracts replacement levels were higher, except for EE and OE. The onset and maximum of starch gelatinization, and highest viscous ratio were detected at higher temperatures in EE and at lower temperatures in OE, PE, and YE. Micrographs of C dough showed a uniformly distributed protein network. In OE, micrographs displayed more interconnected strains of protein than C, while in PE and YE there was less or no protein network formation and interconnection. EE micrographs showed a protein network more elongated, or less protein network formation and interconnection. Regarding dough characteristics, significant differences ($p<0.05$) were found in every extracts for maximum dough height (Hm) and time to reach the maximum dough height, and only in EE for final height of dough (h). Concerning gas properties, significant differences ($p<0.05$) were found for every parameter in EE, while for PE they were observed for maximum height of gaseous production and time to reach the maximum gas formation rate. No significant differences were detected with OE and YE. Bread volume and specific volume decreased at the highest concentrations in every extract. Considering cell area distribution, more than 60% of the cells had an area ≤ 0.1 mm^2. Significant differences were detected in every extracts for cells with area > 5 mm^2. All bread texture parameters considered had significant differences ($p<0.05$) in EE and PE. For both extracts, springiness, cohesiveness, and resilience decreased with higher concentrations, while adhesiveness and stringiness increased. Hardness and chewiness decreased in EE and increased in PE.

The impact of extract incorporation had on dough and bread varied with extract type and concentration. Nevertheless, it was possible to detect the negative effect of replacement at higher concentrations in every extract. Further studies should be conducted on breads with 4% replacement, in order to assess consumer acceptance and contribute to agroindustry BP valorization.

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Valorization of edible flowers as new food ingredients: nutritional and chemical characterization of petals and corresponding infusions

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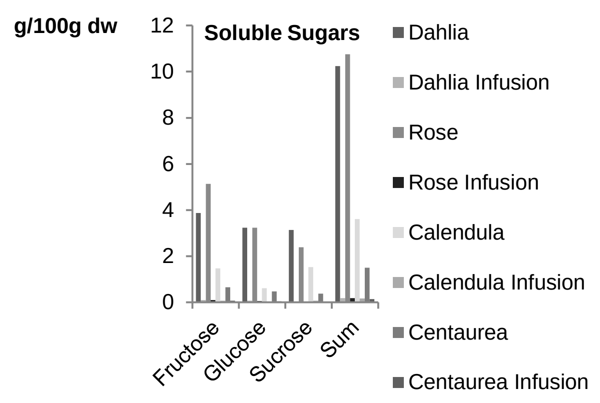
The consumption habits are becoming more diversified and directed towards more sustainable food options [1]. The range of plant species used for food is also becoming more varied, seeking to combine new ingredients with some potential health benefits that could improve the health of the consumers but also with a major importance in ecological sustainability [2].

In this study, the edible petals of Dahlia mignon (commercial seeds mixture), *Rosa damascena* 'Alexandria' and *R. gallica* 'Francesa' draft in *R. canina*, *Calendula officinalis* L. and *Centaurea cyanus* L. provided by the company RBR Foods (Portugal), were characterized in terms of macronutrients, energy value and individual profile of fatty acids and tocopherols (GC-FID and HPLC-fluorescence, respectively). The petals and respective infusions were further characterized regarding its composition in soluble sugars and organic acids (HPLC coupled to RI and DAD detectors, respectively).

Carbohydrates were the most abundant macronutrients, followed by protein and ash. The polyunsaturated fatty acids predominated over saturated fatty acids, mainly due to the presence of linoleic acid. *C. officinalis* petals had the highest concentration of tocopherols, especially α-tocopherol. Fructose, glucose and sucrose were identified in all petals and infusions (Fig. 1). Rose petals and the infusion of calendula gave the highest levels of organic acids, mainly due to the presence of malic acid and quinic acids, respectively (Fig. 2).

These results demonstrate the potential of edible flowers to be introduced into a regular diet.



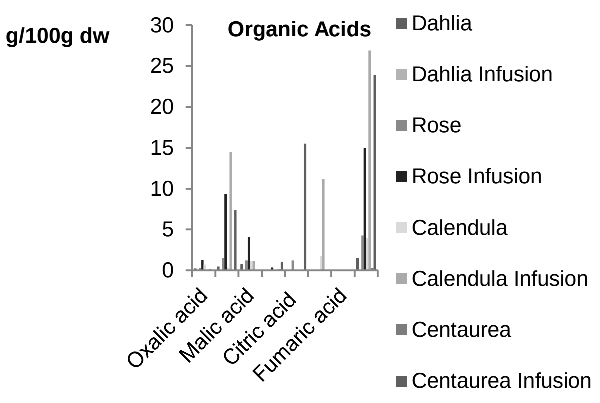


Fig 1. Soluble sugars composition of dried petals and their infusions

Fig 2. Organic acids composition in dried petals and corresponding infusions

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Effect of gibberellic acid and seaweed based biostimulant on the phenolic profile and antioxidant activity of sweet cherries

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Sweet cherry (*Prunus avium* L.) is one of the most popular temperate fruits in the world. Cherries are a very attractive fruit to consumers, for their taste and colour attributes, as well as for their nutritional value [1,2]. Additionally, the consumption of cherries has been associated with beneficial health effects [3]. Producers of sweet cherry continuously search for new and updated agronomical strategies to obtain high quality fruits, such as the pre-harvest application of growth regulators and fertilizers [4-7]. The aim of this study was to evaluate the effect of gibberellic acid (GA3) and a commercial seaweed based biostimulant (*Ascophyllum nodosum*) (SBB) in the biometric properties, chemical profile of polyphenols, ascorbic acid content and in the antioxidant activity of two sweet cherry cultivars (Skeena and Sweetheart) of *Prunus avium* L., grafted on Gisela 6.

The study was carried out in an orchard placed in Carrazedo de Montenegro, northeast of Portugal, during the year of 2015. The treatments consisted of GA3 (10 ppm) and SBB (0.05%) application of on three times during fruit development: four weeks after the full bloom (30 DAFB), seven weeks after the full bloom (49 DAFB) and 30 days before harvest. Phenolic compounds were determined spectrophotometrically and by HPLC-DAD/UV, ascorbic acid was determined by HPLC-DAD/UV and antioxidant activity was determined using DPPH (2,2-diphenyl-1-picrylhydrazyl) and CUPRAC (cupric reducing antioxidant capacity) methods. Biometric measurements and routine analysis were also performed.

GA3 promoted a significant increase ($p<0.001$) of the 'Skeena' cherry weight and size and a slight increase in soluble sugars content (SSC). GA3-treated cherries showed a large increase (24%) compared to control of total phenolics content ($p<0.001$) correlated with a significant increase ($p<0.001$) of catechin, cyanidin-3-*O*-rutinoside and cyanidin-3-*O*-glucoside contents, as well as, higher antioxidant activity of the fruits. The SBB promoted a significant ($p<0.001$) increase (17%) compared to control the ascorbic acid concentration in 'Skeena' cherries. For the Sweetheart cultivar, SSB-treated cherries had higher ($p<0.05$) carotenoids content (18% compared to control) and GA3-treated cherries increased fruit weight (16% compared to control) and total anthocyanins content (17% compared to control) without increasing the antioxidant activity.
To conclude, our study showed that the application of GA3 enhanced cherry quality through the increase of phenolics content and antioxidant activity with potential benefits in human health. Moreover, GA3 promoted the increase in weight and size of sweet cherries.

Acknowledgments
This work was supported by national funds by FCT - Portuguese Foundation for Science and Technology, under the project PEst-OE/AGR/UI4033/2014, the project “CherryCrackLess - Cherry cracking & mitigation strategies: towards their understanding using a functional metabolomic approach” - PTDC/AGR-PRO/7028/2014 and the project "GoldCherry – Enhancing the production of cherry quality" - PA 53626 financed by the European Agricultural Fund for Rural Development (EAFRD) and by national funds through Measure 4.1. Cooperation for Innovation PRODER program. Sofia Correia acknowledge grant from the Portuguese Foundation for Science and Technology (SFRH/BD/52541/2014). The authors thank to Rosa Carvalho, Sara Bernardo, Sílvia Afonso, Maria Cristina Morais and Ivo Oliveira for help in field work and laboratory analysis.

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Effect of heat processing on selenium content and antioxidant activity of several beans

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After cereal grains, legumes are the second most important food crop produced and consumed worldwide [1]. They represent an important component of the diet in several regions of the world, being especially important in developing countries [2]. Nutritionally, dry beans are an excellent source of protein, complex carbohydrates and dietary fiber, and low in fat, being recommended by health organizations as an essential food [3].

The present study aims to investigate the effects of different cooking conditions such as atmospheric (100˚C) or pressure boiling (121˚C), and draining of cooking water after thermal treatment on the phenolic compounds, antioxidant activity and selenium content.

In this work different varieties of *Phaseolus vulgaris* (kidney bean, pinto bean, black bean and borlotti bean), *Vigna unguiculata* (cowpea) and *Glycine max* (soybean) were used. For the antioxidant activity and phenolic content, extracts were made with methanol:water (80:20, v/v). The phenolic content and the antioxidant activity were determined by colorimetric assays. The selenium content was determined by the AOAC fluorometric method based on the digestion with nitric acid and hydrogen peroxide. Processing significantly increased the phenolic content and antioxidant activity in all extracts except in soybean. Draining of cooked beans significantly reduced the phenolic contents and antioxidant capacity in all beans, when compared to not-drained samples, with the exception of soybean. Furthermore, independently of the cooking temperature, the total phenolic content, antioxidant capacities and selenium content were greater in treatments where the cooking water was not discarded.

The crude phenolic extracts evaluated in the present study, obtained from raw and processed beans, as well as beans in general, exhibited potential health-benefiting properties by their antioxidant activities and high amount in selenium. The present study encourages a wider utilization of legumes in the human diet and the development of new food products using raw and processed legumes.

Acknowledgments
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Substituição de sorbato de potássio por extratos de funcho e camomila: comparação do desempenho em iogurtes

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Os consumidores estão cada vez mais atentos à informação disponibilizada nos rótulos dos alimentos, existindo uma tendência crescente de escolha de produtos mais saudáveis e com o mínimo de aditivos artificiais. A indústria alimentar recorre ao uso desses aditivos para melhorar a aparência e/ou propriedades específicas dos alimentos [1], no entanto, alguns autores têm identificado alguns efeitos adversos para a saúde do consumidor relacionados com a exposição excessiva a aditivos artificiais [2]. Para evitar esses problemas e, simultaneamente, atender às expetativas atuais dos consumidores, a indústria alimentar tem apostado na utilização de aditivos naturais, nomeadamente extratos vegetais, sobretudo na classe dos conservantes [3].

Este trabalho teve como objetivo comparar o desempenho de ingredientes naturais e aditivos artificiais em iogurtes. Como ingredientes naturais utilizaram-se extratos obtidos por decocção em água de *Foeniculum vulgare* Mill. (funcho) e *Matricaria recutita* L. (camomila); e como conservante artificial utilizou-se o sorbato de potássio (E202). Os extratos naturais revelaram possuir maioritariamente quercetin-3-*O*-glucósido e ácido cafeoil-2,7-anidro-3-desoxi-2-octulopiranosónico, respetivamente [4,5].

Foram preparados quatro grupos de amostras: iogurtes controlo (sem adição de qualquer ingrediente/aditivo), iogurtes com decocção de funcho, iogurtes com decocção de camomila e iogurtes com E202. As propriedades antioxidantes das amostras foram avaliadas através de dois ensaios *in vitro* (efeito captador de radicais livres e poder redutor) imediatamente após a incorporação e após 7 e 14 dias de armazenamento a 4ºC. Foi realizada também a avaliação do valor nutricional das amostras, bem como a cor e pH nas mesmas condições de armazenamento.

Os resultados demonstram que nem os extratos naturais nem o aditivo sintético causaram alterações significativas no pH ou no valor nutricional dos iogurtes quando comparados com as amostras controlo. No entanto, a presença dos extratos naturais conferiu propriedades antioxidantes aos iogurtes principalmente, no caso da adição do extrato de camomila.

Estes resultados permitem-nos concluir que os extratos aquosos de funcho e camomila ricos em compostos fenólicos podem representar uma alternativa aos conservantes sintéticos melhorando desta forma as propriedades funcionais dos iogurtes sem, no entanto, provocar alterações no perfil nutricional dos mesmos.

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Calcareous soil interactions of synthetically produced azotochelin and its application to amend iron deficient induced chlorosis in soybean (*Glycine max*)

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Amino polycarboxylic acids, e.g. ethylenediaminedi-(2-hydroxyphenylacetic) acid (EDDHA) or ethylenediamine tetraacetic acid (EDTA), are currently the main synthetic chelating agents used to tackle iron chlorosis. Although effective, these chelating compounds pose an environment risk due to heavy metal leaching from soils to groundwaters [1], especially when they are not readily biodegradable and persist in the environment [2]. Therefore, there is a demand for more environmental friendly alternatives. With this work, we tested synthetized azotochelin for its suitability to mend iron chlorosis in soybean. With this purpose, the interaction of Fe-azotochelin complexes with soils and with its components were studied, as well as the dissolution rates of iron minerals in soil and the chelate stability *versus* pH. Secondly, ^{57}Fe-azotochelin chelates were applied to the soil of chlorotic soybean plants in pots, and their growth and SPAD index evaluated. The iron isotope levels on plants (leaves, steam and roots) were measured after 7 and 21 days. Results have shown that azotochelin interacts slightly with soils and its main constituents, such as calcium carbonate, organic matter, montmorillonite-Ca and iron oxides. Iron oxide solubilization was also satisfactory with the highest dissolution rate reached at about 24h. The results of the Fe-chelate soybean application evidenced an increase of the SPAD index levels in compassion to the control plants, followed by a significant increase of Fe determined in leaves and roots. However, isotope deconvolution results suggest that most iron does not come from the supplied iron on the chelates but probably from iron oxides present in the soil, possibly dissolved by azotochelin (shuttle effect) [3]. These results show that azotochelin is a good alternative environmental friendly chelating agent for application in iron chlorosis mend in calcareous soils due to its stability and effectiveness.

Acknowledgments
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Phenolic composition of skins and seeds of six red grape *Vitis vinifera* varieties from the Douro region

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With the increasing interest in characterizing grape varieties in order to improve winemaking procedures, the aim of this study was to evaluate the phenolic composition of skins and seeds of Touriga Nacional (TN), Touriga Franca (TF), Tinta Roriz (Tempranillo, TR), Tinta Barroca (TB), Tinto Cão (TC) and Cabernet Sauvignon (CS) from the Douro region.

The analysis were made on hydroalcoholic solution 50% (H_2O:EtOH) obtained from a dry extract of skin and seeds of each grape variety. Total phenols, total anthocyanins and total tannins were evaluated through spectrophotometric analysis. The monomeric anthocyanin profile was determined using RP-HPLC analysis.

In skin hydroalcoholic extract, TC was the grape variety that showed the highest total phenolic and total anthocyanin content, making this grape variety one to be chosen when a deeper red colour is desired in the wine. In opposite, CS grape variety presented the lowest values, probably due to the adverse conditions where it is grown in Douro region [1].

In seed hydroalcoholic extract, approximately all of the grape varieties show the same value (~ 8 AU/g) for total phenolic content, except for TN grape variety that showed a lower value (~ 4 AU/g). Considering total tannin content, the highest values were obtained for the grape varieties TB, TN and TF and much lower values were determined for TC, TR and CS (Fig.1).

Results of HPLC analysis of monomeric anthocyanin content revealed that all grape varieties skins hydroalcoholic extract present high content in monomeric anthocyanins, being TF the grape variety with the highest content in almost all monomeric anthocyanins studied.

This result will permit winemakers to select the most suitable grape variety according to the type of wine desired.

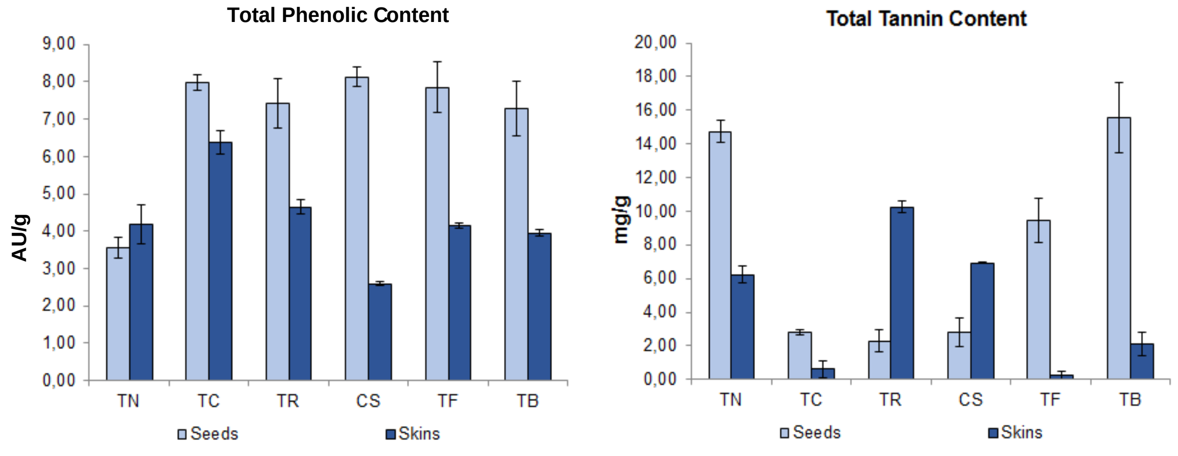

Fig.1. Total phenolics and total tannins content of grape seeds and skins

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Efeito da aplicação de taninos enológicos na evolução das características fenólicas e sensoriais de um vinho tinto

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Com o objetivo de potenciar e melhorar as características qualitativas dos vinhos, os produtores têm vindo a recorrer à utilização de vários produtos enológicos, como seja o uso de taninos enológicos comerciais, que se encontram definidos no Codex Enológico, através da Resolução Oeno 12/2002. Os taninos enológicos podem ser divididos em 2 grandes grupos: os taninos condensados, que são obtidos a partir das grainhas ou da pelicula da uva, e os taninos hidrolisáveis, extraídos a partir de diferentes madeiras [1]. A aplicação deste tipo de produtos enológicos, e sobretudo o seu impacto na evolução ao longo do tempo da composição fenólica e das características sensoriais em vinhos nacionais tem sido objeto de poucos estudos com um carácter aprofundado.

Assim, este trabalho teve como objetivo avaliar o efeito da adição de diferentes tipos de taninos enológicos comerciais disponíveis no mercado e de diferentes origens, na evolução das características fenólicas e sensoriais de um vinho tinto da região do Douro. Assim, seis diferentes taninos enológicos comerciais de diferente natureza (extraídos a partir da película da uva, da madeira de carvalho e da madeira de quebracho) foram adicionados numa dose de 15g/hL num vinho tinto (colheita 2015). A fim de atingir os objetivos propostos, foi avaliada a composição fenólica ao longo de 120 dias de estágio e as características sensoriais ao fim de 20 e 85 dias de estágio, por comparação dos diferentes vinhos com a testemunha (vinho sem adição de tanino).

Os resultados obtidos ao longo dos 120 dias objeto de análise, evidenciam que a aplicação de qualquer tipo de tanino no vinho, induziu a um maior incremento dos teores em pigmentos poliméricos, fenóis totais e flavonóides; e teores mais baixos de pigmentos totais e antocianinas totais e coradas em relação à testemunha. De entre todos os taninos aplicados, destacou-se de forma significativa a aplicação de um dos taninos elágicos (obtido a partir da madeira de carvalho) com o maior efeito no aumento dos teores em fenóis totais e fenóis flavonóides e responsável por uma menor perda de pigmentos totais. A intensidade de cor e a tonalidade evoluíram de forma semelhante em todos os vinhos, incluindo o vinho testemunha. Dos compostos fenólicos individuais detetados por HPLC, verificou-se que de todos os vinhos estudados, o vinho testemunha apresentou concentrações superiores em ácido cafeico e em antocianinas monoméricas glucosidicas (cianidina-3-monoglucósido, petunidina-3-monoglucósido, peonidina-3-monoglucósido e malvidina-3-monoglucósido), ao fim de 120 dias de estágio. Na análise sensorial apenas foram detetadas diferenças significativas ao fim de 85 dias de estágio para o descritor qualidade de aroma, apresentando o vinho em que foi aplicado um dos taninos elágicos uma maior pontuação.

Os resultados obtidos podem, pois contribuir para fornecer informação útil aos produtores de vinho, em particular na seleção dos taninos enológicos mais apropriados para melhorar a qualidade dos vinhos.

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Using lipid nanoparticles to bypass rumen digestion

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The ruminant digestive tract is composed of several organs that are exclusive to this class of animals. When considering feeding and nutrition of these animals, one of the main challenges is the rumen. The rumen is the largest portion of the ruminant stomachs and where extensive microbial fermentation occurs. The microbiota of the rumen ferments the feed, the protein fraction being degraded and the resulting products incorporated into their own microbial proteins. Rumen-protected products have been developed with the aim to bypass digestion in the rumen and increase the amount of nutrients that reach the small intestine and can be absorbed into the bloodstream. The majority of these products are meant to deliver specific amino acids (AAs) to the small intestine. However, these products have shown some limitations, since most of them only deliver small amounts of AAs into the intestine and do not promote their absorption into the bloodstream. In order to overcome these limitations, we propose a new approach that takes advantage of nanotechnology to bypass the microbial fermentation in the rumen, but also to increase the absorption of the nutrients into the bloodstream.

Considering that lipids, mainly saturated fatty acids, are able to pass through the rumen virtually untouched by the microbial digestion, they may be good candidates for building the intended nanoparticles (NPs). Nine different formulations were proposed and tested: six formulations that are composed of lipids that are solid at room temperature (solid lipid nanoparticles - SLNs) and three formulations composed by a mixture of lipids that are solid and lipids that are liquid at room temperature (nanostructured lipid carriers - NLCs). All nine formulations were assessed for their stability in rumen inoculum for 24h, at 39 ºC under slow stirring and with a nitrogen saturated atmosphere, to mimic the natural rumen conditions. Samples were collected at 0h and 24h of incubation to better evaluate if changes occurred in NPs and if they were due to the incubation in the rumen inoculum or other factors related to the inoculum itself. All of the samples were then separated by fractioned centrifugation and analyzed by dynamic light scattering (DLS) in terms of size and zeta potential. Transmission electron microscopy (TEM) was also used to assess if nanoparticles resisted the incubation and retained their physical properties, such as size and spherical morphology.

DLS results showed that only SLNs formulations composed of stearic acid and arachidic acid were able to resist digestion in the rumen inoculum, maintaining their size range of 300-500 nm after incubation and with a highly negative surface charge of around -35 mV. TEM photographs confirmed that both formulations were able to resist digestion and maintain both their size and morphology.

To conclude, this preliminary study showed that SLNs could be synthesized, with adequate physical properties, and with the ability to resist digestion in the rumen, retaining their size, zeta potential and spherical morphology. The proposed formulations are, therefore, promising candidates for future rumen-bypass applications in ruminant nutrition and may help to surpass the current limitations of the existing technologies and products.

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Antioxidant and chelating activities of fermentation broths containing fructooligossacharides

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Fructooligossacharides are present in plants and fruits at low concentrations and with varying individual relative proportions. So, for industrial application, fructooligossacharides extraction from natural sources may not be economically viable. Recently, several works have been published within this field of research usually aiming to establish the best experimental conditions to maximizing fructooligossacharides yield/synthesis [1-3]. However, although it is known that these compounds may have a great health impact, it is also reported that beneficial health effects may depend on the relative fructooligossacharides composition, seeming that nystose-rich diet is preferable compared to a kestose-rich preparation, exhibiting a higher anti-hydroxyl radical activity [4,5]. So, in this work it is reported the results regarding a screening study concerning the bioactivity activity of the fermentation broth extracts obtained using fungi with potential for producing fructooligossacharides. The potential use of five fungi (*i.e.*, *A. aculeatus, A. japonicus, A. opinicosulum, P. thoumii and P. cornyphipum*) was evaluated. Batch fermentation were carried out during 96 hours, at constant temperature (27 ºC) and agitation (100 rpm), being the initial sucrose concentration fixed at 30 g/L. Samples were taken at 24-h intervals and the radical scavenging activity as well as the iron binding ability of chelators, of the different broth extracts, were determined using the DPPH and ferrozine. The overall results obtained showed that although the extracts possessed relatively low bioactive activity; it was possible to set some preliminary insights that allowed selecting the most promissory(s) mold(s), which could enable achieving, in a near future, a final fructooligossacharides formulation with the greatest antioxidant capacity.

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Comparison between FTIR-ATR and NIR spectroscopy for *Lavandula* honey characterization

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Spectroscopic methods have been widely used in the quality assessment of different matrices, among which food products [1,2,3]. The advantage of these analytical techniques is related to the minimal or no sample preparation, quickness of the procedure and potential to run multiple tests with only one sample. However, different methodologies may be applied, emphasizing the importance of identifying the most accurate method and equipment.

The aim of this work was to compare the performance of Near-infrared spectroscopy (NIR) and Fourier Transform infrared spectroscopic method with Attenuated Total Reflectance (FTIR-ATR) for the multivariate characterization of honey's chemical composition. In the first approach, the analysed parameters were: protein content (%), ascertainedby the Kjeldahl method; and apparent sucrose content (%), evaluated according to the regulatory standards of International Honey Commission.

Partial least squares (PLS) regression was used to build the calibration model for these parameters, in comparison to the data obtained with the reference methods.

For the 150 *Lavandula* honey samples two different methodologies were tested: i) a calibration with cross validation followed by ii) a cross validation (70% of the samples) with a test set (remaining 30% of the samples).

The obtained models of suitable accuracy for protein content presented an r^2 ranging from 96.7% to 81.8% (RPD = 5.5 to 2.4) for FTIR-ATR and between 89.4% and 77.6% (RPD = 3.1 to 2.1) for NIR. Concerning sucrose content, r^2 was between 96.9% and 70.0% (RPD = 5.7 to 1.9) for FTIR-ATR, and between 88.5% and 64.4% (RPD = 3.0 to 1.9) for NIR. The root means square error of cross validation and prediction was lower using FTIR-ATR.

The precision achieved using these two parameters suggests that the infrared spectroscopy is a suitable technique for the characterization of honey samples. However, in general, FTIR-ATR appeared to be the most accurate method. Different models are in development for other chemical parameters comparing these two techniques.

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Efeito da adição de pólen na produção de hidromel

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Em Portugal, a apicultura é uma atividade dirigida essencialmente para a produção de mel de alta qualidade. No entanto, ocorrem perdas de mel significativas durante os processos de extracção, embalamento e lavagem dos recipientes. Assim, para valorizar a região e aumentar o rendimento dos apicultores é importante aproveitar uma fracção do mel desperdiçado, como por exemplo, para a produção de hidromel. O hidromel é uma bebida alcoólica tradicional, que contém entre 8 a 18% (v/v) de etanol, que resulta da fermentação do mel diluído realizada por leveduras. No entanto, quando esta bebida é produzida com mel claro observam-se paragens e amuos da fermentação, provavelmente devido à limitação em nutrientes deste tipo de mel [1]. A utilização de pólen como ativador da fermentação apresenta-se como uma aposta favorável, devido à sua composição em proteínas, vitaminas, minerais e lípidos [2].

Este trabalho teve como objectivo avaliar o efeito da adição de diferentes concentrações de pólen (10, 30 e 50 g/L) na produção de hidromel, nomeadamente no desempenho fermentativo e nas características do produto final.

Para a preparação do mosto foram utilizadas ceras de mel claro que foram lavadas de modo a atingir 23 ºBrix. O mel diluído foi suplementado com nutrientes comerciais e seguidamente, dividido para adicionar as diferentes concentrações de pólen. Paralelamente, foi preparado um mosto, sem adição de pólen, como controlo. Todos os mostos foram inoculados com a levedura enológica seca ativa *Saccharomyces cerevisiae* Lalvin QA23. As fermentações foram monitorizadas diariamente através da leitura da densidade óptica, determinação das unidades formadoras de colónias e quantificação dos açúcares redutores. No final das fermentações, a qualidade dos hidroméis foi avaliada através da determinação dos parâmetros enológicos pH, acidez volátil, acidez total, azoto assimilável, SO_2 total e teor alcoólico.

Na fermentação controlo observou-se uma paragem no consumo dos açúcares, ficando o hidromel com cerca de 100 g/L de açúcar residual. Por outro lado, a adição de pólen ao mosto, independentemente da sua concentração, estimulou a cinética de fermentação com o consumo completo dos açúcares. O hidromel produzido com concentrações de pólen de 30 e 50 g/L apresentou um teor alcoólico mais elevado. No entanto nestes hidroméis, também se verificou uma concentração mais elevada de azoto residual, sugerindo que a concentração de pólen adicionada poderá ter sido excessiva.

Resumindo, neste estudo verificou-se que o pólen, particularmente adicionado em concentrações baixas, pode ser um ativador apropriado para suprimir a limitação de nutrientes, existente na produção de hidromel a partir de mel claro. Apesar dos resultados serem bastante promissores, é importante avaliar a influência da adição de pólen no perfil aromático e nas propriedades sensoriais do hidromel.

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Caracterização nutricional e propriedades bioativas de *Geranium robertianum* L .: da planta à fração mais bioativa

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Geranium robertianum L., vulgarmente conhecida como Erva de São Roberto, é uma planta pertencente à família Geraniaceae utilizada em medicina popular no tratamento de uma variedade alargada de doenças [1]. Embora as propriedades terapêuticas tornem esta espécie muito apreciada, estudos sistemáticos da sua composição fitoquímica e bioatividade são ainda escassos.

No presente trabalho foram caracterizadas amostras silvestres de *G. robertianum* provenientes de Trás-os-Montes, Portugal, quanto à sua composição centesimal - proteínas, gorduras, hidratos de carbono e cinzas - bem como em açúcares livres, ácidos orgânicos, ácidos gordos e tocoferóis. A infusão e a decocção (formas comuns de consumo desta planta) e diferentes frações orgânicas, obtidas por extração sequencial, foram avaliadas e comparadas quanto à sua atividade antioxidante (capacidade de captação de radicais livres, poder redutor e inibição da peroxidação lipídica) e citotoxicidade em várias linhas celulares tumorais humanas (MCF-7, NCI-H460, HeLa e HepG2) e numa cultura de células primárias de fígado de porco (não tumorais). Foi ainda determinado, por HPLC-DAD-ESI/MS, o perfil de compostos fenólicos da fração mais bioativa.

G. robertianum demonstrou ser uma planta mais abundante em hidratos de carbono e proteínas e pobre em gordura, proporcionando açúcares, tocoferóis, ácidos orgânicos e ácidos gordos essenciais. A fração de acetona apresentou o maior teor de fenóis e flavonóides totais, bem como as maiores atividades antioxidante e citotóxica. Esta fração mostrou conter taninos hidrolisáveis como principais compostos fenólicos. Este trabalho, detalhado numa publicação recente dos autores [2], visa, juntamente com a presente comunicação, recuperar e valorizar a utilização tradicional desta planta.

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Estudo do perfil carbonílico do café recorrendo à microextração por difusão gasosa (GDME)

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O perfil aromático do café é um atributo essencial na avaliação organolética de um café. Esse perfil depende fundamentalmente das características do café verde, particularmente do grau de maturação, pré-processamento e proveniência geográfica do grão. Na literatura encontram-se descritos mais de 900 compostos voláteis provenientes do café torrado, presumindo-se, contudo, que apenas 5% destes compostos tem impacto efetivo sobre o aroma percecionado [1].

Neste trabalho, será objeto de estudo o perfil carbonílico do café devido à correlação positiva entre alguns compostos desta classe e o aroma desta bebida.

Para este efeito, será explorada a microextração por difusão gasosa (GDME) [2]. O GDME é uma técnica de tratamento de amostra desenvolvida recentemente que é capaz de extrair compostos voláteis de matrizes complexas. Esta técnica baseia-se num processo de difusão gasosa dos compostos voláteis, através de uma membrana, e na recolha desses compostos numa solução aceitadora. As principais vantagens desta técnica são a recolha dos analítos em estudo em soluções aceitadoras, onde podem ocorrer, em simultâneo, reações de derivatização e a simplicidade do procedimento experimental. A solução aceitadora é posteriormente analisada por HPLC/UV e por HPLC/MS.

Serão apresentados os resultados relativos ao perfil carbonílico dos cafés testados obtido pela técnica referida, em função do grau de torra e espécie de café.

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Recuperación de compuestos fenólicos de *Sargassum muticum* en resinas comerciales

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Las algas marinas representan una fuente abundante de productos naturales y productos químicos importantes. *Sargassum muticum* (Yendo) Fensholt es una especie invasora de la familia de Phaeophyta que se caracteriza por poseer diversos compuestos bioactivos, entre ellos, los compuestos fenólicos o florotaninos, que están despertando gran interés [1]. Los florotaninos, oligómeros cuya unidad monomérica es el floroglucinol (1,3,5-tridroxibeceno), se encuentran en algas pardas y se caracterizan por poseer actividad antioxidante, antitumoral, antiinflamatoria, anticancerígena, etc. [2,3].

En estudios recientes se ha confirmado la posibilidad de emplear resinas poliméricas no iónicas para recuperar estos compuestos de corrientes acuosas obtenidas por tratamiento de autohidrólisis o de extractos brutos, y para obtener fracciones purificadas [4]. En este trabajo se pretende comprobar si esta tecnología es adecuada para recuperar y concentrar compuestos fenólicos presentes en corrientes acuosas. Se considerarán la corriente resultante tras el descongelado de las muestras y la fracción escurrida del prensado. También se comparará la capacidad de eliminar agua de esta técnica con otras tecnologías de secado empleadas previamente.

La biomasa algal recogida manualmente en la Praia Mourisca, Pontevedra, en julio de 2015, se descongeló y se filtró para separar la corriente líquida (LD) de la fase sólida, que se prensó hasta 70 KN para obtener la corriente líquida (LP). Ambas corrientes se sometieron a precipitación con cloruro cálcico para precipitar el alginato, y el sobrenadante a extracción con acetato de etilo en relación 1:3 (v:v). Las fracciones solubles en acetato de etilo se concentraron en rotavapor y se caracterizaron para evaluar el contenido fenólico total, como equivalentes de ácido gálico (mg equivalentes ácido gálico (EAG)/g extracto) y floroglucinol (mg equivalentes floroglucinol (EF)/g extracto) y su actividad antiradicalaria (TEAC) [5]. Se obtuvieron valores de contenido fenólico del orden de 6 mg EAG/g y 5 mg EF/g. Los valores de TEAC de 9 mmol Trolox/100g extracto. El rendimiento fue de 2,4 g extracto/100 g alga.

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Volatile and polyphenolic characterization of Tinta Negra wines during Madeira wine ageing processes: *canteiro vs. estufagem*

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Madeira wine is a fortified wine with high international recognition and a huge impact on the Madeira Island economy. Tinta Negra is the grape variety responsible for 80% of the total Madeira wine production, being very versatile and can produce wines with different sweetness degree (from dry to sweet). This fortified wine can be submitted to both ageing processes: *canteiro* and *estufagem*. *Canteiro* consists on ageing the wines in wood casks usually for 3 years, in cellars lofts warmed at room temperature while the *estufagem* system consists on heating the wine at 45ºC for at least 3 months and then wines are submitted to wood casks, accelerating the wine maturation. Several studies were performed in order to study the volatile profile [1,2] as well as the polyphenolic content [3,4] in Madeira wines produced by Tinta Negra.

This study evaluates the volatile profile and the polyphenolic content from the initial wines until 2 years of ageing (*canteiro* and *estufagem* processes) of Madeira wines produced from Tinta Negra grape variety. Three stages were analyzed namely: 0 (initial wine), 120 (wine after *estufagem*) and 720 (2 years of ageing). The extraction using the Solid Phase Micro Extraction (SPME) followed by gas chromatography couple with the mass spectrometry (GC-MS) analysis was used to evaluate the volatile profile of these wines while the polyphenols analyses were performed on a high performance liquid chromatographer (HPLC) equipped with diode array detection (DAD).

The results indicated that the volatile fraction is composed mostly by esters and alcohols but also by others minor compounds such as fatty acids, carbonyls, furans and others compounds. Dry wines revealed higher amounts while sweet wines showed greater number of compounds during ageing. The results found for *canteiro* and *estufagem* processes were similar along ageing.

Regarding polyphenols, results indicate that hydroxybenzoics and hydroxycinnamates represent the major compounds when compared to stilbenes, flavonols and flavanols in these wines. Also, hydroxybenzoics tend to increase while hydroxycinnamates tend to decrease with ageing, both in *canteiro* and *estufagem*.

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Solubility studies of trans-cinnamic acid in mixed solvents

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Phenolic acids are a subclass of phenolic compounds with chemical and biological properties of interest in the pharmaceutical and food industries. The design of their extraction and separation processes includes the knowledge of their thermophysical properties as well as multicomponent solid-liquid equilibria data.

For these compounds, even essential solubility data in pure organic solvents and water are scarce. Therefore, in this work, trans-cinnamic acid was chosen as a model compound for which only a few solubility data in pure water and alcohols can be found in the literature [1-3].

The solubility of trans-cinnamic acid in the mixed solvents water + ethanol, and water + methanol was measured, at 298.15 K, using the isothermal shake-flask method and quantitative analysis either by gravimetry or UV spectrophotometry. As can be seen in Fig. 1, the solubility of the acid can significantly increase with the addition of the alcohol, with a more pronounced effect induced by ethanol. In a complementary approach and aiming to search for other methods to increase the aqueous solubility of trans-cinnamic acid, the phase-solubility diagram was determined for systems containing α-cyclodextrin.

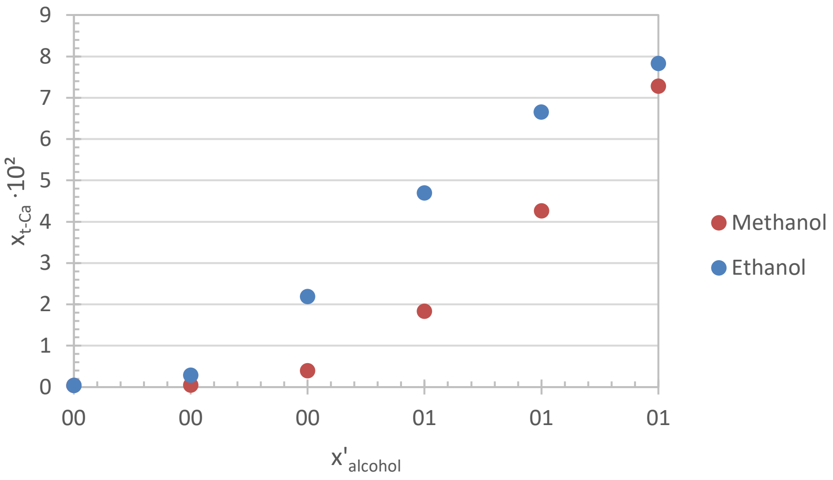

Fig.1. Solubility of trans-cinnamic acid in mole fraction ($x_{\text{t-Ca}}$) in mixtures of alcohol + water at 289.15 K versus the mole fraction of alcohol in solute-free basis

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Caracterização química de clones Verdelho usados na produção de vinho DOP “Madeira”

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O Verdelho é uma casta *Vitis vinifera* L. recomendada para a produção de vinho com dominação de origem protegida (DOP) “Madeira”. Produz cachos pequenos com bagos obovoides, médios e com película espessa. Por ser uma casta que apresenta índices de produção baixos é importante estudar os clones e o seu comportamento vitícola [1]. Os primeiros estudos de seleção clonal em Portugal datam do fim dos anos 70, o que veio permitir um avanço na qualidade dos vinhedos portugueses. Este tipo de seleção tem como objetivo permitir a escolha de plantas mais adaptadas ao clima a que estão sujeitas, de plantas com produções de melhor qualidade e mais resistentes a agentes bióticos [2]. A videira é uma cultivar que desde a sua plantação necessita de um bom par de anos para vir a ter uma produção consistente e de qualidade, pelo que a seleção errada do tipo de planta tem um custo dispendioso [3].

Este estudo teve como objetivo preliminar comparar 5 clones diferentes de Verdelho num campo experimental do Instituto do Vinho, do Bordado e Artesanato da Madeira (IVBAM), situado no Estreito da Calheta, de forma a apurar que clones produzem uvas de melhor qualidade para a produção de vinho DOP “Madeira”. Os clones analisados foram o M1/5, o M2/2, o M2/3, M2/4 e M2/5. As respetivas uvas foram analisadas em termos de açúcares residuais e ácidos orgânicos por cromatografia liquida de alta performance (HPLC) e de composição volátil por cromatografia gasosa acoplada à espectrometria de massa, após extração por micro-extração em fase sólida (SPME).

Observou-se que os clones M1/5 e M2/4 apresentavam níveis de açúcares residuais de 15,6%, mais elevados relativamente aos outros clones, em média com concentrações de 53,7 g/L em frutose e 61,6 g/L em glucose. Em termos do total de ácidos orgânicos, foram os clones M1/5, M2/3 e M2/4 que apresentaram as concentrações mais elevadas, entre 5,6 a 6,4 g/L. Em termos de composição volátil, o perfil do clone M2/3 foi o que apresentou maior abundância, sobretudo nos seguintes compostos: 2-hexanal; 2-hexanol; 2-hexen-1-ol e linalool.

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Molecular level insights on the interaction between a celiac disease peptide and polyphenols by ^{1}H-NMR spectroscopy

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Polyphenols are a group of plant secondary metabolites with several biologically significant functions [1]. Among the high diversity of polyphenols, tannins have been described as the most reactive towards proline-rich proteins, which are structurally similar to gluten peptides responsible for the onset of Celiac Disease (CD), a prevalent genetic autoimmune disorder were the ingestion of gluten proteins leads to damage of the small intestine. As these polyphenolic compounds present low intestinal absorption and suffer reduced metabolism in the human digestive system, they remain in the small intestine for extended periods of time, a feature that should allow their interaction with celiac reactive peptides through essentially hydrophobic and hydrogen bonding [2-3]. To date, several poorly digested proline and glutamine-rich peptides from disease-associated grains have been identified. Some of them stand out because of their immunoreactivity while others appear to be essentially cytotoxic [4].

This work intended to bring insights into the interaction between some common food tannins with a previously described CD immunodominant 32-mer peptide [5]. Peptide assignment and characterization of peptide binding was assessed by means of both homonuclear 1D and two-dimensional (2D) ^{1}H-NMR experiments. NMR data was recorded on a Bruker Avance III 600 HD spectrometer equipped with a 5 mm CryoProbe Prodigy. All experiments were run at a temperature of 300 K and pH 7.4.

While TOCSY assays allowed to characterize the peptide-ligand binding by following the ^{1}H chemical shifts of specific residues in the 32-mer peptide, NOESY experiments were performed in order to identify changes in nuclear Overhauser effects (NOEs) when food phenolics bond to the 32-mer peptide. The dissociation constants between the 32-mer peptide and three different phenolic ligands namely procyanidin dimer B3, procyanidin dimer B6 and procyanidin trimer C2 were determined through Saturation-Transfer Difference (STD) NMR. Accordingly, the procyanidin trimer C2 had a higher affinity towards the 32-mer peptide as a result of a higher number of aromatic rings and hydroxyl groups available for hydrophobic and hydrogen bonding while the position of the inter-flavanic bond has no apparent influence on complex formation ($4\alpha\rightarrow8$ of procyanidin B3 vs $4\alpha\rightarrow6$ of procyanidin B6). Additionally, the differences in the STD amplification factor for the different procyanidin B3 hydrogens were used to map the ligand structural moieties that are in close proximity with the 32-mer peptide.

Overall, our experiment findings provide molecular insights on the binding process between a CD bioactive peptide and plant polyphenols, highlighting the potential importance of natural phenolic compounds in a nutritional context to prevent CD.

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Glucosinolate metabolism and functionality: responses to elicitor's treatment

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Plants have developed diferente strategies against biotic and abiotic stressors. One of them is the accumulation of defense compounds. The induction of such compounds is mediated by signaling molecules, such as jasmonic acid (JA), ethylene, amino-acids (including tryptophan (TF)), salicylic acid (SA) [1-3] and several others, which acts by activation of corresponding transduction pathways. One class of such defense compounds, largely present in Brassicaceae plant family is the class of glucosinolates (GLS) [3]. GLS are β-D-thioglucoside-N-hydroxysulfates linked with a variable side chain derived from different amino acid precursors [4], and most of the knowledge about the effect of signaling molecules on glucosinolates biosynthesis is known from studies with Arabidopsis thaliana as plant model [4]. Less studies have been conducted with other species, particularly *Brassica rapa*. Moreover, it is often reported that hydrolysis products of indole glucosinolates are bioactive compounds that may act as preventive or poison against insects or pathogens [5, 6].Thus, plants with indole GLS could be very useful to control pests in a process known as biofumigation [7]. In this regard, plants with enhanced GLS levels are looked for their ability to produce particular hydrolysis compounds of indole GLS.

In this context, we set a study in which the interaction of jasmonic acid (JA), tryptophan (TF) and salicylic acid (SA) in regulation of glucosinolates accumulation in Brassica rapa is evaluated. The induction of indolic and aliphatic glucosinolates after treatment JA, TF and SA was evaluated. The treatments with signaling molecules were performed on seedlings Brassica rapa to determine differences in glucosinolate accumulation. Both profile and content of glucosinolate levels and indole breakdown derivative compounds were assessed using HPLC-DAD/UV-Vis, with special focus on induction of indole glucosinolates and indole isothiocyanates.

The results indicate a variation of both profile and content of indole compounds, suggesting a variation in their biosynthetic pathway. The increment of indole compounds with treatments of JA and TF suggest an interference accompanied by an increment of the gene expression involved in the indole glucosinolate biosynthetic pathway. The eliciting effects of signaling molecules on specific biosynthetic pathways might be used as a tool to develop Brassica species with desired GLS profiles and levels.

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Pesquisa de histamina em patês e conservas de peixe

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A intoxicação por histamina nos peixes é também designada por intoxicação escromboide [1], termo que deriva da família Scrombidae, que inclui várias espécies de peixes, designadamente atum, cavala e agulhão (espécies que têm, em comum, um elevado nível de histidina livre nos tecidos musculares [2]. As más condições de conservação após a captura do peixe (e.g. temperatura) permitem a metabolização bacteriana de histidina em histamina [1,3].

O objetivo deste trabalho foi avaliar o risco do consumo de potenciais produtos alimentares à base de patês e conservas de peixe, com possível contaminação por histamina.

A amostragem (40 amostras) foi realizada durante o mês de Fevereiro de 2015, em várias superfícies comerciais, de forma a garantir uma maior representatividade dos produtos disponíveis no mercado. A informação recolhida foi obtida através dos respetivos rótulos da embalagem. Todas as amostras estavam 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 conservas de peixe 2,5mg/kg e patês 100mg/kg).

No presente estudo, a histamina não foi detetada em nenhuma das amostras analisadas. Considera-se que um peixe de boa qualidade apresenta menos de 10mg/kg de histamina, sendo que entre os 10 e 30mg/kg o peixe já apresenta uma deterioração significativa e acima dos 50mg/kg uma evidente decomposição.

A utilização de peixe de má qualidade bem como o maneio incorreto do mesmo são as principais causas da elevada concentração de histamina em conservas de peixe impróprias para consumo [4].

Os resultados obtidos no presente estudo diferem dos reportados em estudos anteriores [3, 4, 5], nos quais foram detetados valores até 383,41 mg/kg.

Os presentes resultados indicam que a produção das conservas e patés analisados é segura, no que diz respeito à prevenção da contaminação por histamina.

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Qual a quantidade de aspártamo em bebidas comercializadas?

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O aspártamo, um dos edulcorantes mais utilizados a nível mundial, incluindo Portugal [1], é permitido, na União Europeia, desde a década de oitenta, sendo o valor Máximo Permitido por Lei (MPL), em bebidas, de 600mg/L [2], estabelecido para que a ingestão diária não ultrapasse a Ingestão Diária Admitida (ADI) [3].

Em fevereiro de 2016, foram adquiridas 75 amostras de bebidas em superfícies comerciais de Coimbra para determinação da ocorrência de aspártamo. Toda a informação recolhida sobre o produto foi obtida a partir do rótulo. A determinação analítica foi efetuada por cromatografia líquida de elevada eficiência associada a um detetor V/VIS, de acordo com metodologia previamente descrita [3], após revalidação.

Foi detetado aspártamo em cinquenta e seis (74,67%) amostras analisadas, com concentrações entre 23,70 e 365,32mg/mL (média 97,79mg/mL) (Tabela 1). Nenhuma das amostras apresentou concentrações superiores ao MPL. Em sete amostras não foi detetado aspártamo, apesar da indicação da sua presença no respetivo rótulo. A ocorrência mais elevada foi observada em bebidas aromatizadas. Apesar de a concentração mais elevada de aspártamo ter sido encontrada num refrigerante gaseificado, este grupo apresentou a menor média de concentração. Os néctares apresentaram a média das concentrações mais elevada. Apesar das bebidas energéticas e solúveis apresentarem uma média superior às restantes, o baixo número de amostras comprometeu a sua representatividade. Em comparação com um estudo anterior [3], realizado em Portugal, verificou-se uma diminuição da concentração máxima detetada (568,3 vs. 365,32mg/L). A média total também apresentou um decréscimo de aproximadamente um terço (154,8mg/L). Num estudo similar, em Espanha, Lorenzo e col. [4] determinaram uma ocorrência de 26% e uma concentração média de 67,5mg/L (21-563mg/L), e portanto inferiores ao presente estudo.

Tabela 1. Descrição dos resultados de ocorrência e níveis de aspártamo nas amostras analisadas

Amostra	Ocorrência (%)	Média (mg/L)	[Mín; Máx] (mg/L)
Refrigerantes gaseificados	22/31 (70,96%)	58,07	[23,7; 365,32]
Refrigerantes não gaseificados	13/20 (65,00%)	75,18	[26,55; 137,64]
Bebidas energéticas	2/2 (100%)	200,08	[181,19; 218,98]
Bebidas de água aromatizada	6/6 (100%)	68,45	[57,66; 166,13]
Solúveis	3/5 (60,00%)	172,76	[149,52; 185,32]
Néctar	10/11 (90,91%)	120,40	[26,20; 191,08]

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Composição química e propriedades bioativas de suplementos alimentares à base de cardo mariano

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O cardo mariano é uma planta medicinal nativa da bacia do Mediterrâneo pertencente à família das Asteraceae. É amplamente reconhecido pelas suas propriedades terapêuticas muitas vezes associadas aos princípios ativos presentes nas suas sementes [1]. Neste trabalho, avaliou-se o valor nutricional do cardo mariano bem como a sua composição em ácidos orgânicos, açucares, tocoferóis e ácidos gordos. Estudou-se ainda a bioatividade de três formulações baseadas nesta planta (infusões, comprimidos e xaropes), nomeadamente as atividades antioxidante, citotóxica e antimicrobiana. Uma vez que as suas propriedades terapêuticas são muitas vezes atribuídas à sua composição fenólica, analisou-se também o perfil em compostos fenólicos das três formulações estudadas [2].

Nas amostras de planta seca analisadas, os hidratos de carbono (87,2±0,3 g/100 g) foram o macronutriente maioritário, seguido pelas cinzas (6,9±0,3 g/100 g), proteínas (4,44±0,07 g/100 g) e lípidos (1,46±0,01 g/100 g). A frutose (2,16±0,04 g/100 g) foi o açúcar detetado em maior concentração, tendo sido também encontradas a glucose (0,97±0,07 g/100 g) e a sacarose (0,47±0,08 g/100 g). Quanto aos ácidos orgânicos, foram detetados os ácidos químico (2,8±0,2 g/100 g), oxálico (1,39±0,05 g/100 g), málico (0,96±0,05 g/100 g), cítrico (0,24±0,02 g/100 g), xiquímico e fumárico, estes últimos em quantidades vestígiais. Foi observada uma prevalência de ácidos gordos polinsaturados (45±1%), com a contribuição significativa do ácido linoleico (42±1%), seguidos pelos ácidos gordos saturados (35±1%) e monoinsaturados (19,70±0,01%). Relativamente aos tocoferóis, a amostra revelou duas isoformas: o γ-tocoferol (0,88±0,01 mg/100 g) e o α-tocoferol (0,42±0,01 mg/100 g).

O xarope e a infusão de cardo mariano demonstraram a melhor atividade antioxidante, com o xarope a revelar valores de EC_{50} ligeiramente inferiores aos da infusão (0,018±0,02 a 0,32±0,01 mg/mL para o xarope e 0,36±0,08 a 2,5±0,2 mg/mL para a infusão). O xarope foi ainda a única formulação capaz de inibir o crescimento de uma linha de células tumorais humanas HepG2 (carcinoma hepatocelular; GI_{50} = 0,28±0,02 mg/mL), não revelando toxicidade em culturas primárias de células de fígado de porco, PLP2. No que respeita à atividade antimicrobiana em isolados clínicos com elevados perfis de resistência, o xarope foi uma vez mais a formulação a revelar os melhores resultados, inibindo o crescimento de *Escherichia coli*, *E. coli* produtora de β-lactamases de espetro estendido (ESBL), *Staphylococcus aureus* resistente à meticilina (MRSA) e *Pseudomonas aeruginosa* (MICs de 0,2 a 1,3 mg/mL). A infusão revelou capacidade de inibir o crescimento destas mesmas estirpes ainda que em concentrações mais elevadas (MICs de 31,3 a 500 mg/mL), enquanto os comprimidos apenas inibiram o crescimento de *E. coli* ESBL (15 mg/mL). Quanto ao perfil fenólico, os compostos maioritários foram: apigenina-7-*O*- glucorónido e luteolina-7-*O*-glucorónido (3,1±0,1 e 1,17±0,09 mg/g) na infusão, silibinina hidroxilada e taxifolina (1,565±0,007 e 0,284±0,007 mg/g) nos comprimidos, e isoramnetina-*O*-desoxi-hexósido-*O*-hexósido e isoramnetina-3-*O*-rutinósido (7,26±0,04 e 5,75±0,04 mg/g) no xarope. De um modo geral, o cardo mariano revelou ser uma boa fonte de compostos fenólicos, apresentando diversas formulações com propriedades bioativas.

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Estudo de aldeídos e cetonas como marcadores voláteis para a avaliação da fermentação ruminal

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Tendo em vista o aumento da população mundial com o consequente aumento da procura de produtos de origem animal e as baixas perspetivas de expansão da área agrícola arável, é necessário melhorar a eficiência da produção animal. Tendo a alimentação um impacto económico significativo na produção de leite ou carne de animais ruminantes, é essencial maximizar a eficiência de conversão alimentar (quantidade de produto produzido por kg de matéria seca ingerida). Nestes animais, o rúmen tem um papel crucial no processo digestivo. Os produtos finais da fermentação no rúmen têm diferentes funções no metabolismo dos animais e, consequentemente, no perfil nutricional dos produtos obtidos.

Durante a fermentação ruminal são formados diversos compostos voláteis cuja natureza química está diretamente relacionada com a composição dos alimentos ingeridos. Esses compostos voláteis podem servir para avaliar a eficiência da conversão dos alimentos e diagnosticar problemas digestivos e metabólicos através da análise de conteúdo ruminal, fezes, urina e leite. A fermentação ruminal é habitualmente avaliada pela medição do gás produzido no rúmen, ou através da determinação de marcadores voláteis característicos da degradação de hidratos de carbono e proteínas, tais como os ácidos gordos voláteis, sulfureto de hidrogénio e amoníaco [1-2]. No entanto, existem ainda outros marcadores voláteis (sulfureto de metilo, dissulfureto de metilo, acetaldeído) [3] da decomposição dos alimentos no rúmen, mas cuja determinação é pouco utilizada para a avaliação nutricional da dieta.

Com este trabalho pretende-se estudar aldeídos e cetonas voláteis resultantes da fermentação ruminal com vista à identificação de novos marcadores voláteis para a avaliação da eficiência da digestão dos alimentos em ruminantes. Foram analisadas amostras de fluido ruminal recolhidas de vacas leiteiras fistuladas no rúmen e alimentadas com dietas de composição conhecida. Os extratos das amostras em estudo foram obtidos por microextração por difusão gasosa (GDME, *gas-diffusion microextraction*) [4] e analisados por cromatografia líquida de alta eficiência com deteção espetrofotométrica e por espetrometria de massa (HPLC-UV-MS/MS) para identificação dos compostos.

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Identificação de aminas biogénicas em fluido ruminal de vacas alimentadas com diferentes dietas

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No tubo digestivo dos animais ruminantes, os alimentos são extensamente fermentados no rúmen pela população microbiana produzindo maioritariamente ácidos gordos voláteis, metano, dióxido de carbono e amoníaco. Existem, ainda, outros compostos formados em menores quantidades, tais como o sulfureto de metilo, aminas, álcoois, aldeídos e cetonas. As aminas biogénicas resultam maioritariamente da descarboxilação dos aminoácidos no rúmen [1] e podem constituir um bom indicador da degradação proteica dos alimentos nestes animais. Além disso, a influência destes compostos na saúde dos ruminantes tem vindo a motivar o seu estudo [2].

Com este trabalho pretendeu-se estudar a presença de aminas biogénicas em fluido ruminal e relacionar a sua composição com a dieta alimentar. As amostras em estudo provenientes de vacas fistuladas no rúmen e alimentadas com diferentes dietas (feno-silagem e palha) foram sujeitas a um novo procedimento de extração baseado em difusão gasosa desenvolvido para este trabalho. As aminas biogénicas volatilizadas diretamente a partir da amostra são retidas numa coluna de extração em fase sólida (SPE). Posteriormente, as aminas são derivatizadas na coluna de SPE fazendo passar uma solução de *o*-ftalaldeído (OPA). De seguida, procede-se à eluição dos derivados com um solvente orgânico para análise por cromatografia líquida de alta eficiência com deteção fluorimétrica (HPLC-FLD).

A metodologia de preparação da amostra foi otimizada através do estudo de diversos parâmetros da extração e da derivatização, tais como tempo e temperatura de extração, pH e concentração de OPA. A metodologia otimizada foi aplicada à análise de amostras de fluido ruminal. As principais aminas detetadas nas amostras analisadas foram a metilamina, etilamina, tiramina e *iso*-pentilamina. No conteúdo ruminal do animal alimentado com feno-silagem verificou-se um maior teor destas aminas relativamente ao de palha. Foram também detetados outros compostos nos extratos obtidos, que serão identificados recorrendo à espetrometria de massa.

Agradecimentos
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Phenolic extraction from almond hulls: effect of time, temperature and ultrasound

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Almond represents one of the most important crops worldwide, concerning nut trees, whilst its production generates huge amounts of by-products, including hulls, shells and skins. The edible part, kernel, is usually consumed fresh or processed, while the by-products are manly discarded. The greatest amount of residues, in almond production, corresponds to the hulls of this fruit, which production is estimated to exceed 6 million tons annually, being usually used as livestock feed [1].

However, it has already been reported that almond hulls contain phenolic compounds with beneficial biological activities [2, 3] that can be used as natural antioxidants replacing the synthetic ones. So far, concerning their recovery, there is no optimal extraction processes available for all the matrices, while a plethora of distinct factors can influence the efficiency of the extraction of phytochemicals. Thus, the development of reliable and accurate extraction methods, concerning these compounds, constitutes an important step for a proper valorization of these agro-food by-products.

Therefore, the aim of this study was to evaluate the optimal extraction conditions for the recovery of polyphenolic contents, and simultaneously the antioxidant capacity of these almond hull extracts. Different extracting conditions (ultrasound during 10 min, 20 min and 30 min; shaking during 30 min, 60 min and 120 min, and temperatures of 30°C, 50°C and 70°C) were assessed, in which respects to phenolic composition and antioxidant radical scavenging capacity, of the corresponding almond hull extracts obtained. The solvent used was food grade ethanol, in order to obtain extracts suitable to be used by the food and pharma industries. The phenolic composition was assessed by the Folin-Ciocalteu method, for total phenols; and complexation with sodium molybdate and aluminium chloride for *ortho*-diphenols and flavonoids, respectively. The antioxidant capacity was determined resorting to two different radical scavenging assays (ABTS and DPPH).

The optimal values, concerning all the assays performed, were obtained with resort to the extraction method of ultrasound, with the time of 30 minutes corresponding to the highest content of phenolics, and the highest antioxidant activity.

The results retrieved from these extraction methods, have supported the potential application of this agro-food waste as a source of bioactive compounds to be applied in the food industry. However, further extraction optimization procedures should be assessed, accounting with other processes and ranges (such as % and pH of solvent).

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Raw material influence in mead production

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Honey can be fermented to produce different types of mead given their sugar concentration [1]. Mead is a beverage produced by the alcoholic fermentation of diluted honey. This beverage present an alcoholic strength ranging between 8 – 18 % volumes [2].

The aim of this work is characterize the quality of honey mead with different kinds of raw-material: *Lavandula* honey; *Castanea* honey and a mixture of waxes and *Castanea* honey resulting from the bee-keeper uncaps process.

To produce the honey must the different raw materials was diluted with natural spring-water (37 g of honey/100 mL of water) and mixed to homogeneity. The honey must was inoculated with a commercial wine yeast *Saccharomyces cerevisiae* QA 23 at a concentration of 0,3 g/hL and incubated at 25 0C. Throughout the fermentation process biomass concentrations and reducing sugar of the must were regularly measured. At the end of fermentations the meads were treated with bentonite (100 g/hL). In the meads produced, °Brix, pH, total acidity and assailable nitrogen concentration were evaluated.

It was observed that the yeast grow is more efficient in the *Castanea* honey than in the other samples. Given the results showed in Table 1 it is possible conclude that the meads produced with different raw material are similar and the differences could be attribute to the differences of honey, with different chemical composition. According to the obtained results it can be concluded that it is possible produce mead also with a mixture of waxes and honey resulting from the bee-keeper uncaps process with an important economical benefice.

Table 1. Physicochemical characteristics of honey-meads obtained with different raw materials

Analytical parameters	*Castanea* honey	*Lavandula* honey	*Castanea* honey with waxes
pH	3.43	3.31	3.47
Reducing sugars (g/L)	35.25	23.54	24.09
Titrable acidity (g/L tartaric acid)	3.75	3.64	4.35
Volatile acidity (g/L acetic acid)	0.57	0.69	0.75
Final nitrogen (mg/L YAN)	38.5	87.5	42.0
Total SO_2 (mg/L)	32.0	30.7	30.7
Alcohol (%)	10.5	12.7	12

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Direct analysis of vitamin A, vitamin E, carotenoids, chlorophylls and free sterols in animal and vegetable fats by NP-HPLC-DAD/FD

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Alongside their many functional roles in human health, vitamin A and E, carotenoids, chlorophylls and sterols are also essential components of plants growth, development and metabolism. Therefore, they can be found in a large number of foods as nuts, seeds, fruits, vegetables, dairy products, but mostly in fats and oils. Some of these lipophilic substances are usually present in such a unique combination that even the most subtle adulteration can be detected, thus their estimation is often a good tool to assess authenticity, especially in vegetable oils.

The method presented herein was developed and validated for the direct and simultaneous analysis of vitamin A, vitamin E, carotenoids, chlorophylls and derivatives as well as of total free sterols (20 analytes) in animal (Azores butter and fish oil-based food supplement) and vegetable fats (extra-virgin olive oil and margarine).

The method is based on direct sample weight (ca. 75mg), internal standards addition, dissolution in *n*-hexane, followed by dehydration with anhydrous sodium sulfate, and a single centrifugation step, after which the supernatant was analyzed immediately. The chromatographic separation was achieved with a normal-phase column (Luna Silica; 100mm x 3mm, 3µm; Phenomenex) eluted with a total run gradient time of 28.5min. of 3% to 25% (v/v) of 1,4-dioxane in n-hexane with a flow rate of 1mL/min, at 22ºC. Quantification was based on either UV/Vis or fluorescence signal response, using the internal/external standard method.

Validation of the proposed chromatographic method included linearity, specificity, limits of detection (LOD) and quantification (LOQ), precision and accuracy. High correlation coefficients (R^2 >0.998) and high chromatographic resolution (R_s > 1.5) were achieved, thus confirming method reliability for a wide working range. Instrumental LODs and LOQs ranged from 0.36ng/mL to 1.57µg/mL and from 1.20ng/mL to 5.22µg/mL, respectively. Moreover, intra-day and inter-day precisions below 5% together with an overall 89 – 116% recovery range supported this method's precision and accuracy for all tested compounds. The method was applied to several commercial samples.

In conclusion, this study provided a new cost- and time-efficient method for the accurate analysis of twenty micronutrients in animal and vegetable fats. By not requiring saponification or extraction, the proposed method is not only faster but also more environmental-friendly than existing procedures.

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Estudo da composição química de seis genótipos de *Portulaca oleracea* L.

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Portulaca oleracea L. (vulgarmente designada por beldroega) é uma erva daninha cujas partes aéreas são comestíveis, sendo consumidas cruas, em saladas ou cozidas [1]. Existe uma variação genética significativa entre os genótipos de beldroegas [2], e esta diversidade pode ser utilizada no desenvolvimento de cultivares de alto rendimento com elevado conteúdo em ácidos gordos ómega-3, por exemplo.

O objetivo deste trabalho foi analisar a composição química de seis genótipos de beldroega: três ecótipos silvestres provenientes do mar Cáspio da região do Irão (genótipo A, B e C: das cidades de Sari, Gorgan e Aliabad, respetivamente), uma variedade local proveniente da região de “Domokos” na Grécia central (genótipo D) e duas cultivares comerciais beldroega comum de Gemma S.A. (genótipo E) e beldroega verde escura (genótipo F).

Os açúcares foram determinados por cromatografia líquida de alta eficiência (HPLC) acoplada a um detetor de índice de refração; os ácidos orgânicos foram analisados por HPLC acoplada a um detetor de fotodíodos e os ácidos gordos por cromatografia gasosa acoplada a um detetor de ionização de chama.

Verificou-se que a composição química de beldroegas é dependente do genótipo. O teor em açúcares totais foi mais elevado no genótipo B; o teor em ácido oxálico foi menor no genótipo D e maior no genótipo C. Os ácidos gordos mais abundantes foram o ácido palmítico (C16:0), o ácido oleico (C18:1), o ácido linoleico (C18:2n6) e o ácido alfa-linolénico (C18:3n3), com diferenças significativas nos teores presentes nos diferentes genótipos avaliados. O genótipo D apresentou maior percentagem relativa do ácido alfa-linolénico. O genótipo E revelou possuir uma composição equilibrada de ácidos gordos ómega-3 e ómega-6. As variedades comerciais (genótipos E e F) foram bastante similares aos genótipos B e C.

Este estudo fornece novas informações sobre a composição química de beldroegas que podem ser utilizadas na indústria alimentar como produtos de elevada qualidade e valor acrescentado. Assim, estas plantas devem ser valorizadas, nomeadamente como uma fonte de ácidos gordos ómega-3.

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Caracterização físico-química da flor de *Borago officinalis* em dois estados de floração

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A borragem *(Borago officinalis)* é uma planta anual, cultivada para usos medicinais e culinários. As flores de borragem têm despertado algum interesse aos chefs de cozinha gourmet e consumidores, uma vez que podem ser usadas na decoração de saladas e bebidas, conferindo um ligeiro sabor a pepino. No entanto, grande parte dos estudos referentes a esta planta incidem nas sementes, principal constituinte comercial usado para extração de óleo, sendo as flores de borragem pouco estudadas.

Nesse sentido, o presente trabalho teve como objetivo caracterizar o botão e a flor completa, do ponto de vista físico-químico, nomeadamente em termos de: dimensões, cor, a_w, humidade, cinzas, proteína, gordura total, fibra dietética, hidratos de carbono, energia e carotenóides totais, de forma a, avaliarem-se eventuais diferenças entre dois estados de floração. Em simultâneo, avaliaram-se as pétalas.

Relativamente à caracterização do botão e flor completa, correspondentes a dois estados de floração distintos, e às pétalas verificou-se que o botão e a flor completa apresentaram um menor teor hídrico, e consequentemente teores mais elevados de todos os macronutrientes face às pétalas, mas sem significado estatístico. O botão demonstrou ser aquele com maiores teores de fibra dietética e lípidos, enquanto a flor completa apresentou os maiores teores de cinzas e proteína. Para além disso, a flor completa foi aquela que apresentou o maior teor de carotenóides, em comparação com os botões e pétalas, provavelmente devido à sua concentração nas sépalas. Os resultados mostraram que as pétalas são essencialmente constituídas por água (90,5±0,4%). Quanto aos restantes macronutrientes da amostra fresca, a fibra dietética total é o constituinte maioritário (3,84±0,03 g/100g), seguido dos hidratos de carbono (3,49±0,44 g/100g). Nesse sentido, as pétalas frescas de borragem apresentaram um baixo teor calórico (28±2 kcal/100g). Em relação aos valores de a_w, estes foram semelhantes entre as três amostras (0,982-0,983).

Em suma, o presente trabalho permitiu aumentar o conhecimento geral sobre as características físico-químicas da flor de borragem, fornecendo mais informação aos consumidores. Por outro lado, o conhecimento dos constituintes maioritários nos diferentes estados de floração pode favorecer a sua utilização seletiva. Assim sendo, a flor completa deve ser escolhida quando se pretende maximizar a quantidade de carotenóides, enquanto o botão deverá ser selecionado no caso de se pretender ingerir uma maior quantidade de fibras.

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Effect of *Fucus vesiculosus* powder addition on colour and textural properties of gluten-free cookies based on chestnut flour

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Chestnut and *Fucus vesiculosus* (FV) brown seaweed are autochthonous raw materials from Galicia. The use of chestnut as gluten-free raw material is interesting due to its absence of gluten and its health and nutritional benefits [1]. Brown seaweeds, like FV, represent a suitable supplement for food due to their high nutritional value as source of dietary fibre and natural antioxidants. As consequence, the conjunctive use of chestnut and FV is proposed in order to obtain suitable products for coeliac people and to add value of both biomaterials.

Four different chestnut flour-based formulations (2% flour basis, f.b., of guar gum and 1.8% f.b. of salt) enriched with FV at different content (0 (control), 3, 6 and 9%, f.b.) were mixed in a lab kneader (Mixolab®, Chopin Technologies) following a three-step protocol (i: 5 min, 50ºC; ii: 10 min, 50-90ºC (4ºC/min); iii: 4 min, 90ºC). The obtained doughs were allowed to cool (≈30ºC), manually moulded and cut in disks (34 mm diameter, 3.6 mm height) and baked in an oven (180ºC, 25min). Colour was evaluated before (dough) and after baking (cookies) using CIElab coordinates (L*, a*, and b*) employing a colorimeter (CR-400, Konica Minolta). Textural properties of cookies were studied by means of hardness, measured as the force needed to break the cookie employing a cylinder probe P/3 (3 mm diameter) at 2 mm/s in a texture analyser (TA-TXPlus, Stable Microsystems).

Colour studies before baking step showed that FV addition significantly increased green colour (low a* values) and decreased brightness (L*) of enriched doughs, Table 1. After baking, yellow colour raised mainly due to Maillard reactions [2], while little changes in brightness and greenness were observed. As it can be seen in Fig. 1, addition of FV higher than 3% f.b. significantly increased cookies hardness, indicating that it could be a limit of FV addition in relation to textural properties.

Table 1. Colour parameters of doughs (do) and cookies (co) based on chestnut flour enriched with *Fucus vesiculosus*†

	L^*_{do}	a^*_{do}	b^*_{do}	L^*_{co}	a^*_{co}	b^*_{co}
Control	54.68 ± 0.95^a	7.62 ± 0.16^a	17.76 ± 0.27^c	38.19 ± 3.01^b	14.12 ± 0.24^a	28.37 ± 2.28^a
FV03	46.09 ± 0.53^b	3.51 ± 0.11^b	21.82 ± 0.52^a	45.89 ± 2.57^a	$9.70 \pm 1.45^{b,c}$	31.20 ± 1.02^a
FV06	42.25 ± 0.60^c	2.21 ± 0.08^c	22.23 ± 0.36^a	43.86 ± 1.99^a	7.84 ± 1.49^c	30.23 ± 0.95^a
FV09	39.38 ± 0.98^d	1.51 ± 0.11^d	20.53 ± 0.49^b	36.53 ± 3.84^b	9.93 ± 0.51^b	24.24 ± 3.71^b

†Data value of each parameter with different superscript letters in columns are significantly different ($P \leq 0.05$)

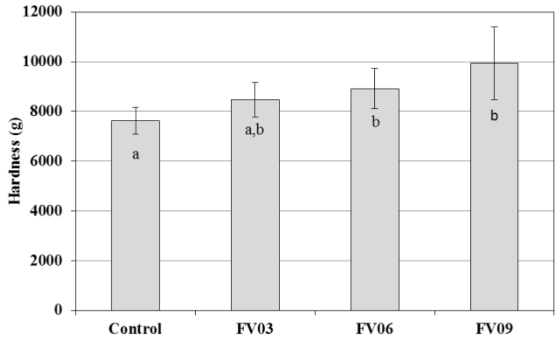

Fig.1. Hardness of gluten-free cookies based on chestnut flour enriched with *Fucus vesiculosus*†

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Chemical composition and oxidative stability of Algerian *Moringa oleifera* whole seed and kernel oils

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Native to the sub-Himalayan regions of Northwest India, the Drumstick tree *Moringa oleifera* possesses multipurpose usability. One of this uses derives from the high content of its seeds in comestible oil (30 to42 %). *Moringa oleifera* seeds oil is liquid at room temperature, pale yellow in colour; unrefined oil has a flavour similar to peanut oil in electronic nose analysis, and resembles olive oil in fatty acid composition [1, 2]. The aim of this work was to detail the chemical composition and oxidative stability of Algerian *Moringa oleifera* seed oil, while aiming to ascertain if the presence of the shells affects or not the composition and stability of extracted oil. For the purpose, whole seeds and kernels from the same crop year and geographical location were extracted with petroleum ether, and the oil was the oils were compared in terms of fatty acid composition, triglycerides, sterols, tocopherols and oxidative stability, following standard procedures.

Unsaturated fatty acids were found to be > 75%, with a clear dominance of oleic acid (71.43%, 71.65%, respectively for whole seeds, and kernel oil). These similarities were also extended to the triglycerides analysis, where the most prominent triglyceride was triolein (44.74%, 45.70%). Total phytosterols were found to be > 4100 mg/kg, with β-sitosterol, stigmasterol, campesterol and Δ^5-avenasterol, as main compounds, and small amounts with other minor sterols. Tocopherols were mainly characterized by the presence of α-tocopherol (263.2, 256.4mg/kg, respectively), followed by ɣ-tocopherol (47.8, 51.2), and small amounts of β-and δ-tocopherol. *Moringa oleifera* whole seed and kernel oils showed a high stability to oxidation in the rancimat method (40.3 h, 42.1 h), probably due to the high amounts of monounsaturated fatty acids together with the presence of natural antioxidants like phytosterols and tocopherols

Our findings showed that, in comparison with literature data from other countries, Algerian *Moringa oleifera* oil presents interesting properties, particularly regarding its stability, that justifies further studies. Additionally, no significant differences in the composition of both oils (whole seed oil and kernel oil)were found, with only a slight reduction in the oxidative stability. However, as the oxidative stability is still very high incomparison with other common oils, including olive oil, the extractive industries couldeconomicallybenefit from avoidingshell removal.

Acknowledgment
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Evaluation of the antioxidant and antibacterial activity of spearmint (*Mentha spicata* L.)

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Aromatic herbs and spices have been used for centuries in gastronomy for seasoning and flavouring purposes. Additionally, several of these herbs are also used in traditional medicine due to their composition in bioactive compounds. In order to control the microbial growth in foods, the food industry often resorts to the use of additives, namely of authorised preservatives. However, recently there has been a growing interest towards the use of alternatives, namely natural additives and extracts from plants, that would allow preventing foodborne diseases and promoting the extension of the shelf life of foods [1]. Due to its potential activity against foodborne pathogens and foodspoilage bacteria and its better acceptability by consumers who are increasingly demanding for more “natural” foods, the use of essential oils can be an interesting alternative to substitute, at least partially, synthetic preservatives [2]. Different types of mints are included among the most widespread perennial aromatic herbs, with different species being also used in folk medicine. Among those, *Mentha spicata* L., commonly called spearmint or garden mint, is widely used in as a flavouring agent in foods, in particular in the European cuisine. This plant is also frequently used in infusions and in folk mainly for its digestive, carminative, antispasmodic and diuretic properties [3].

In this work, the total content of phenolic compounds and of flavonoids, reducing power and antioxidant activity (in vitro measurement of 2,2-diphenyl-1-picrylhydrazyl (DPPH) radical scavenging capacity) of spearmint (*Mentha spicata*) methanolic extracts were evaluated using spectrophotometric techniques. Additionally, the antibacterial activity of the essential oil extracted from the plant by hydrodistillation using a Clevenger apparatus, was also evaluated by the agar-diffusion method against different Gram-positive bacteria (*Bacillus cereus*, *Staphylococcus aureus*) and Gram-negative bacteria (*Escherichia coli*, *Klebsiella pneumoniae*, *Proteus mirabilis*, *Pseudomonas aeruginosa*).

Preliminary results of this study suggest that the inclusion of spearmint as a seasoning/flavouring agent in different dishes or consumed in the form of infusion can offer health benefits due to their antioxidant capacity. Additionally, the essential oil from *Mentha spicata* showed a significant inhibitory capacity against all studied Gram-positive and Gram-negative bacteria, with the exception of *Pseudomonas aeruginosa*, which showed to be resistant. Compared to the antibiotics used as a positive control, for some bacteria, higher inhibition halos were obtained for the essential oil. Therefore, the use of spearmint as a condiment in gastronomy may be beneficial from the point of view of food safety and food shelf-life improvement.

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Evaluation of Tunisian olive oils from different cultivars

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Olive oil is a highly appreciated food product due to sensory and healthy attributes, being quite prone to frauds. So, physicochemical evaluation of olive oils is legally required. In this study, 43 olive oil samples produced in Tunisia from different olive cultivars (groups: Sahli cv – 11 samples; Chetoui cv- 26 samples; and, Other cvs – 4 samples including Leguim cv and Arbequina cv) were physicochemically evaluated taking into account: (i) free acidity (FA), K_{232} and K_{270} extinction coefficients, ΔK, and, peroxide values (PV), required for quality level classification (i.e., extra-virgin, virgin and lampante olive oil: EVOO, VOO and LOO); and (ii) other useful data for olive oil overall characterization (total phenols (TP); antioxidant capacity (DPPH); and, oxidative stability (OS)). Based on the levels found for FA, PV and extinction coefficients (K_{232}, K_{270} and ΔK), the 43 olive oils were classified as: EVOO (4 samples), VOO (5 samples) and LOO (33 samples). It was verified that TP, DPPH and OS levels of EVOO, VOO and LOO samples were statistically similar (P-value ≥ 0.2340 for one-way ANOVA). Also, the olive cultivar (i.e., Sahli cv, Chetoui cv and other cvs) did not statistically influenced the mean levels of the FA, PV, TP, K_{232} and DPPH evaluated (P-value > 0.05), and slightly influenced the mean levels of K_{270} and OS (P-value < 0.05). Finally, as expected an almost linear tendency could be established between DPPH and OS or TP. The possibility of using the 8 physicochemical parameters for classifying olive oils according to cultivar; as well as TP, DPPH and OS for differentiating among olive oil quality levels was assessed through a fusion physicochemical data-chemometric tools approach and further evaluated using a repeated K-fold cross-validation procedure. The results from the linear discriminant analysis (LDA) coupled with a simulated annealing (SA) variable selection algorithm pointed out that the physicochemical data evaluated did not possess the aimed discrimination potential (sensitivities around 80% for cross-validation). So, for these olive oils, the identification of potential putative markers for the recognition of olive oil cultivar and quality level must be performed. Alternatively, the potential use of other analytical procedures like electrochemical analysis should be evaluated considering the satisfactory results already achieved by the research team [1].

Acknowledgments
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Water adsorption and desorption isotherms of *Undaria pinnatifida* brown seaweed

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Brown seaweeds constitute an economically and ecologically important seaweeds group that are used mainly as human food and as a source of alginate for a wide range of industries. However, kelps have many other commercial applications, such as feed for aquaculture and animal husbandry, agricultural fertilizers, feedstock for biofuel production, and medicinal purposes [1]. The knowledge of water exchange between valuable solids and atmospheres is critical to select drying or storage conditions.

Experimental water adsorption and desorption isotherms of *Undaria pinnatifida* brown seaweed were determined, in a wide range of temperatures in order to cover the most common storage (5ºC) and drying (45 and 65ºC) temperatures, using a gravimetric static method detailed elsewhere [2]. Briefly, several saturated salt solutions were selected to obtain atmospheres with constant relative humidity in order to generate water activities, a_w, in the solid between 0.09 and 0.73. Samples were dried up to 0.02 kg/kg dry basis in order to ensure the water adsorption during equilibrium experiments and fresh samples were employed for desorption experiments. Triplicate samples (around 0.5 g) were stored and periodically weighed until to reach constant weight (±0.0005 g). About 2 months were necessary to achieve the equilibrium. Equilibrium moisture content (X_{eq}) was obtained after determination of dry matter of each sample using a vacuum oven (70ºC, 15 kPa).

Experimental data exhibited a concurrent increase in X_{eq} with increasing a_w, suggesting type III isotherms according to the BET classification (Fig. 1). The X_{eq} values at similar a_w were notably larger than those previously reported for other brown kelps [3]. At constant a_w, X_{eq} decreased with increasing temperature. The observed hysteresis loops between desorption and adsorption isotherms can be classified as type H3 following the IUPAC classification. Modelling of adsorption (R^2>0.997) and desorption (R^2>0.983) data was satisfactorily preformed (0.094 < a_w < 0.726) using a proposed model ($X_e=C+A(a_w/(1-a_w))^B$) based on Oswin model. It should be highlighted that A and C parameters followed linear trends (R^2>0.991) with temperature, whereas B remained invariant (4.19 for adsorption and 3.70 for desorption processes).

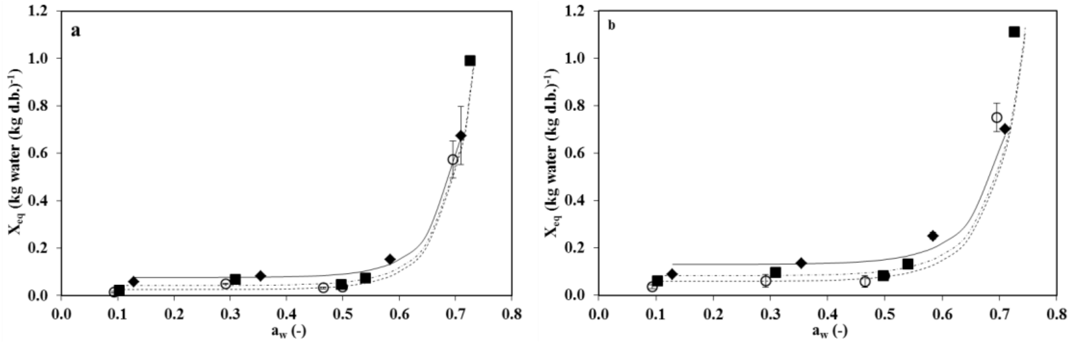

Fig.1. Experimental data for water (a) adsorption and (b) desorption isotherms of *Undaria pinnatifida* seaweed at different temperatures: (♦) 5, (■) 45, (○) 65ºC. Lines correspond to the proposed model

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Estimation of water sorption of sucrose from glucose and fructose data

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Carbohydrates play a major role in biological and food systems. The control of moisture content during processing of foodstuffs with high sugar content is basic in order to avoid the loss of quality of sugars due to microbial and chemical spoilage. Estimating the hygroscopic properties of sugars at different temperatures could be valuable information in order to generate prediction models which will allow obtaining water desorption isotherms, in a wide temperature range of many food materials, taking into account their chemical composition [1].

The experimental equilibrium moisture content of glucose, fructose and sucrose over a wide range of water activities (from 0.09 to 0.91) and temperatures (20, 35, 50, and 65ºC) was determined and the appropriate mathematical model, following statistical criteria [2], was selected. Experimental desorption isotherms were determined using a static gravimetric method reported elsewhere [3]. Note that samples were placed into an environment around 100% relative humidity for a couple of weeks in order to ensure the desorption process. The estimation of the disaccharide (*i.e.* sucrose) desorption isotherms from their monomers (*i.e.* glucose and fructose) was also evaluated. Briefly, the ratio between moles of water per moles of each sugar was plotted against water activity, a_w, for each temperature in order to obtain the corresponding empirical fittings. From these fittings, in terms of a_w, the moles of water per mole of oxygen were easily obtained for each individual sugar at each temperature. Adding these ratios for glucose and fructose and multiplying by a factor of 11/12, desorption isotherms of sucrose were predicted at different temperatures. The factor of 11/12 was employed due to sucrose molecule presents 11 active centres whereas glucose and fructose molecules present 6 each one.

Water desorption isotherms of glucose, fructose and sucrose are clearly influenced by the temperature. Tested isotherms were type III according to Brunauer's classification. Henderson model proved to be an excellent ($R^2 > 0.998$, RMSE < 0.009) model to fit the desorption isotherms of tested sugars [3]. In all cases, the experimental isotherms of sucrose were nicely predicted ($R^2 > 0.990$) from the corresponding isotherms of their monomers (Figure 1).

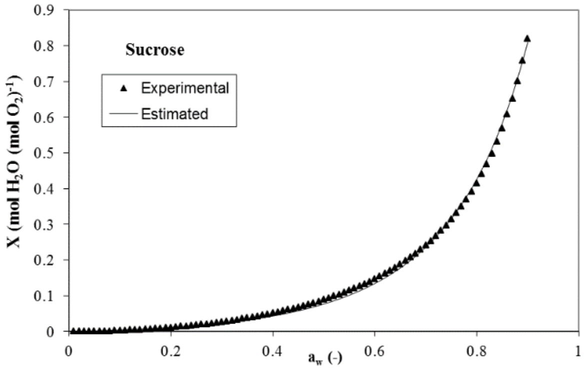

Fig.1. Experimental and estimated water sorption of sucrose at representative temperature, 65ºC

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In silico and experimental analysis of DNA markers for *Citrus aurantium* identification in herbal medicines

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Citrus aurantium L. belongs to the Rutaceae family and it is popularly known as bitter orange, Seville orange, sour orange, bigarade orange, or marmalade orange. In traditional Chinese medicine, the fruits are known as "zhi shi", being used as a stimulant of gastrointestinal function. In addition to the fruit itself, the leaves are used in herbal infusions as aids in digestion, the flowers are used for their sedative properties in cases of flu and the peel of the fruit is used as regulator of digestion. The fruit is traditionally used as an antiemetic, antitussive, diaphoretic, digestive and expectorant. Adrenergic amines (octopamine, synephrine, tyramine, methyltyramine and hordenine) are considered to be the most important active compounds of *C. aurantium*. Synephrine, tyramine and hordenine act in fat metabolism, activating lipolysis through adrenergic action and stimulation of beta-3 receptor [1]. Synephrine is a chiral amine present in nature as (R)-(-)-*p*-synephrine, which is chemically similar to other sympathomimetic amines, such as ephedrine (from *Ephedra sinica*). Therefore, bitter orange has been used in weight-loss formulations with increased popularity [2]. Since plants in herbal preparations can be substituted by others due to adulteration or to misidentification/accidental swap, to ensure consumer's safety and to verify labelling compliance, the development of adequate analytical methods is mandatory. So far, DNA-based methods have been reported as highly appropriate tools for plant authentication [3].

Therefore, the aim of this study was to develop a methodology for the specific identification of *C. aurantium* using DNA-based methods. For this purpose, voucher leaves of *C. aurantium*, as well as other 23 *Citrus* species (including *C. sinensis* – sweet orange) were gently provided by Germplasm Banks. Commercial samples of herbal infusions having bitter orange as ingredient (*n*=6) were acquired in supermarkets. DNA was extracted from all samples using the commercial Nucleospin Plant II kit. An *in silico* study using 263 sequences of *C. aurantium*, available at NCBI database, was performed to eliminate high homology with other *Citrus* spp. Eight genomic sequences (NCBI accession no. HM172529, KM201256, KM201257, HM172529, HM172533, M172528, JN681151.1 and JN681151.1) were selected and used to design new primers. Qualitative PCR results showed the identification of *Citrus* genus targeting a resistance-like protein RGAs4-8-like encoding gene (NCBI accession no. HM172533) and RGAs4-1-like encoding gene for the identification of *C. aurantium* (NCBI accession no. M172528). Real-time PCR coupled to high resolution melting analysis using EvaGreen dye was also performed with *C. aurantium* specific primers. The developed methodologies were further applied to the analysis of the 6 commercial infusions labelled as containing bitter orange. PCR results showed incompliances for 5 of these samples due to the absence of bitter orange DNA. This result can possibly be related to a misidentification/swap of bitter orange (*C. aurantium*) with sweet orange (*C. sinensis*). Future work will comprise the development of a methodology for the specific identification of *C. sinensis* to confirm this hypothesis.

Acknowledgments
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Potencial antioxidante de *Stevia rebaudiana* Bertoni cultivada em Portugal e conservada em diferentes condições térmicas

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A procura de adoçantes naturais tem vindo a ganhar cada vez mais importância devido à grande controvérsia associada à utilização de alguns adoçantes artificiais nomeadamente, ciclamatos, aspartame e acesulfame-K. Os glucósidos de esteviol (E 960) constituem um grupo de adoçantes naturais de utilização generalizada, sendo obtidos a partir de *Stevia rebaudiana* Bertoni, uma planta nativa da América do Sul [1]. No entanto, a referida planta contém outros potenciais de utilização que devem ser explorados, nomeadamente associados à sua capacidade antioxidante.

Esta planta já é produzida em Portugal, no entanto, são necessários estudos que comprovem que a sua composição química se mantém independentemente das condições de cultivo.
Neste trabalho, utilizaram-se amostras de Stevia cultivadas em Bragança num ensaio de campo com condições de cultivo definidas e, que após colheita, foram submetidas a dois tratamentos de conservação diferentes: em fresco (-20ºC) e desidratadas (30ºC). Foi avaliada a sua atividade antioxidante (efeito captador de radicais livres e poder redutor), tendo sido também determinados alguns compostos bioativos tais como fenóis e flavonoides totais (métodos espetrofotométricos), tocoferóis (HPLC-fluorescência) e açúcares livres (HPLC-RI). Foram observadas diferenças significativas entre as diferentes amostras. A desidratação parece favorecer a atividade antioxidante e a concentração em fenóis e flavonoides. Já as amostras conservadas em fresco apresentaram maiores concentrações de tocoferóis (incluindo isoformas α, γ e δ) e açúcares livres, tendo-se identificado e quantificado oito moléculas distintas: ramnose, xilose, arabinose, frutose, glucose, sacarose, trealose e rafinose.

Os resultados confirmam que as plantas cultivadas em Bragança possuem metabolitos secundários bioativos responsáveis pela capacidade antioxidante.

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Estudo da hidrólise do pigmento natural Curcumina presente na planta *Curcuma longa*

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Realizamos o estudo da hidrólise e solubilização do pigmento em água e em soluções aquosas de surfactantes (Brometo de dioctadecildimetilamónia, Plurónico F127 e misturas de ambos) a diferentes valores de pH, utilizando as técnicas analíticas Espectroscopia de Absorção e Titulações Potenciométricas.

Concluímos que a hidrólise depende do tipo de curcumina presente na solução, podendo estar na forma molecular ou em três estados de forma ionizada, a curcumina mostrou apenas ser estável a valores de pH 12 a qual está na forma completamente ionizada. A microencapsulação é efetiva na solubilização do pigmento e na proteção de hidrólise no intervalo de pH estudado.
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Phenolic compounds content, antioxidant and antimicrobial activities of juniper (*Juniperus communis* L.)

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Juniper (*Juniper communis* L.) berries are widely used in different products such as perfumes, pharmaceuticals and to aromatize alcoholic beverages. In particular, they are employed with other botanical ingredients in the production of commonly consumed juniper-based spirits, such as gin [1]. Juniper berries are also frequently used in the European gastronomy to season and flavour foods, being considered the only spice obtained from Cupressaceae plants and one of the few examples of spices produced in cold or temperate regions [2]. In the northeast region of Portugal, the berries are traditionally used in game meat dishes. Besides being used in drinks and for culinary purposes, *J. communis* berries are also used in folk medicine for their diuretic, antiseptic, stomachic, and carminative properties [3], being inscribed in different Pharmacopoeias.

In this work, the total content of phenolic compounds and of flavonoids, reducing power and antioxidant activity (in vitro measurement of 2,2-diphenyl-1-picrylhydrazyl (DPPH) radical scavenging capacity) of the methanolic extracts of juniper (*Juniperus communis* L.) berries and leaves were evaluated using spectrophotometric techniques. Two samples of berries were acquired in a local supermarket and in a specialized store, respectively and one sample of berries and leaves were collected in the wild in Trás-os-Montes region. Additionally, the antimicrobial activity of a sample of essential oil obtained by hydrodistillation was determined by the macrodillution broth assay against several Gram-positive and Gram-negative bacteria and *Candida albicans*.

Total phenolics content, determined by the Folin-Ciocalteu methodology and expressed as mg gallic acid equivalents per gram of sample (GAE/g), ranged from 11.13±1.33 to 16.16±0.64 mg GAE/g for the berries samples, being significantly higher for the leaves sample (141.12±9.56 mg GAE/g). As expected, based on the phytochemicals content determined for the berries and leaves, the leaves showed a higher reducing power (EC_{50}=0.17±0.00 mg/mL) and antioxidant activity, measured as the ability to decrease to 50% the DPPH absorbance (EC_{50}= 0.10±0.01 mg/mL) compared to the berries (reducing power ranging from 2.40±0.04 to 3.48±0.26 mg/mL and antioxidant activity ranging from 1.74±0.04 to 3.84±0.39 mg/mL).

The essential oil was able to inhibit the growth of *C. albicans* and different bacteria (*Bacillus cereus*, *Bacillus subtillis*, *Staphylococcus aureus*, *Escherichia coli*, *Klebsiella pneumoniae* and *Enterococcus faecalis*) to different extents, while showing no activity against *Pseudomonas aeruginosa* and *Proteus mirabilis*.

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Mixing properties of gluten-free dough based on chestnut flour enriched with *Fucus vesiculosus* brown seaweed

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In the last years, new gluten-free products appear in the market due to their suitability for people with coeliac disease. In this sense, the development of new gluten-free products has an increasing demand. This opportunity could be used to add value of autochthonous Galician raw materials like chestnut and seaweeds. Chestnut is an attractive alternative to be used as base for gluten-free products. Moreover, *Fucus vesiculosus* (FV) brown seaweed, common seaweed of Galician coast, has been recently classified like a “novel food” for human consumption [1]. In this context, the main target of this work is to study the effect of FV addition on mixing properties of gluten-free dough based on chestnut flour.

Four different formulations were studied: the control based on chestnut flour (14 % water, flour basis, f.b.) consisted of 2% of guar gum and 1.8% of salt and three formulations (FV03, FV06 and FV09) with FV seaweed powder added to control at different percentages (3, 6 and 9% flour basis, f.b.). Doughs preparation from these formulations and mixing behaviour with water were carried out in a lab kneader (Mixolab®, Chopin Technologies) following a standard protocol [2]. Water addition was adjusted to achieve the target consistency of 1.10 N·m. With this protocol the main dough mixing properties were determined: water absorption (WA), development time (DT, time to achieve the maximum torque) and the stability time (ST, the period at which the dough torque is kept at 1.10 ± 0.07 N·m).

The addition of FV seaweed powder to gluten-free doughs based on chestnut flour significantly modified mixing behaviour of doughs compared to control dough, Fig. 1. WA (f.b.) of dough increased, in the common WA range of commercial doughs, from 58 (control) up to 64 % (FV09). A linear relationship (R^2>0.98) between WA and FV addition was found. The DT was significantly larger for FV09 (2.5 ± 0.2 min) and practically constant for the other doughs (1.9 ± 0.2 min), indicating that FV additions higher than 6% implies longer complete homogenization of the dough. ST was also significantly increased by FV addition. FV09 dough had the highest value (5.8 ± 1.2 min), whereas no significant differences were observed for FV06 and FV03 (3.9 ± 0.4 min). The control sample had the lowest ST (2.7 ± 0.1 min). The addition of FV seaweed powder helps the dough stabilization during mixing.

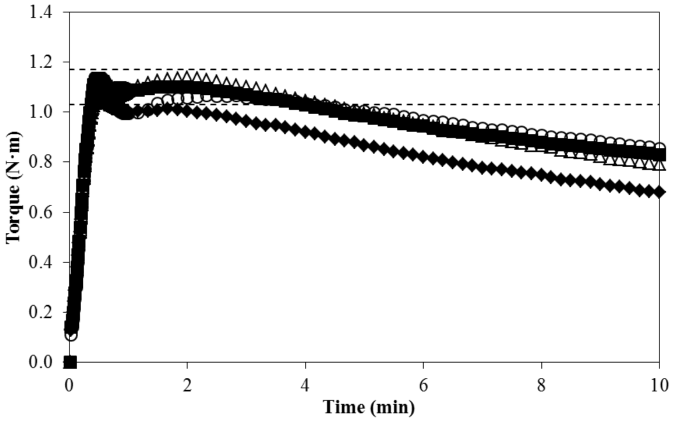

Fig.1. Mixing curves of chestnut flour doughs enriched with *Fucus vesiculosus*: 0%(♦), 3%(∆), 6%(■), 9%(○)

Acknowledgements
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Air drying kinetics modelling of brown seaweed *Undaria pinnatifida*

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Seaweed wakame (*Undaria pinnatifida)* is one of the most valuable brown algae due to their high demand and economic value*,* in markets whose goods are intended for human consumption, which is their principal use today*.* As the supply from wild harvest cannot meet increasing current and future demands, aquaculture of these kelp species is currently a growing enterprise [1]. The drying of these seasonal seaweeds is critically relevant and unexplored step in the industrial processing.

In this context, experimental air drying kinetics of the brown seaweed *Undaria pinnatifida* at different temperatures (35, 50, 60 and 75°C) were studied following the protocol previously reported [2]. Briefly, *Undaria pinnatifida* seaweeds were air-dried in a pilot-scale tray dryer with air velocity of 2 m/s and relative humidity of 30%. Samples were placed on a tray (450×450 mm) with the same initial load density (1.3 ± 0.1 kg/m^2) for all experiments. Drying kinetics were determined by weighing in a balance at selected drying times until sample moisture ratio (MR) achieved around 0.02.

In all cases, experimental air drying kinetics exhibited a concurrent decrease in moisture ratio with increasing time (Figure 1a). As expected, drying time decreases with increasing air temperature from 170 min at 35 °C up to 120 min at 75 °C. Air drying kinetics at each tested temperature were satisfactorily (R^2> 0.99) fitted using the two-parameter Page model (n and k) [3]. It can be considered that n is constant (1.16 ± 0.01) in the range of tested temperatures. Drying temperature significantly increases k parameter, from 11.4 ± 0.1 10^{-3} min^{-n} at 35ºC to 17.9 ± 0.3 10^{-3} min^{-n} for drying above 50ºC, indicating that temperature rise from 35ºC to 50ºC significantly increased drying rate. Drying rates, w, achieve maximum values depending on air drying temperature, and after that, a falling drying rate period is observed at all tested temperatures (Figure 1b). At high moisture content, induction periods can be observed and they are related to the initial heating of the seaweed samples.

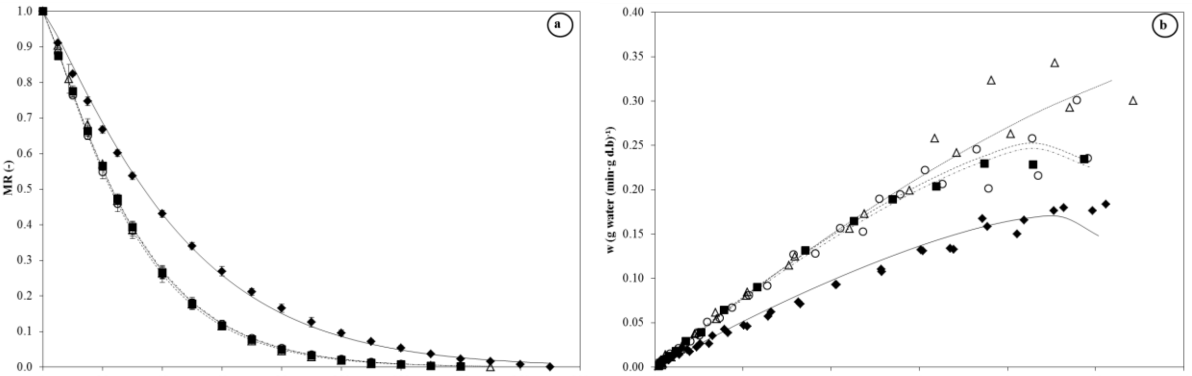

Fig.1. Experimental drying curves and drying rates for *Undaria pinnatifida* brown seaweed at different temperatures (ºC): 35 (♦), 50 (Δ), 60 (■), and 75 (○). Lines correspond to Page model, 35 °C (──), 50 °C (···), 60 °C (- · -) and 75°C (- - -)

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Tratamento de *Melissa officinalis* L. com irradiação gama e feixe de eletrões aumenta a concentração de compostos fenólicos

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O consumo crescente de infusões implica a necessidade de processar uma quantidade cada vez mais elevada de espécies vegetais [1]. Nestas plantas, os compostos fenólicos, considerando a sua natureza hidrofílica, estão entre os compostos químicos naturais mais importantes nas infusões. Tendo em atenção os diversos tipos de bioatividade dos compostos fenólicos, o material vegetal a ser utilizado em infusões deve ser processado utilizando técnicas que tenham a capacidade de preservar o mais possível o seu perfil fenólico.

As técnicas de irradiação têm vindo a ser destacadas pelo seu potencial como tecnologias de conservação promissoras aplicáveis a diferentes tipos de alimentos [2]. Assim, os perfis fenólicos de amostras de *Melissa officinalis* L. (cidreira) irradiadas com feixe de eletrões ou irradiação gama foram caracterizados e comparados com os de amostras-controlo (não submetidas a irradiação), tendo por objetivo verificar a ocorrência de possíveis efeitos potenciadores.

Em geral, verificou-se que as amostras irradiadas apresentavam maiores teores de compostos fenólicos individuais, o que representa um resultado favorável à validação da irradiação como tecnologia adequada de conservação. Além do mais, foi possível identificar quais os compostos fenólicos que eram incrementados por cada um dos tipos e doses de irradiação, o que pode ser útil para otimizar a produção de compostos fenólicos específicos.

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Nutritional profile of *Phaseolus lunatus* and *Cajanus caja* seeds

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Legumes (Fabaceae) are one of the most economically important crop families in the world. They are growing on about 15% of the world's arable land and provide 33% of dietary protein around the world [1]. When combined with cereals, for instance rice or corn, a complete amino acid profile is achieved that can replace animal protein, being the diet basis of many people of low socio-economic strata all over the world. Moreover, the partial replacement of animal protein by vegetable protein results in lower land and water demands and shorter times of production [2].

Legumes are also a unique source of bioactive compounds, with documented antimicrobial, pharmaceutical, and/or nutraceutical properties [1]. Indeed, to make the society more aware about the importance of legumes role in the promotion of health, nutrition, food security and environmental sustainability, the United Nations declared the year of 2016 as the International Year of Pulses [2].

In this work, the nutritional profile of two different species (*Phaseolus lunatus* and *Cajanus cajan*) was assessed. Samples were selected in local markets and adequately prepared. Moisture content was instrumentally determined (SMO 01, Scaltec Instruments, Germany). Ash content was determined by incinerating the sample in a muffle furnace at 500 °C (AOAC 920.153); protein was quantified by Kjeldahl method (AOAC 928.08); and total fat determined according to Soxhlet procedure (AOAC 991.36). Fiber was analysed using an enzymatic - gravimetric method (985.29 AOAC). Total carbohydrates were determined by difference.

The results show that both types of seeds are rich sources of protein, as expected, but also of fiber.

Table 1. Moisture, ash, protein, lipids and total carbohydrate contents of analysed seeds (contents expressed in %)

Samples	Ash	Protein	Lipids	Total Fiber	Carbohydrate
Cajanus cajan	2.98 ± 0.07	23.43 ± 0.01	2.27 ± 0.15	29.9	41.68 ± 0.22
Phaseolus lunatus	5.16 ± 0.04	30.53 ± 0.67	1.12 ± 0.04	31.2	31.58 ± 0.28

Mean values of triplicate determinations ± standard deviations.

As described in table 1, these results contribute to enhance knowledge of nutritional composition of these legumes that grow in arid regions. Given their nutritional and socioeconomic importance, it is expected that this study also contributes to boost family farming of legumes, while reinforcing social, economic and environmental sustainability policies.

Acknowledgments
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Extraction of phenolic compounds from *Juglans regia* L. optimized by response surface methodology

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The studies on plant secondary metabolites extraction, namely phenolic compounds, are increasing due to their *in vitro* bioactivity and marked effects on oxidative process related to several health diseases. Moreover, they have been widely used in pharmaceuticals, functional foods and natural cosmetics [1].

The solid-liquid extraction of these compounds from biomass is usually carried out using organic solvents such as methanol, ethanol, acetone and ethyl acetate. In this context, microwave assisted extraction (MAE) is one of the most employed alternative extraction methods commonly using methanol or ethanol in different concentrations by dilution with water. Ethanol will be selected in this work due to its lower toxicity. In addition, this alcohol can be obtained from renewable sources and is safe for human consumption. Among the advantages reported for MAE are its lower extraction times and solvent consumption, when compared to conventional methods [2-4].

Our research group is interested in the green extraction of valuable compounds from biomass and there are previous evidences that walnut leaves are rich in phenolic acids and flavonoids [5]. In the present work, a 5-level full factorial Box–Behnken design was successfully implemented for maceration and MAE optimization, in which the ethanol concentration (*Et*), processing time (*t*), temperature (*T*), and solid/liquid ratio (S/L) were relevant independent variables. HPLC-DAD results showed that MAE is more effective extracting higher contents of phenolic compounds than conventional maceration in a lower processing time.

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Teor de flavonóides numa chávena de chá

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O chá é uma das bebidas mais consumidas no mundo. O facto do consumo de chá estar, normalmente, associado a efeitos benéficos para a saúde, tem contribuído para a procura de compostos bioactivos nesta bebida em particular de flavonóides, compostos cuja função na prevenção doenças degenerativas e cardiovasculares é conhecida.

No mercado existem diversas variedades de chá de *Camellia sinensis* as quais advêm do diferente grau de maturação das folhas que são usadas e do tipo de processamento aplicado na produção do chá. O fabrico do chá preto envolve um processo de fermentação, importante para o desenvolvimento da cor e sabor da bebida. No chá verde, as folhas de *Camellia sinensis* são sujeitas a uma vaporização cujo objectivo é inactivar as enzimas responsáveis pela oxidação. O chá branco é obtido apenas por secagem rápida das folhas ou seja, resulta de um tipo de processamento mais suave [1].

O presente trabalho teve como principal objetivo determinar o teor total de flavonóides em diferentes amostras de chá verde (Hysson e Encosta de Bruma) e chá preto (Pekoe, Broken Leaf e Orange Pekoe) produzidos nos Açores a partir de folhas de *Camellia sinencis* e comparar os resultados com os obtidos para o chá branco, de modo a avaliar a influência do tipo de folhas e da forma de processamento usados no fabrico do chá.

As infusões foram preparadas com cerca de 1.5 g de folhas de chá em 200 mL de água quente (volume correspondente a uma chávena). Foram também efectuados ensaios com folhas de chá moídas de modo a avaliar a eficiência da extração. O teor em flavonóides foi determinado através de um método colorimétrico a 510 nm com uma curva de calibração de catequina em etanol a 10% (concentração das soluções padrão entre 5-300 mg/ L) [2].

A utilização de folhas moídas mostrou poder aumentar a eficiência da extração de flavonóides até 40%. O chá que revelou maior teor de flavonóides foi o chá verde Encosta de Bruma (31,8 ±1,0 mg/g chá), seguido do chá verde Hysson e preto Pekoe com concentração muito semelhante (18,0±1,1 e 18,3±0,5 mg/g de chá, respectivamente). O chá preto Broken Leaf, Orange Pekoe e o chá branco apresentaram os teores mais baixos mas semelhantes em flavonóides (12,0±0,3,11,3 ±0,9 e11,4±0,2 mg/g de chá, respectivamente). Encontrou-se uma boa correlação entre a actividade antioxidante dos chás (método FRAP) e o seu teor em flavonóides (r^2=0,926) o mesmo não se verificando em relação ao teor em polifenóis (r^2=0,775).

A comparação de resultados evidenciou que o grau de maturação das folhas de *Camellia sinencis* bem como o processamento a que são sujeita influenciam no teor total de flavonóides que se encontra presente nas diversas variedades de chá.

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Production of acidic oligomers with prebiotic potential from lemon peel wastes by chemical hydrolysis under mild conditions

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Pectin-rich agro-industrial by-products (including lemon peel wastes) constitute renewable sources of pectic oligosaccharides (POS), a type of indigestible carbohydrates that have been recently suggested as novel prebiotics [1], [2].

When samples of lemon peel wastes are subjected to a water extraction (to remove sugars and other soluble compounds) followed by hydrothermal treatment under non-isothermal conditions at 160ºC, a mixture of POS are obtained in aqueous solution, which contains acidic oligomers such as oligogalacturonides (OGalA) and neutral oligomers such as arabinooligosaccharides and galactooligosaccharides [3].

The aim of this work was to develop a method to separate the acidic POS fraction from the neutral one, based on their different susceptibility to acid hydrolysis and the use of membrane technology to fractionate the resulting solution. In a first step, POS mixtures were treated with diluted HCl or H_2SO_4 (under mild conditions) to hydrolyse neutral chains keeping the acidic fraction of OGalA practically intact. Afterwards, membrane filtration (1kDa cut-off) was used to separate the acidic oligomers from the neutral monomers generated by the acid hydrolysis.

This approach allowed obtaining a purified fraction of OGalA susceptible to be employed in future works to evaluate its prebiotic potential and to elucidate structure-function relationships. Furthermore, the current study constitutes a promising alternative to valorise this type of industrial by-products.

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XXII Encontro Luso-Galego
Química

COMUNICAÇÕES ORAIS E EM PAINEL

Química Analítica

Validação de um método de quantificação de elementos essenciais e potencialmente tóxicos em músculo de peixe - desafios

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A alimentação deve ser equilibrada e variada, oferecendo todos os nutrientes necessários para colmatar as necessidades humanas e garantir uma vida saudável. Para garantir que os alimentos sejam seguros, estes devem estar isentos de contaminantes. É importante monitorizar a qualidade e segurança dos alimentos a fim de avaliar os riscos e benefícios do seu consumo. A quantificação da componente inorgânica em alimentos, i.e., dos elementos essenciais e dos potencialmente tóxicos, tem merecido poucos estudos apesar de ter um impacto relevante na saúde humana [1].

A escolha de apenas um tipo de matriz para a realização deste trabalho deveu-se a vários fatores, de entre os quais se destaca a necessidade de adotar diferentes estratégias de preparação de amostra e posterior análise, consoante a matriz alimentícia em questão, devido essencialmente à diferente composição que os alimentos possuem, o que introduz diferentes abordagens durante o processo de validação do método.

Na literatura não existe um consenso sobre a utilização de métodos para a preparação de amostras de músculo de peixe e, por isso, torna-se imperativo estabelecer e validar métodos eficazes para a sua digestão e análise [2].

O objetivo deste trabalho consistiu em validar uma metodologia para a digestão e análise de amostras de músculo de peixe, recorrendo a técnicas de análise multi-elementares tais como emissão ótica e espectrometria de massa associadas a plasma indutivamente acoplado (ICP-OES e ICP-MS). As amostras de músculo de peixe foram digeridas em meio ácido com recurso a um sistema de micro-ondas.

Neste trabalho, foi possível validar com sucesso os elementos Mn e Sr por ICP-MS e os elementos Cu, Fe e Zn por ICP-OES. Para outros elementos, o controlo de qualidade estipulado pelo laboratório não foi atingido, evidenciando o desafio que é analisar com adequada qualidade o músculo de peixes.

A estimativa da incerteza associada a cada elemento validado, foi feita utilizando os valores obtidos no processo de validação, combinando a justeza e a precisão. A incerteza estimada para os elementos validados foi de 13.2% para o Mn, 13.6 % para o Cu, 14.9% para o Sr, 18.8% para o Fe e 19.7% para o Zn. O Fe e o Zn foram os elementos que apresentaram uma maior incerteza, associada a um maior erro de justeza e uma menor precisão.

O método após validação foi aplicado a diferentes amostras de peixe, o que permitiu comparar os níveis de elementos essenciais e potencialmente tóxicos existentes nos tecidos de um alimento tradicionalmente presente na dieta Portuguesa, como é o peixe.

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TXRF instrumentation for direct metal analysis and preconcentration strategies in combination with nanoparticles

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The determination of metals and metalloids in environmental, food and related samples continues being of paramount importance. Therefore, the development of strategies easily extended to a routine basis is desired. For this purpose, the technique Total X-Ray Fluorescence Spectrometry (TXRF) has been increasingly applied in the last years as an alternative to inductively-coupled plasma mass spectrometry (ICP-MS), electrothermal-atomic absorption spectrometry (ETAAS), flame-atomic absorption spectrometry (FAAS) avoiding the use of cooling water and the high consumption of gas, and to conventional X-ray fluorescence spectrometry improving its sensitivity [1]. Mainly, TXRF consists of the application of the sample as a thin film (or liquid drop which is then dried) over a sample carrier. Since the incidence and reflected angle are approximately ≈0º/90º, the reflection of the X-ray incident beam is almost total and scarcely penetrates into the substrate resulting in a reduced absorption and scattering of the radiation, and consequently, in lowered background noise and improved detection limits [1].

Recently, several research works has been published in our research group focused on the metal analysis in a wide variety of samples using ultrasonic-slurry sampling and ultrasound-assisted extraction with diluted acids or surfactants as sample preparation approaches in combination with TXRF analysis [2,3,4]. Benefits of TXRF include multielemental character, ability to handle microsamples, low amount of required reagents, simple calibration and decreased background noise and matrix effects with no-consumption of gasses or cooling water. Accurate and precise results were reached in certified reference materials and real samples of different origin. Additionally, the use of ultrasound energy allows faster extractions with high sample throughput systems (e. g., cup-horn sonoreactor) than conventional extractions approaches.

Nevertheless, the limit of detection of this techniques is µg/g-mg/g depending of the element and it is limited to volatile elements. Thus, new sample preparation procedures based on preconcentration strategies are required to solve these limitations. Following the recent trend on the use of nanomaterials as sorbents of metals due to the high surface area and affinity. Several research works have been developed in our research group using nanoparticles of Ag and Pd as new platforms for trapping of Hg, Se, hydrides of Sb and Se [5,6,7]. Increased sensitivity and high enrichment factors were achieved.

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Miniaturized spectrophotometric and fluorimetric assays for selenium determination in pet foods

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Selenium (Se) is an essential micronutrient that should be provided to companion animals according to their nutritional requirements [1]. Therefore, there is a need to determine the total amount of Se in order to make formula adjustments and fortification of pet foods. Inductively coupled plasma mass spectrometry (ICP-MS), among other techniques, has been successfully implemented for the determination of trace levels of Se in foods [2]. However, expensive equipment and skilled operators are required, which may preclude its use for routine analysis. Colorimetric and fluorimetric techniques are classical approaches to determine Se at levels found in food [3], providing benefits for industrial application due to simplicity, easy operation and ready access in most laboratories. Nevertheless, current protocols use hazardous solvents and laborious procedures that render techniques time-consuming. In this context, the aim of this work is to develop an environment-friendly method for the determination of Se in pet food using miniaturized spectrophotometric and fluorimetric assays.

The spectrophotometric determination is based on the formation of a piazselenol complex in acidic medium from the reaction between 3,3-diaminobenzidine (DAB) and Se(IV). A pre-concentration and clean-up step were performed by salting-out assisted liquid-liquid extraction (SALLE) using acetonitrile and Na_2CO_3 precipitation. Subsequently, an aliquot of the supernatant was transferred to a microplate well and absorbance was read at 420 nm. Limits of detection (LOD) and quantification (LOQ) were 0.05 and 0.1 µg mL^{-1}, respectively. A similar approach was implemented for the fluorimetric determination based on the reaction between 2,3-diaminonaphthalene (DAN) and Se(IV) allowing the formation of the fluorescent DAN-Se complex. The fluorescence intensity was read at λ_{exc} = 370 nm and λ_{emmis} = 590 nm. Preliminary results provided LOD and LOQ values 10 times lower compared to the spectrophotometric method. Further application to pet food samples and validation by comparison with ICP-MS are currently under way.

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Rapid and simple determination of formaldehyde content in cork agglomerate products

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Formaldehyde is one of the most relevant indoor air pollutants, since it is carcinogenic and toxic and can adversely affect human health. It is well-known for its preservative and disinfectant properties and is mostly applied in the production of adhesives and resins. The production of urea and melamine resins is the main usage of formaldehyde by the industrial sector. Due to the hazardous effects of formaldehyde in health, it is necessary to accurately measure its content in different materials, in particular in products used in buildings.

In this work, a rapid and simple methodology was developed for the extraction and determination of formaldehyde in samples of cork agglomerate products commonly used as building material. Gas-diffusion microextraction (GDME) [1, 2] was used for the extraction of formaldehyde directly from the samples, with simultaneous derivatization with acetylacetone in the presence of ammonia (Hantzsch reaction). The derivative was then determined by spectrophotometry at 412 nm. Several extraction parameters (extraction temperature, sample mass, volume of acceptor solution, extraction time and concentration of acetylacetone) were optimized by means of an asymmetric screening design (two factors at four levels and three factors at three levels). The developed methodology proved to be a reliable tool for the determination of formaldehyde in the samples with suitable method features: low LOD (0.14 mg kg^{-1}) and LOQ (0.47 mg kg^{-1}), $r^2 = 0.9994$, intraday and interday precision of 3.5% and 4.9%, respectively. Seven samples were analysed and contents between 1.9 and 10.0 mg kg^{-1} were determined. The results of the developed methodology were compared with the standard method EN 717-3 and no significant differences (*t*-test, p=0.05) were obtained. The GDME-based procedure proved to be an inexpensive, fast, simple and robust alternative for the determination of formaldehyde.

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Determination of free formaldehyde in cosmetics containing formaldehyde donors, using gas diffusion microextraction

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Formaldehyde is one of the most abundant compounds used in the industrial production of consumer goods. It is used in the production of resins, textiles, insulation materials and plastics but is also added to cosmetics and hygiene products due to its antimicrobial properties. Despite its widespread usage, formaldehyde is considered to be carcinogenic, toxic, and exposure to formaldehyde can lead to contact dermatitis, asthma and allergies. For these reasons the analytical control of the free formaldehyde content in cosmetics and hygiene products is of the uppermost importance.

Nowadays, directly adding formaldehyde to cosmetics and hygiene products is rarely the common practice. As a substitute, substances called formaldehyde donors are added. These substances are added to release small amounts of formaldehyde over time. Methods for the determination of formaldehyde are usually straightforward. Nonetheless, these techniques are not appropriate for the assessment of free formaldehyde in cosmetics with formaldehyde donors [1]. The reason is that direct reaction between the derivatization reagent and cosmetic sample, which is typically the most common procedure, will induce the liberation of all the formaldehyde that has not been released by the formaldehyde donors.

In this work, gas-diffusion microextraction (GDME) technique [2, 3] was used for the extraction of formaldehyde from cosmetic and personal hygiene products. Acetylacetone in the presence of ammonia was used as derivatization agent. This derivatization process was used for the spectrophotometric determination of formaldehyde because of its high selectivity. The developed methodology showed acceptable limits of detection (3.7 mg kg^{-1}) and quantification (12.3 mg kg^{-1}) which are perfectly reasonable values for the determination of formaldehyde in these samples. For comparison purposes, an alternative method found in the literature using a liquid-liquid extraction with dichlomethane, was also used for the determination of formaldehyde [4]. No significant differences (t-test, $p=0.05$) were obtained by the two different techniques, and concentrations between 100 and 370 mg kg^{-1} were found. The GDME-based procedure proved to be a fast, simple, inexpensive and robust alternative for the determination of formaldehyde in cosmetics containing formaldehyde donors.

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Pioneer use of cucurbit[uril] as ionophore in ion selective electrodes

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The macrocyclic methylene-bridged glycoluril hexamer dubbed by "cucurbituril (CB(6)) due to its fundamental binding properties such as high affinity, highly selective and constrictive binding interactions has been applied in waste-water remediation, as artificial enzymes and as molecular switches. The shape, solubility and chemical functionality may now be tailored by synthetic chemistry to play a role in molecular recognition, self-assembly and nanotechnology [1]. As far as the author knows, there isn't any research work concerning the application of CB in the development of chemical sensors, namely in the potentiometric sensors. So, in this work it is our aim to evaluate the use of CB as ionophore in ion selective electrodes (ISE). For that, etilefrine a sympathomimetic amine of the 3-hydroxy-phenylethanolamine series, a cardiac stimulant used as an antihypotensive [2] was chosen to be determined by a ISE based on CB.

Several polymeric membranes were prepared by using the CB(6) as ionophore. The lipophilicity of the membrane was varied by the incorporation of different solvent mediators, such as dibutyl sebacate (ε=5.4), 2-nitrophenyl octyl ether (ε=23.9) and 2-fluorophenyl 2-nitrophenyl ether (ε=50.0). The use of lipophilic salt was also considered. The best membrane was evaluated by changing the CB(6) for a cyclodextrin CD(6), another recognition molecule composed of six α-(1,4)-linked glycosyl units [3], with toroidal three-dimensional configuration.

The calibrations performed with etilefrine solutions showed a marked influence of the plasticizer used in the sensors membrane. The less lipophilic 2-fluorophenyl 2-nitrophenyl ether appears to impair small interaction between the ionophore and the etilefrine. The increase of the lipophilicity of the plasticizer resulted in higher interaction with the ionophore. So, the use of dibutyl sebacate leads to the improvement of the linear response range that was only surpassed by the absence of lipophilic salt (potassium tetrakis(4-chlorophenyl)borate) in the membrane composition. The potentiometric response of the latter presents a lower limit of linear range (LLLR) of $(1.35\pm0.00)\times10^{-6}$ M and are insensitive in the pH range of [4.0;10.0]. A similar membrane using CD(6) as ionophore was also evaluated and exhibit a slight increase of the LLLR $(2.65\pm0.00)\times10^{-6}]_{n=4}$ and a reduction of one decade in the operational plateau. The obtained results enable the envisagement of using cucurbit[uril] as an alternative to the described sensors based on CD ionophore.

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A laccase biocathode for oxygen reduction implementation

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Lately, attention has been centered in biocathodes performance, namely to materials and additives used for electrode construction as well as to immobilization process. These features enables the substitution of precious metals used in fuel cells due to selectivity of the biocatalysts towards the analyte/fuel, allowing working conditions at neutral pH and ambient temperature, eliminating the need of physical separation between anolyte and catholyte.

Laccase enzyme is widely used as biocatalyst since catalyzes the four electron reduction of O_2 to H_2O, a freely available oxidant and due to the capacity to undergo direct electron transfer when the immobilization process is efficient. Unmediated electron transfer and selectivity are two important characteristics for assembly of self-powered biofuel cells and miniaturization for implants applications. Katz and col [1] introduced in 2001 a self-powered biofuel cell generating a power of 1uW and analytical signals nernstian related with the monitored analyte at the same time. In order to increase the power output or simply get further miniaturization, new bioelectrodes with high efficiency must be developed.

In the present work, a carbon nanostructured air-breathing electrode with *Rhus vernicifera* immobilized was characterized in terms of electron transfer efficiency and oxygen electroreduction capacity using cyclic voltammetry and amperometric techniques.

Bioelectrodes were constructed as follows: graphite electrodes were home made with a 2 mm commercial pencil mines over which 10 µL of graphene oxide (1mg/ml) were dropped and further electro-reduced in the interval of -1.3 to 0.8 V vs. Ag/AgCl, at 50 mV/s for 2 hours. The graphene surface was then casted with 10µL of a mixture consisting of laccase and carbon nanotubes, dried and followed by drop casting of 4ul of sol gel solution silicon titanium tetraglycerolate and left to dry at ambient temperature for about 5 hours.

The electrochemical impedance spectroscopy results for the nanostructured electrode without enzyme immobilization showed a reduction in the heterogeneous electron transfer resistance in the order of magnitude from kΩ to Ω when graphene is dropcoated in the graphite surface compared to the bare graphite resulting in an increase of the voltammetric current density of 10 times. Relatively to the immobilization process, in oxygen saturated solution the biolectrode performance improves when carbon nanotubes is used as enzyme wiring compared to functionalized carbon black. The biocatalytic response increases with the temperature and pH reaching a maximum of 40ºC in temperature range studied and optimum alkaline pH around 9. Finally the bioelectrode showed good response to the amperometric determination of diluted oxygen in quiescent buffer solution.

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Development and validation of HPLC method for quantification of dapsone and clofazimine loaded in nanoparticles targeting bioavailability assessment

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Leprosy is a chronic infectious disease caused by *Mycobacterium leprae*. This disease is a serious public health problem in several developing countries, namely in India and Brazil [1]. The current treatment of leprosy is a multidrug therapy that includes the antimicrobial agents dapsone (DAP) and clofazimine (CLZ) [2, 3]. Many patients develop potentially harmful side effects that may occur during or after treatment with these drugs [2, 4]. The use of a nanotechnological approach for the delivery of these drugs can improve their efficacy, bioavailability and reduce unwanted toxic effects. Based on their different physico-chemical properties, DAP was incorporated in solid dispersions whereas CLZ had to be loaded in polymeric nanoparticles. Therefore, the main objective of this work was the development and validation of a high performance liquid chromatography (HPLC) method with UV/Vis detection for quantification of DAP and CLZ loaded in nanoparticles, targeting the future application to bioavailability assessment, namely during intestinal permeation assays.

Chromatographic separation was achieved using a reversed phase Kinetex core-shell C18 column (250 × 4.6 mm; 5 µm particle size; 100 Å). The mobile phase consisted of a mixture of aqueous acetate buffer (final concentration 50 mM, pH 4.8) and acetonitrile. Gradient elution mode was performed increasing acetonitrile content from 27 to 60% (v/v), at a flow rate of 1.0 mL min^{-1}. Detection wavelength was set at 280 nm and the injection volume was fixed at 20 µL. The developed HPLC method was validated for selectivity, linearity and range, accuracy, precision, detection and quantification limits (LOD and LOQ), stability, matrix effect and recovery, in accordance with EMA guideline on bioanalytical method validation [5], providing results suitable for its application to the targeted samples.

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Development and application of high-throughput microplate-based ORAC-pyranine method for evaluation of antioxidant capacity

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An antioxidant is defined as any substance that when present at low concentrations, compared to those of an oxidizable substrate, significantly delays or prevents oxidation of that substrate. Among the several methodologies to evaluate the antioxidant properties of a vast array of compounds and biological matrices, Oxygen Radical Absorbance Capacity (ORAC) must be highlighted [1]. ORAC measures the protection afforded by an antioxidant compound to a target molecule against oxidation by oxygen radical species (ROS), including peroxyl radicals.

Hence, one of the objectives of the present work was the utilization of pyranine (PYR) and pyrogallol red (PGR) as alternative probes to fluorescein. Furthermore, depending on the target molecule employed, ORAC values translate different information due to kinetic differences in probe oxidation upon oxygen radicals attack. This fact justifies the need of performing ORAC protocols employing different probes in order to profile the mechanistic behaviour of a given antioxidant compound. This can be assessed through the free radical scavenging capacity (ORAC-PYR) and through the reactivity towards oxygen radicals (ORAC-PGR) [2].

Therefore, this work proposes a novel high-throughput microplate-based ORAC method for the evaluation of antioxidant capacity wherein PYR was employed as probe/target molecule and 2,2′-azobis (2-amidinopropane) dihydrochloride (AAPH) as free radical generator. The conditions that provide the best relationship between time and sensitivity were 10 μM of PYR and 10 mM of AAPH. RSD values were < 5.4 % and < 6.4% for intra- and inter-assay precision, respectively. A limit of detection of 0.3 μM Trolox equivalents combined with a sampling rate of 38 determinations per hour was achieved. The applicability of the developed method was demonstrated by conducting a structure-antioxidant activity relationship study of antioxidant compounds commonly present in food and biological samples. Several beverages containing compounds with antioxidant properties were also analysed by the proposed ORAC-PYR and by ORAC-PGR for comparison purposes, establishing their total scavenging capacity and reactivity.

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Cromatografia de afinidade baseada em lectinas – um modelo com aglutinina de *Sambucus nigra*

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O estudo dos proteomas tem constituído um dos principais meios para detectar alterações a nível celular e bioquímico, decorrentes de várias patologias. Contudo, a presença de proteínas séricas muito abundantes dificulta significativamente a descoberta e análise de proteínas e glicoproteínas pouco abundantes, que podem ser potenciais biomarcadores de doenças [1].

Diversas técnicas têm sido utilizadas para realizar o fraccionamento do proteoma sérico, nomeadamente a cromatografia de afinidade baseada nas proteínas A e G, na IgY aviária, em anticorpos monoclonais ou em lectinas [2,3]. As lectinas são particularmente adequadas para se unirem e isolarem selectivamente determinadas estruturas de glicanos presentes em amostras complexas, como são as biológicas. As lectinas unem-se reversivelmente a glicoproteínas presentes nas amostras em diferentes concentrações, originando, depois da eluição, um conjunto de glicoproteínas enriquecido, para posteriores estudos de Glicoproteómica.

No entanto, a cromatografia de afinidade com lectinas (CAL) para aplicações bioquímicas é ainda realizada, sobretudo, de forma discreta (em *batch*), o que implica um procedimento demorado, o uso de reagentes ou colunas comerciais dispendiosos e instalações com temperatura controlada. Este trabalho propõe o desenvolvimento e optimização de uma metodologia de fluxo para realizar a CAL, utilizando como modelo a aglutinina de *Sambucus nigra* imobilizada em partículas de agarose, para isolar o glicano sialilTn (um biomarcador pan-carcinoma) presente em glicoproteínas séricas de pacientes de cancro. Em condições de fluxo, a metodologia CAL desenvolvida permite a automatização do processo de fraccionamento, o que é especialmente importante quando o número de amostras a analisar é elevado, minimizando a manipulação e perda de amostras durante o procedimento. Adicionalmente, o sistema de fluxo apresenta uma montagem simples, pouco dispendiosa e não requer instalações específicas ou experiência técnica muito especializada. Outra vantagem da metodologia proposta é a sua elevada versatilidade, uma vez que pode ser adaptada para efectuar a CAL com qualquer lectina, de acordo com o objectivo da análise glicoproteómica.

Agradecimentos
As autoras agradecem aos hospitais participantes a autorização para recolha das amostras de sangue humano.

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On-line post-column HPLC-DPPH assay for evaluation of antioxidant compounds

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The identification of antioxidant compounds in food samples is of high importance due to a growing interest on natural antioxidants, as phenolic compounds, and their contribution for the prevention of oxidative damage induced by radical species. For this reason, the development of methodologies that allow the simultaneous identification of antioxidants on complex matrices and a rapid screening of the antioxidant activity of different samples is of extremely importance.

The principal aim of this work was the development and optimization of an analytical methodology for the separation, identification and quantification of compounds with potential antioxidant activity in different matrices, namely food samples. The methodology is based on the separation and identification of individual compounds by HPLC, followed by the post-column determination of the antiradicalar capacity (DPPH method) using an on-line system (Fig.1).

In a first approach, the optimization was conducted using phenolic compounds standards due to their importance in food samples as antioxidants. Relevant parameters such as concentration of DPPH, flow and reaction time were optimized in order to achieve higher resolution and sensitivity. Tests were carried out at a flow rate of 0.2 ml/min for the DPPH solution and 0.8 mL/min for HPLC mobile phase. The best results were obtained using 0.01 mM DPPH and 4 min reaction time.

The on-line post-column HPLC-DPPH assay results were in accordance with off-line conventional DPPH method. Additionally, the developed methodology presents advantages comparatively to conventional DPPH methods due to its simplicity, high sensitivity and application potential, allowing the rapid screening of individual constituents and simultaneous determination of radical scavenging capacity in different samples.

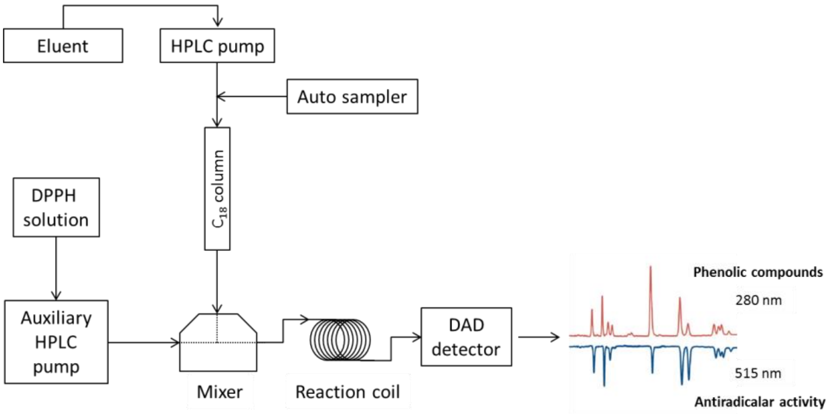

Fig.1. Instrumental setup for on-line post-column HPLC-DPPH assay

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Vapor bromine generation and trapping/reaction onto a fluorescein-containing aqueous microdrop: an efficient approach for the fluorimetric determination of bromide in water samples

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This work reports on the development of a novel method for determination of bromide in water samples. The method is based on the *in situ* generation of bromine, transfer of the volatile to the headspace and trapping/reaction onto a fluorescein-containing aqueous drop exposed to the gas phase above the sample. The in-drop reaction of bromine with fluorescein gives rise to a decrease in the analytical signal due to the formation of tetrabromofluorescein (eosin). The proposed methodology involves the combination of two miniaturized techniques, namely, headspace single drop microextraction (HS-SDME) and microvolume fluorospectrometry. Remarkably, dilution of the enriched microdrop was not required to perform the fluorimetric determination and, as a result, the method showed excellent sensitivity for bromide detection. The reported approach yielded an enrichment factor of 243 under optimal conditions. The limit of detection (LOD) and quantification (LOQ) were 1.1 and 4.4 µg L^{-1}, respectively. The repeatability, expressed as relatively standard deviation, was found to be 4.4% (n=6). The methodology was applied to the analysis of water samples, and recovery studies were carried out to evaluate for potential matrix effects. Satisfactory recoveries in the range of 95-110% were obtained in all cases. In comparison with alternative approaches reported in the literature, our method provided lower or comparable LODs. The results presented herein show the great potential of the coupling HS-SDME-microvolume fluorospectrometry for the sensitive determination of bromide in waters.

Agradecimientos
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Estimación del contenido de polifenoles en vinos mediante detección electroquímica basada en dispositivos electroanalíticos integrando nanotubos de carbono

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El empleo de técnicas electroanalíticas para el análisis rutinario del contenido de polifenoles en vinos se presenta actualmente como una alternativa interesante a los métodos espectrofotométricos tradicionales. La oxidación electroquímica de los polifenoles a potenciales moderados permite su cuantificación en muestras de interés agroalimentario de forma sencilla, pudiendo simplificar los procesos de tratamiento de muestra. En este sentido, la integración de nanotubos de carbono en la interfase sensora mejora notablemente la respuesta electroquímica de los dispositivos electroanalíticos utilizados para estos fines, siendo especialmente destacable el incremento en la estabilidad de las señales.

En esta comunicación se muestra como la incorporación de películas de nanotubos de carbono en la superficie de electrodos de carbono vítreo permite llevar a cabo la estimación del contenido de polifenoles en muestras de vinos blancos sin más tratamiento que su dilución y/o filtrado, mejorando significativamente la estabilidad, reproducibilidad y sensibilidad de las señales obtenidas respecto al comportamiento observado en electrodos no modificados. Los dispositivos electroanalíticos utilizados se han acoplado a sistemas de análisis por inyección en flujo (FIA) y electroforesis capilar (EC), permitiendo evaluar el contenido de grupos de polifenoles mediante FIA así como la obtención de perfiles electroforéticos mediante EC, estos últimos relacionados con el contenido de polifenoles individuales. Los resultados obtenidos en ambos casos al analizar vinos elaborados con uva *airén* o *verdejo* han mostrado que pueden haber diferencias en el contenido de polifenoles en función del tipo de uva empleada en estos vinos. A partir de las señales obtenidas con estos dispositivos electroanalíticos ha sido posible generar modelos de clasificación con ayuda de técnicas quimiométricas (Análisis de Componentes Principales y Análisis Discriminante), capaces de asignar correctamente en función del tipo de uva más del 70% de las muestras de vino analizadas.

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Implementação de uma metodologia rápida para avaliação da capacidade antioxidante em extratos de plantas medicinais

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As análises por injeção em fluxo vieram revolucionar profundamente a forma como as análises e ensaios são realizados [1]. Os sistemas de análise em fluxo têm conquistado cada vez mais espaço no contexto laboratorial e industrial devido à sua simplicidade, robustez, rapidez e eficiência o que torna estes sistemas uma importante ferramenta para a prática de “química verde”. A tudo isto acrescenta-se ainda a possibilidade de estes sistemas serem automatizados o que permite aumentar a quantidade de informação produzida e a facilidade na gestão e análise dessa mesma informação.

O ensaio de DPPH$^\bullet$ [2] é um dos métodos mais comuns na caracterização e quantificação das propriedades antioxidantes de moléculas ou extratos. Este ensaio é frequentemente utilizado na investigação para a determinação da capacidade anti-radicalar de inúmeros compostos bioativos como vitaminas, flavonoides e fenóis bem como em extratos mais ou menos complexos, como de plantas.

Este método baseia-se na mudança de coloração de uma solução de DPPH$^\bullet$ (2,2-difenil-1-picrilhidrazilo), que sendo um radical relativamente estável de cor violeta, se converte num composto mais estável de coloração amarela quando é reduzido por agentes antioxidantes pela transferência de um átomo de hidrogénio. A reação é então monitorizada espetrofotometricamente pela variação da absorvância da solução de DPPH$^\bullet$ a 515 nm.

Na sua forma tradicional, o ensaio de DPPH recorre ao consumo elevado de soluções com solventes orgânicos (geralmente metanol) e intervalos de tempo longos para desenvolvimento da reação. Assim, apesar de ser um método muito comum e relativamente simples de ser executado, este pode revelar-se um ensaio extremamente fastidioso, principalmente quando o número de amostras a serem analisadas é elevado.

Neste contexto, a implementação do método de determinação da capacidade antioxidante pelo radical DPPH$^\bullet$ num sistema de análise em fluxo por multi-impulsão (MPFS, [3]) permite a automatização do método, a diminuição de reagentes e solventes gastos e resíduos produzidos, o aumento do ritmo de determinação e a diminuição do custo por análise.

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Microsphere biofunctionalization for meso/microfluidic-based automated immunoassays

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Immunochromatography and enzyme-linked immunosorbent assay (ELISA) represent selective and sensitive procedures based on solid-phases for separation/detection and quantification of anthropogenic pollutants in the aquatic environment. In contrast with batch-wise procedures, such as microplate-based platforms, automated methods reduce manual handling of reagents, thus increasing overall precision and decreasing time-to-result.

Microparticles have been shown to be an adequate support for carrying out immunoassays in meso and microfluidic systems. They offer a wide range of coupling sites for biomolecules such as antibodies, combined with specialised anti-fouling surfaces to prevent non-specific binding and high compressibility for optimum fluidics.

In this work we investigated the protein-coupling behaviour of two commercially available microsphere supports (Tentagel® polystyrene-PEG-COOH and PolyAn® PMMA beads with 3D antifouling surface) using DCC/EDC and NHS/S-NHS activation chemistry. The study of coupling conditions (pH, proportion of reagents and type of buffering system) was addressed. The success of the biomodification of the supports was demonstrated by using self-prepared fluorophore-protein conjugates (Fig. 1). Laser-scanning microscopy and flow cytometry were applied for further characterization of the functionalized particles. The applicability of the developed particles will be demonstrated through the design of suspension multiplex assays for the detection, quantification and preconcentration of bioactive substances such as caffeine and carbamazepine, using Lab-on-valve (LOV) platforms.

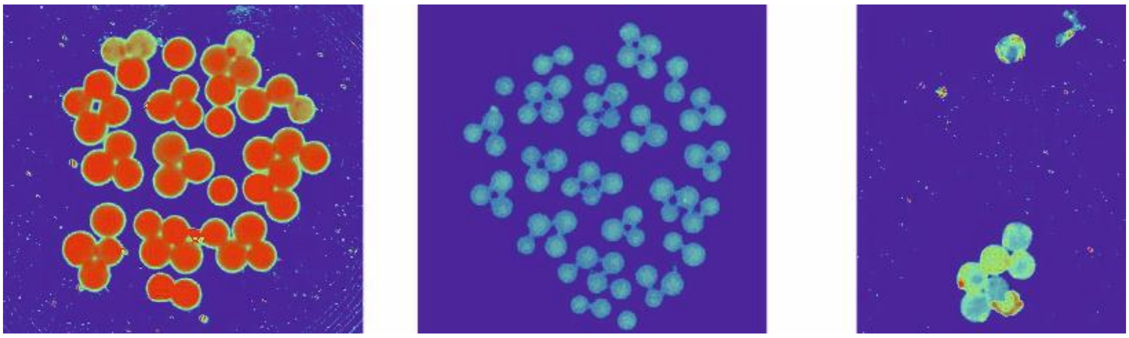

Fig.1. Laser-scanning microscopy images obtained for Tentagel® polystyrene-PEG-COOH microspheres after conjugation with IgG-Alexa647 sec.AB (left) through DCC/NHS reaction. The same beads were incubated with PBS (middle) and IgG without NHS activation (right) as negative controls

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Design, construction and application of an electrochemical immunosensor

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Thyroxine (T_4) is a thyroid hormone with a key role in metabolism regulation. Its actions spread from regulating bone grown, to temperature changes, adequate cell development and differentiation, or changes on the body's sensitivity to other hormones, among many others effects not fully studied. Hence, both an excess and a deficiency of T_4 can cause several diseases, from Graves disease to neurodevelopmental disorders or even depression, being its quantification in the human body essential. This work focuses on the design, construction and application of a self-assembled monolayer (SAM)-based electrochemical immunosensor for the quantification of the thyroid hormone T_4. The biosensor was developed based on the use of a mixed SAM for the immobilization of the anti-T_4 antibody onto a gold screen-printed electrode (SPAuE); 6-mercaptohexanol (6-COH) and 11-mercaptoundecanoic acid (MUA) were applied for the covalent binding of the antibody, creating the appropriate linker between the golden surface and the anti-T_4 (Figure 1).

Electrochemical impedance spectroscopy and cyclic voltammetry techniques were used for the modification procedure control and characterization of the modified electrodes surface. Furthermore, the analytical application of the developed biosensor was carried out by EIS after incubation of the sensor with different concentrations of T_4 hormone and using $Fe(CN)_6^{3-}/Fe(CN)_6^{4-}$ as redox probe.

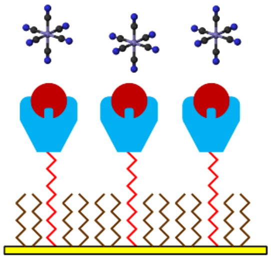

Fig.1. Schematic representation of the immunosensor construction, comprising the coverage of the SPAuE surface with MUA and 6COH, creating the appropriate link between the golden surface and the anti-body

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Development and validation of a new method for the determination of metformin in pharmaceutical formulations

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Metformin hydrochloride (MTF), chemically is 1,1-dimethylbiguanide hydrochloride with a molecular formula of $C_4H_{12}ClN_5$ (Fig. 1). It is an oral antidiabetic drug that has been used in the treatment of noninsulin dependent diabetes [1] which improves control of glycaemia primary by inhibiting hepatic gluconeogenesis and glucogenolysis and seems to ameliorate hyperglycemia by improving peripheral sensitivity to insulin, reducing gastrointestinal glucose absorption and hepatic glucose production [2].

In this work, a new spectrophotometric method was described for the determination of the metformin (MTF) in pharmaceutical formulations through charge transfer complex formation, using *p*-chloranil (CL) in presence of hydrogen peroxide. The experimental conditions were optimized using chemometric experimental designs. The absorption spectrum of the coloured product shows maximum absorption at 532 nm. Beer's law is obeyed in a concentration range of 9.05×10^{-3} at 6.33×10^{-2} mol l^{-1} MTF with a good determination coefficient ($R^2 = 0.99683$). The limit of detection ($3.SD_{blank}$/slope of curve) and limit of quantification ($10.SD_{blank}$/slope of curve) were 7.65×10^{-4} mol l^{-1} and 2.32×10^{-3} mol l^{-1} MTF, respectively. The developed method was optimized and validated as per the guidelines of International Conference on Harmonization (ICH) [3] and demonstrated excellent specificity, linearity, precision and accuracy for MTD.

The proposed method is free from the disadvantages of interference of the excipients normally found along with MTF in tablet dosage formulations and does not involve any extraction step. The results obtained by applying the proposed method agreed fairly well with those obtained by the Farmacopeia Brasileira standard procedure [4] at 95% confidence level. Thus, the proposed method is simple and applicable as well as for routine analysis of MTF in tablets.

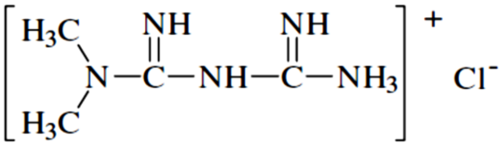

Fig.1. Chemical structure of Metformin hydrochloride (MTF) [2]

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Aplicación del diseño experimental a la optimización de la Microextracción Líquido-Líquido Dispersiva (DLLME) para el análisis de drogas de abuso en humor vítreo

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El objetivo de este estudio es la optimización de la microextracción líquido-líquido dispersiva (DLLME) [1,2] para la determinación de catorce drogas de abuso: Morfina, Metilona, N-Etilcatinona, 6-MAM, Mefedrona, Pentedrona, BEG, Cocaína, MDPV, Cocaetileno, Pirovalerona, EDDP, Buprenorfina y Metadona en muestras de Humor Vítreo humano seguido de su separación mediante cromatografía líquida de ultra eficacia (UPLC) combinada con detección UV. Los analitos fueron separados en una columna Acquity Shield RP 18 (100 mm x 2.1 mm, 1.7 µm) usando una fase móvil binaria compuesta por H_2O milliQ/0.1% ácido fórmico y ACN/0.1% ácido fórmico usando el modo de gradiente de elución (4.1 min de tiempo de análisis).

Durante la optimización del método, fueron estudiados parámetros como el tipo de fase móvil para la separación en UPLC, el tipo y volumen de los disolventes de dispersión y extracción. Para estudiar la influencia de los factores (efecto salino, volumen de muestra de humor vítreo, volumen de disolvente dispersante, volumen de disolvente extractante, tiempo en el ultrasonidos (US) y pH de la muestra) en el proceso de extracción se realiza un diseño de cribado o screening asimétrico $2^2 3^3 4^1//16$ que permite estudiar diferentes factores multinivel en 16 experimentos. El objetivo es determinar cuáles son los factores realmente importantes con el fin de optimizarlos, reduciendo el número de experiencias a realizar. A continuación, para optimizar los factores, volumen de dispersante y volumen de extractante, se utiliza un diseño central compuesto (CCD) de superficie de respuesta y funciones de deseabilidad.

En las condiciones óptimas, el método ofrece una alternativa atractiva para el análisis de drogas de abuso en muestras de humor vítreo, proporcionando varias ventajas, tales como una corta preparación de muestra y una reducción del volumen de disolvente en comparación con metodologías tradicionales.

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Development of a cystatin C biosensor for the diagnosis of chronic kidney disease

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Chronic kidney disease (CKD) is characterized clinically by a progressive loss in renal function and affects around 600 million people worldwide [1]. Cystatin C is a novel serum marker for the diagnosis of CKD which is particular useful for detection in the early stages [2]. Any small change in glomerular filtration rate (GFR) is reflected by a modification of cystatin C levels in the serum [2], which means that this protein is a good indicator of kidney function. Useful automated methods for cystatin C determination give slightly different results, which impairs precise diagnosis. Therefore, new methods are needed in order to get more accurate results in the early detection of CKD [3].

In this work we are developing a novel biosensor for cystatin C monitorization in CKD, based in the well-known interaction mechanism of cystatin C with cysteine proteinases, such as papain. Papain has been isolated from Papaya fruit latex and its enzymatic activity is inhibited by cystatin C [4]. Furthermore, the interactions between cystatin C and papain, which are easily available and inexpensive substrates, should provide the necessary information for the development of biosensors [5].

Two strategies were applied in designing this biosensor. First, the immobilization of gelatin (papain substrate) on screen-printed carbon electrodes (SPCEs) was studied by chronoamperometry. The electrical current change was followed by the application of a ferrocyanide/ferricyanide redox couple with the papain on the top of gelatin. Cystatin C quantification was evaluated by the changing of the diffusion process, due to the papain inhibition by cystatin.

Secondly, papain immobilization on screen-printed gold electrodes (SPGEs), using amino-terminated self-assembled monolayers (SAMs), was monitored using electrochemical impedance spectroscopy (EIS). For that, different experimental conditions including the use of different alkanethiols molecules and papain and cystatin C concentration range were analyzed in order to get us the most reliable biosensor.

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Sample preparation procedures based on QuEChERS for assessment of 3-monochloropropane-1,2-diol esters in vegetable edible oil

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3-monochloropropane-1,2-diol (-3MCPD) is a food contaminant induced by heat, several toxicological studies has described its genotoxical activity reason why this compound has been cataloged as "Possibly Carcinogenic to human" by IARC (Category 2B) [1]. Although there is no toxicological data available for its esterified forms, their recent interest lays on the fact that free 3-MCPD formation from its esters may occur in human digestive track during enzymatic hydrolysis [2].

Vegetable edible oils are subjected to distinct processing methods in order to obtain specifics organoleptic properties, which could be performed at high temperature, situation that allows formation of this kind of food contaminants [3].

Direct determination methods based on HPLC are the most suitable since their do not require nether hydrolysis nor derivatization steps. Solid phase extraction (SPE) [4] is widely used for isolation of this compounds from oil matrices but it involves two stage of clean up with a large amount of organic solvent and a long time of processing. The objective in this work is to simplify and shorten the hole sample preparation time by develop a protocol based on QuEChERS (Quick, Easy, Cheap, Effective, Rugged and Safe) which reduce the organic solvent consumption and at the same time enables the combinations of different kinds of sorbent at the same stage. In this study, different sorbents (PSA, C18, SiSAX, Z-Sep+, OASIS HLB, etc) were tested in order to optimize the clean up step. Another method known as SALLE (Salting-out Assisted Liquid-Liquid Extraction) was assessed for the isolation of 3-MCPD diesters in vegetable edible oils samples.

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XXII Encontro Luso-Galego
Química

COMUNICAÇÕES ORAIS E EM PAINEL

Química dos Polímeros

Development of amino resin with flexible performance

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Amino-formaldehyde resins are thermosetting polymers. They are divided into three main types: urea formaldehyde (UF), melamine formaldehyde (MF) and melamine urea formaldehyde (MUF). These resins are characterized, after cure, by high crosslink density, high stiffness and high tensile strength [1]. However, this stiffness may be undesirable when a final product with some flexibility is desired.

Cork agglomerates are cork-based products that can be used for surfacing, flooring and insulation purposes. They are composed of cork granules with variable dimensions, bound together by rubber, polyurethane adhesive or MUF resin [2]. Cork agglomerates can be sold as flat panels or as a rolled panels (so called “cork roll”). MUF resins cannot be used for the latter form, since its stiffness causes the material to crack when flexed.

The aim of this work is to develop an amino resin with high flexibility, enough to allow its use in cork roll production. Good adhesive properties, hydrolysis resistance and low formaldehyde emissions are also key features. The strategy applied to address this challenge consists in the modification of the MUF resin with the incorporation of long and linear chain compounds that act as flexible segments in the MUF structure. Glycols with different molecular weights were used for this purpose.

The results show different performance for glycols with different molecular weights. Namely, the adhesive properties decrease with increasing molecular weight. The glycol with molecular weight of 200 g/mol yielded a promising formaldehyde-based flexible adhesive polymer.

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Exploring oxypropylation to prepare liquid and biphasic polyols from the pine-fruit shell of *Auraucaria angustifolia*

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This work comprises the characterization of pine-fruit shell, the residue of the edible seeds of *Araucaria angustifolia*, a coniferous tree native of South America with economic importance in the South and Southwest of Brazil, and their subsequent use to produce polyols trough oxypropylation. Two different alternatives have been followed: (i) total oxypropylation to produce liquid polyols and (ii) partial oxypropylation to produce biphasic polyols (liquid polyols reinforced with biomass of the same nature). The first polyols were characterized in what concerns unreacted biomass, homopolymer content, hydroxyl number and viscosity, and their properties compared with equivalent products to foresee future applications (e.g. production of rigid polyurethane foams). The second ones were subjected to homopolymer extraction and tested to produce composite materials by hot pressing.

The used pine-fruit shell, obtained from fresh pine fruit purchased in a local market of Campo Mourão PR (Brazil), presented ash and moisture contents of 1.9% and 5.0%, respectively. The lignocellulose composition (dry-basis) comprised cellulose (26.9%), hemicellulose (13.8%) and lignin (35.0%). Moreover, the obtained extractables indicate a major presence of hydroxylated substances (5.9% extracted with methanol) and polar components (6.9% extracted with water), comparatively with nonpolar components (extraction with hexane and dichloromethane).

For total oxypropylation, a set point temperature of 160 °C was used, and 12 polyols have been produced using a pine-fruit shell to propylene oxide ratio (PFS/PO) of of 30/70, 20/80 and 10/90 (g/ml) with 4 catalyst levels (KOH, at contents of 5, 10, 15 and 20%, biomass-based). The resulting liquid polyols were characterized by an homopolymer content ranging from 4-65%, a hydroxyl number between 257-605 mg KOH/g and very high viscosities for the series 30/70 (>500 Pa.s, 20°C). The series 30/70 was the one presenting the higher amount of unreacted PFS (34.9-77.4 %) and for the series 10/90 reasonable amounts were obtained (usually inferior to 10%). In general, the use of low PFS/PO ratios favours the liquefaction process.

In comparison with total oxypropylation, partial oxypropylation was conducted under moderate process conditions, namely at lower set point temperatures (135 and 150 °C). Different PFS/OP ratios, KOH contents (5 and 10%) and productive scale (50 and 100 g) were tested. Subsequently to oxypropylation, the biphasic polyols were subjected to homopolymer extraction that ranged from 3-40%, and the obtained products hot pressed using an in-house built apparatus. The following conditions were used: 135 ºC and 50 bar during 3 minutes. In a general way the assays using a set point temperature of 150 ºC give rise to material's thermal degradation, nevertheless the used productive scale. According to these preliminary studies, the biphasic polyols produced using a PFS/PO ratio of 25/75 (100 g), and a set point temperature of 135 °C, showed good binding characteristics and adequate proportions of oxypropylated/non oxypropylated material, thus representing suitable conditions for the partial oxypropylation reaction having in view the production of composite materials.

To the best of our knowledge no other works concerning pine-fruit shell oxypropylation are available in the literature. In this context, the results presented here pointed out for the viability of using this agro-forestry residue to produce both liquid and biphasic polyols.

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Aplicação de análise térmica (DSC) na identificação e caracterização de materiais têxteis

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A identificação de fibras é uma necessidade constante quer a nível de investigação quer industrial e é feita através de um conjunto de ensaios que implicam grande consumo de tempo e recursos e que incluem tais como a observação microscópica, comportamento ao calor e à chama, ponto de fusão, solubilidade, testes de coloração, índice de refração e massa volúmica. O presente trabalho pretende analisar a utilização da calorimetria diferencial de varrimento (DSC) na identificação e caracterização de fibras têxteis.

As características dos materiais que podem ser identificadas usando análises térmicas, incluem a temperatura de transição vítrea; cristalinidade; temperatura de fusão; temperatura de cristalização a frio; processos térmicos associados à libertação de água e degradação térmica [1,2,3].

Neste trabalho, serão apresentados vários casos práticos, sobre a aplicação desta técnica analítica nas fibras naturais e sintéticas. Um dos estudos realizados refere-se à identificação de fibras naturais, como o algodão e sintéticas, como a poliamida. É também descrita a caracterização de polímeros modificados, em que um dos exemplos se refere à caracterização do poli (álcool de vinilo) (PVA) modificado por indução fotoquímica na presença de um iniciador (Fig 1).

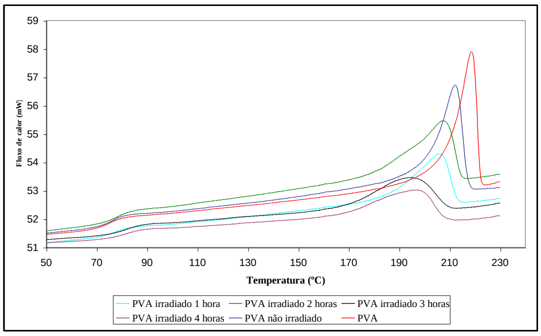

Fig.1. Curvas de DSC do PVA original (MM=72000 g/mol, 98 % mol) e irradiados durante 1 a 4 h na presença de 6% de benzoato de sódio.

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Polymer additives - the influence on ultrasonic metal welding

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In the ultrasonic metal welding process, metals are joined by the application of high frequency vibrations, under moderate pressure, in which the vibrations are applied parallel to the interface between the parts. The high frequency relative motion between the parts forms a solid-state weld through progressive shearing and plastic deformation over the surface asperities that disperses oxides and contaminants and brings an increasing area of pure metal contact between adjacent surfaces.[1] The problems of oxides, high thermal conductivity, high electrical conductivity, intermetallic and brittle alloys are not significant in the ultrasonic welding since the ultrasonic equipment should be capable of monitoring energy and controlling the critical welding variables.[2] However, on automotive industry, for applications that involve the ultrasonic welding of cables it has been seen that depending on the insulation material of cables the metal bonding is not always stronger as it should be.

PVC being largely used on automotive industry and it is considered one of the most versatile polymers due to their ability to react with various additives before being processed into final products. By the choice within a wide range of chemicals, it is possible to obtain PVC compounds with the necessary features for each application. [3] There are a large number of variables that affect the properties of PVC such as the degree of crystallinity, the glass transition temperature, molecular weight or morphology. The mechanical, thermal or chemical properties of the manufactured product may have specific characteristics, primarily due to two main factors: 1) Inclusion of appropriate additives in PVC formulations (plasticizers, pigments, lubricants, colorants, flame retardants, etc.) and 2) a variety of manufacturing processes such as extrusion, injection, etc. [4]

In the insulation of cables, PVC is used in the flexible form, but due to PVC thermal instability, processing it is virtually impossible without the addition of additives. The additives are generally high molecular weight thermoplastic and are added in small quantities with three main functions, accelerate the fusion process; improve the rheological and mechanical properties. [4] The biggest disadvantage of PVC is the easiness to degrade by the action of temperature or ultraviolet radiation. [5]

In order to identify if polymer additives are influencing the ultrasonic welding process ability, a study was conducted using electrical cables with PVC insulation.

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XXII Encontro Luso-Galego
Química

COMUNICAÇÕES ORAIS E EM PAINEL

Química e Ambiente

Environmental impact of the mycoestrogen zearalenone from agriculture runoff: risk assessment in surface waters

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Zearalenone (ZEA) – the only known mycoestrogen – is a non-steroidal estrogenic mycotoxin produced by several species of fungi of the genus Fusarium [1]. ZEA toxicity is related to the chemical structure of this estrogenic mycotoxin, similar to the naturally occurring estrogen, being classified by the International Agency for Research on Cancer in the group 3 [2]. Most surveys indicate that ZEA occurs primarily in pre- or post-harvest maize and other cereals [3]. Previous Portuguese studies have, in fact, demonstrated the occurrence of ZEA in different type of flours [4] and in maize bread [1], showing that the presence of this mycotoxin in maize crops is unmistakable. Nonetheless, while much research has been carried out on the analysis of mycotoxins in food and feed matrices, human and husbandry animal exposure, and related health effects, the environmental exposure to mycotoxins has been scarcely investigated [5].

This study provides the first environmental risk assessment (ERA) of ZEA based on a broad-scale investigation on its incidence in surface waters, from Portugal. Good analytical performance was obtained through sample filtration and immunoaffinity columns (IAC) cleanup and detection and quantification by liquid chromatograph with-tandem mass spectrometry (LC/MSn).

ZEA levels were evaluated in 38 samples, collected upstream wastewater treatment plants (WWTPs), from 7 Portuguese rivers and 1 creek, in two different seasons. Overall, 23.7% were contaminated, at levels ranging between 5.6 and 82.6 ng/L. The greatest mycotoxin concentration was observed during spring, however no statistical differences were observed when compared to the autumn sampling campaign. ZEA potential ecotoxicological risk to different trophic levels of aquatic organisms was evaluated by means of risk quotients (RQ) calculation. Fish appeared to be the most sensitive species followed by daphnids and algae. Although all the RQs calculated were lower than 1, a certain risk could be expected for fish with a RQ between 0.1 and 1.

Our results confirm that this mycotoxin can be a relatively frequent contaminant on surface waters upstream WWTPs, providing evidence of its agricultural runoff into the environment. ZEA might contribute to the overall estrogenic activity in the environment and could therefore pose a risk for wild fish in their natural habitat, enhancing their estrogenic endocrine disruption. Such exposure can also be dangerous due to potential accumulation with other mycotoxins and might represent further hazard especially if the contaminated water is used in food production for humans and animals.

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Descontaminação de águas com resíduos alimentares – uma alternativa promissora?

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A contaminação por metais em águas é uma preocupação global devido à elevada toxicidade de alguns elementos e ao seu caráter persistente no ambiente. Elementos como arsénio, chumbo, mercúrio e cádmio continuam a ocupar os primeiros lugares na lista de substâncias perigosas prioritárias que devem ser reduzidas/eliminadas do ambiente, nomeadamente das águas [1]. Por este motivo, a remoção destes elementos de águas tem originado grande interesse científico, tendo sido realizados vários os estudos com diferentes tipos de materiais com o objetivo de diminuir o grau de contaminação das águas.

A biosorção é considerada uma área de grande potencial e uma alternativa atrativa para a remoção de metais de águas contaminadas, pelo baixo custo e elevada disponibilidade dos materiais usados, podendo ser considerado, na maioria dos casos, um método "amigo do ambiente". No entanto, a maioria dos trabalhos encontrados na literatura sobre biosorção, corresponde a estudos com concentrações dos elementos potencialmente tóxicos que são ambientalmente pouco realistas e utilizam elevadas quantidades de material no processo de remoção [2]. Para além disso, a maior parte dos trabalhos foca-se em sistemas mono-elementares e há ainda pouca informação sobre sistemas multi-contaminante e ainda menos sobre sistemas com águas reais. [3].

Neste trabalho estudou-se a capacidade de biosorção de diferentes resíduos alimentares tais como casca de banana, casca de batata, casca de batata doce e casca de ovo, aplicados a sistemas multi-elementares, usando baixas quantidades de material e concentrações realistas de contaminantes em água da torneira. A eficiência dos materiais foi testada em sistemas quaternários de Hg, Cd, Pb e As com concentrações de 50 µg/L para todos os contaminantes, com uma massa de material sorvente de 500 mg/L. A análise de Hg foi efetuada por espectroscopia de fluorescência atómica com vapor frio (CV-AFS) e os restantes elementos foram quantificados por espetrometria de massa por plasma acoplado indutivamente (ICP-MS).

Nas condições testadas, a afinidade dos materiais estudados para os contaminantes selecionados teve a seguinte ordem Hg>Pb>Cd>>As. A casca de banana foi o material mais eficiente, apresentando elevadas percentagens de remoção de Hg (95%) e Pb (80%).Embora com percentagens de remoção mais baixas, os restantes materiais também se mostraram eficientes, essencialmente na remoção de Hg (90%) e foram ligeiramente menos eficientes para Cd e Pb (entre 40 e 65%).No caso do arsénio, nenhum material provou ser eficiente na remoção deste elemento. Este trabalho evidencia a valorização de resíduos alimentares de baixo custo e bastante disponíveis, sem custos adicionais de pré-tratamento dos materiais, permitindo reduzir significativamente os níveis de contaminação numa água da torneira que tenha sido sujeita a poluição.

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Environmental friendly techniques for zinc selective recovery from spent alkaline batteries

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Alkaline batteries are considered as hazardous solid wastes for the environment, when they are spent, due to their heavy metals content. Growth of the world population and demand for a better quality of life cause increment of batteries consumption. Since the storage capacity of hazardous waste dumpsites are constraint and the cost of raw materials are increasing, there is an essential tend for developing battery recycling processes [1, 2].

Hydrometallurgical processes are usually based on the dissolution of metal phases in acid or alkaline solutions [3, 4]. Since these processes need high temperature and concentrated solutions in a long reaction time to overcome these disadvantages ultrasound- and microwave-assisted leaching were used to minimize the energy and optimize the reaction conditions [5, 6].

The main aim of this work was to evaluate the efficiency of ultrasound and microwave-assisted leaching to selective recovery zinc from spent alkaline batteries and compares the results with conventional leaching [7]. For this purpose, H_2SO_4 was used, as a leaching agent, for all extracting strategies. For conventional leaching, optimized conditions resulted in 90% of Zn extraction (H_2SO_4 1.5 mol/L, 3 h, 80ºC). The use of microwave energy reduced the time and promoted Zn extraction to 96% (1 cycle, 30 s, H_2SO_4 1 mol/L) while these results evidenced that no significant differences, in terms of selectivity, were achieved when microwave was used instead of conventional conditions. For the optimum determined conditions of ultrasound-assisted leaching method (2 min, 0.1p 20% amplitude, H_2SO_4 1 mol/L), 92% of Zn extraction was obtained. Both, ultrasound and microwave-assisted leaching strategies were very adequate for Zn recovery in low acid concentration and short period of process. However, higher purity grade of Zn solution (83.3%) in ultrasound made this method more selective.

Acknowledgments
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Degradação de compostos fenólicos por radiação gama

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O processo de transformação da cortiça envolve o uso de grandes quantidades de água e, consequentemente, uma elevada produção de águas residuais, principalmente na etapa de cozedura das pranchas de cortiça. O efluente que resulta deste processo apresenta uma carga orgânica elevada com pH baixo (pH ~ 4.5) devido à extração a quente de compostos solúveis em água, como os ácidos fenólicos (ácido gálico, ácido quínico, ácido protocatecuico, ácido vanílico, ácido siríngico e ácido elágico) e taninos. Estes compostos recalcitrantes e tóxicos [1] não são degradados pelos métodos de tratamento convencionais, causando impacto ambiental.

Os Processos de Oxidação Avançados (POA), e em particular a radiação ionizante, têm demonstrado ser eficientes no tratamento de efluentes [2, 3], pela formação de espécies altamente reativas, como o radical hidroxilo. Esta tecnologia não requer a adição de reagentes químicos e não forma substâncias poluidoras e radioativas.

Neste trabalho, pretendeu-se estudar a degradação de compostos fenólicos por radiação gama utilizando diferentes condições experimentais. As irradiações foram realizadas utilizando um equipamento experimental Co-60 (C^2TN-IST) e doses de radiação gama de 5, 10, 20 e 50 kGy com débito de dose de 1.6 $kGyh^{-1}$. Os compostos selecionados, usados como modelo, são o ácido gálico, ácido protocatecuico, ácido vanílico e acido siríngico. As soluções (dos compostos isolados e em mistura quaternária) foram preparadas a diferentes pH (natural, 3, 7 e 10), arejadas ou saturadas em óxido nitroso (N_2O) ou oxigénio (O_2), de modo a promover a formação de diferentes radicais. A degradação dos compostos foi posteriormente analisada por HPLC-DAD.

Os resultados obtidos indicaram diferenças significativas na degradação dos compostos alvo em mistura comparativamente com os compostos isolados. Na mistura, poderá ocorrer uma competição entre os ácidos fenólicos, o que resulta numa menor degradação de cada um, mesmo com doses de radiação mais altas. Relativamente aos compostos isolados, são notórias as diferenças entre as amostras arejadas e as que estão sob atmosfera de N_2O e O_2. Foi verificado um aumento da degradação nas amostras de ácido gálico (pH natural) saturadas em O_2, bem como nas amostras de ácido protocatecuico (pH natural e pH 3) saturadas em N_2O e O_2.

A identificação dos mecanismos de radiólise de compostos fenólicos é importante para a otimização de processos de tratamento de efluentes com tecnologias alternativas como a radiação gama e está presentemente em curso.

Agradecimentos
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Previsão da ocorrência de *blooms* de cianobactérias na Albufeira do Roxo

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O aparecimento de cianobactérias nas origens de água superficiais acarreta sérios impactes ecológicos e económicos. Estes são resultantes da presença de cianotoxinas, metabolitos secundários produzidos por estes microrganismos, prejudiciais para o Homem (efeitos neurológicos, hepatotóxicos e dermatóxicos) [1]. O fenómeno dos *blooms* de cianobactérias em Albufeiras do sul de Portugal apresenta particular severidade do ponto de vista operacional e de desempenho das infraestruturas de abastecimento de água [2]. Nesse sentido, as entidades gestoras de serviços de água têm que se dotar de ferramentas expeditas que permitam a antevisão desses fenómenos num período que lhes permita adotar em tempo útil protocolos de prevenção, controlo e tratamento de água [3].

No caso em estudo – Albufeira do Roxo, em Beja – foram recolhidos e sistematizados dados de monitorização da qualidade de água disponibilizados por diversas entidades. Após a sua análise e tratamento estatístico, foram utilizadas ferramentas lineares (PLS) e não lineares (redes neuronais artificiais) para a criação de modelos preditivos da ocorrência de *blooms* de cianobactérias. No final do período de modelação selecionou-se o modelo que melhor se adequa às previsões da ocorrência de *blooms* na Albufeira em questão.

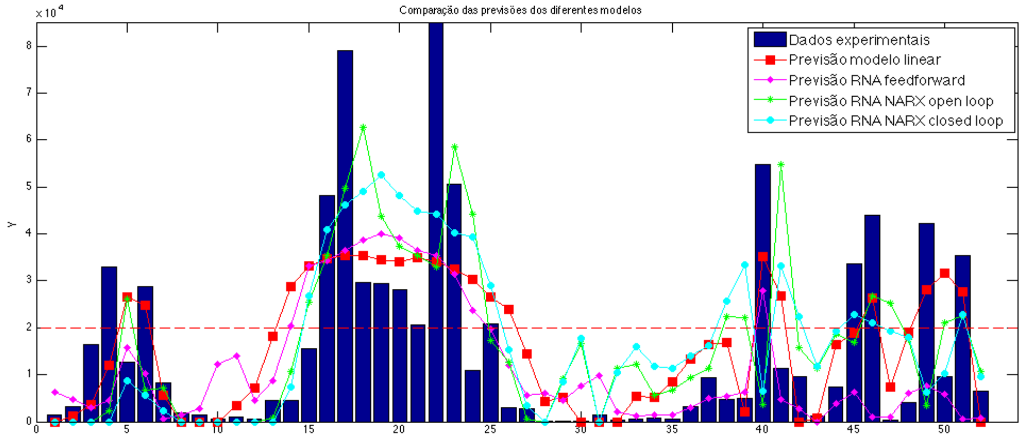

Fig.1. Comparação entre os valores experimentais de *blooms* de cianobactérias e os previstos através de diferentes abordagens de modelação.

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Porphyrin sensitized-graphitic carbon nitride for photocatalytic hydrogen production in water

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Currently, the world energy demand is largely dependent on fossil fuels, such as petroleum, coal, and natural gas, raising serious sustainability and economic issues. Consequently, the quest for alternative, renewable and sustainable energy sources is of great significance. Among various potential solutions, solar hydrogen (H_2) production from water splitting offers an environmentally clean energy for the future and exhibits a method for solar energy storage and chemical energy conversion [1,2]. An ideal route for H_2 evolution is semiconductor-based water splitting under solar light irradiation [3]. The most challenging task in photocatalytic water splitting is to develop efficient and stable photocatalysts which are capable of sufficiently absorbing solar light for splitting water.

Graphitic carbon nitride (g-C_3N_4) [4] is an inexpensive metal-free semiconductor that presents an appealing electronic structure with a suitable band gap for both water reduction and oxidation, as well as physical stability [5]. The utilization of g-C_3N_4 as a photocatalyst for H_2 evolution has been intensively studied in recent years [5]. However, the photocatalytic efficiency of pristine g-C_3N_4 is still not satisfactory due to the rapid recombination of photoinduced electron-hole pairs, low visible light utilization efficiency (band gap of ~2.7 eV with an absorption edge just at ~450 nm) and small surface area [5]. Among the various strategies developed to extend the spectral response region of semiconductors, dye sensitization seems to be very promising [5]. Besides their similarity to the key dyes of natural photosynthesis (chlorophyll), porphyrins and metalloporphyrins present several advantageous coordination, redox and photoinductive properties (high thermal and photostability, spectral response in the visible range, long-lived excited-states and high excited-state redox potential), which can be exploited for the formation of hybrid heterostructures that may overcome the limiting steps of visible light absorption and charge recombination [5].

In the present study we report the results of the photocatalytic hygrogen production using hybrid composites of *meso*-tetra(3-carboxyphenyl)porphyrin, abrreviated as m-CO_2HTPP, and g-C_3N_4, prepared by a simple impregnation method. The structure and morphology of the materials was characterized by several techniques (X-ray diffraction, UV-vis diffused reflectance spectra, photoluminescence, thermogravimetric analysis, Fourier transform infrared spectra and N_2 adsorption-desorption isotherms). Deaerated aqueous solutions containing the *as*-prepared hybrid material, a sacrificial electron donor, an electron acceptor and Pt as co-catalyst were tested towards H_2 production by irradiation with UV-vis light. The efficient sensitization of g-C_3N_4 with *m*-CO_2HTPP porphyrin was evidenced by UV-vis, infrared and X-ray diffraction analysis. The photocatalytic experiments show that the hybrid (g-C_3N_4+*m*-CO_2HTPP) duplicates the amount of H_2 evolved when compared with *m*-CO_2HTPP porphyrin alone (202 μmol and 105 μmol, respectively). The improved performance of the hybrid composite can be attributed to the increase of the specific surface area, enhancement of visible light absorption and the efficient separation of the photogenerated electron-holes pairs. This work demonstrates the potential application of carbon nitride sensitized porphyrins for solar energy conversion.

Acknowledgements

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Minimization of the release of endotoxins and trihalomethanes in the aquatic system

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The occurrence of endotoxins and trihalomethanes in the effluents of wastewater treatment plants (WWTPs) might suppose an important threat to the environment and, if water reuse is considered, even by potential consumers. The presence of endotoxins (bioaerosol constituents) seems to play a causal role in the gastrointestinal diseases for workers in the wastewater industry [1], while the water chlorination process leads to the appearance of halogenated disinfection by-products, such as trihalomethanes, with mutagenic and toxic adverse effects. The aim of this research is to determine the best physic—chemical treatment to reduce the release of endotoxins and trihalomethanes in the effluents of WWTPs and the inlet of drinking water plants (DWP). Different advanced alternatives were applied: adsorption with activated carbon, tertiary membrane filtration and ozonation.

Comparing the concentration of endotoxins in the effluent of two alternative biological wastewater treatments, a considerably higher concentration of these pollutants was detected in the outlet of a secondary conventional activated sludge (CAS) plant (843 EU mL^{-1}) than in the effluent of a membrane bioreactor (MBR) system (100 EU mL^{-1}) [2]. The best posttreatment alternative was the membrane filtration (above 90%) in order to reduce the release of endotoxins after the biological applied treatments (fig.1), whereas only removals of 30% were achieved when the powdered activated carbon was used as adsorbent even at long contact times. In the case of the ozonation, low removals were observed (<40%) and more toxic intermediates were generated at low contact times (below 30 min).

In the inlet of a DWP, the trihalomethanes found were chloroform (16%), bromodichloromethane (<3%), bromoform (74%) and dibromochloromethane (6%). The active carbon was a strong adsorbent of these pollutants and removals above 80%, were achieved, mainly in the case of the bromoform. However, no effect of the use of ozone in the removal of trihalomethanes was observed.

In conclusion, if both types of pollutants are targeted, the best alternative is the combination of a membrane filtration with the use of as activated carbon due to result in a high reduction of the release of endotoxins and trihalomethanes (more than 80%) in the environment.

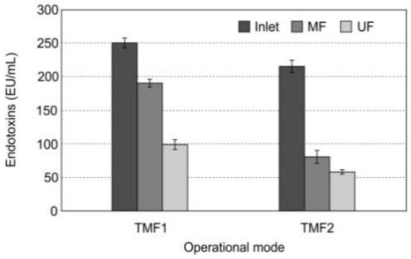

Fig.1. Removal efficiencies of endotoxins by a tertiary filtration membrane: MF (microfiltration), UF (ultrafiltration). *In the absence (TMF1) and presence (TMF2) of suspended biomass.*

Acknowledgments
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The influence of the water matrix on the performance of sulfamethoxazole removal by catalytic wet peroxide oxidation

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Laboratory grade purified ultrapure water (UP) is an attractive matrix to evaluate the performance of advanced water treatment technologies, mainly due to its easy manipulation, simplicity and reproducibility of the experimental results. However, antimicrobial agents like sulfamethoxazole (SMX) are typically found in much more complex matrices throughout the urban water cycle, such as in raw and in conventionally treated urban wastewater (UWW) [1] or drinking water (DW) [2], or in surface water and groundwater [3]. Bearing this in mind, the influence of the water matrix on the performance of SMX removal by catalytic wet peroxide oxidation (CWPO) – an advanced oxidation process typically operated at atmospheric pressure and mild temperature, was assessed in this work using secondary treated UWW and DW spiked with SMX (500 μg L^{-1}). Synthetic water (SW) containing humic acid (HA; 40 mg L^{-1}), bicarbonate (500 mg L^{-1}), sulphate (60 mg L^{-1}) and chloride (200 mg L^{-1}), was also tested in order to mimic the presence of the typical constituents of conventionally treated UWW and DW. As observed in Fig. 1a, the performance of CWPO decreases with the increasing complexity of the water matrix. This phenomenon was ascribed to the scavenging effect promoted by the different anions considered, as well as to the negative impact of dissolved organic matter typically found in secondary treated UWW, as simulated by the presence of HA (cf. Fig. 1b).

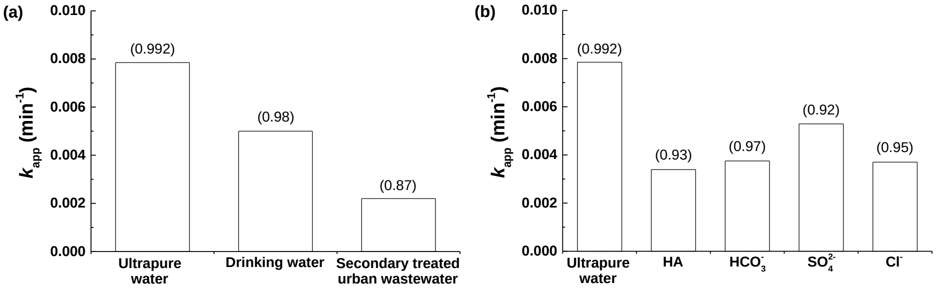

Fig.1. Apparent first order reaction rate constants (k_{app}) for SMX degradation by CWPO (6 h), when using (a) UP, DW and UWW and (b) UP and synthetic UWW, under the same operating conditions.

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Do by-products of oxytetracycline retain its antibacterial activity after irradiation under sunlight?

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Oxytetracycline (OTC) is one of the authorized antibiotics most used in aquaculture. The main concern related to the use of antibiotics, as is the case of OTC, is the emergence of bacterial resistance. Some authors refer that about 70-80 % of antibiotics used in fish feed in aquaculture are excreted in water [1], contributing to contamination of aquatic systems, which can act as a reservoir of resistance genes [2]. The resistance can reach humans through transfer of drug-resistant pathogens from the aquatic environment [3].

In this work, several irradiation experiments of OTC were performed using simulated sunlight, with an irradiance of 550 W/m^2, in the following aqueous matrices: aquaculture's waters collected from two different aquaculture companies and aqueous solutions of phosphate buffer (0.001 M) without and with synthetics sea-salts (21 ‰). Detection of OTC and its photoproducts was made by HPLC-DAD and HPLC-fluorescence. The well-diffusion method was chosen to perform the antibacterial assays, before and after OTC photo-degradation. The bacterial strains considered to these experiments were *Escherichia coli*, *Vibrio* sp. and *Aeromonas* sp.

The results revealed firstly that different photo-products are formed in the different aqueous matrices, justifying the study of the antibacterial activity in all of them. During the irradiation, the biological activity decreased in all matrices and, in some cases, no biological activity was detected, suggesting that, in these cases, the OTC by-products do not retain its antibacterial activity after irradiation under sunlight.

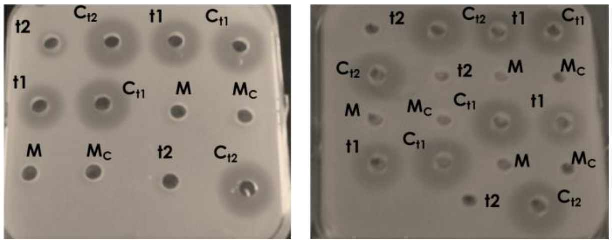

Fig.1. Antibacterial assays with *Vibrio* sp. in synthetic (left) and natural (right) water samples.

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Cleaning up metal contaminated water through living algae: experiments with *Ulva lactuca*

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Sustainable management of water resources under climate change, population growth and economic development is a current environmental challenge. Because wastewater treatment, particular the removal of metals and metalloids can be very difficult and costly [1], the European Water Framework Directive [2] encourages the development of innovative, cheap and effective technologies for water treatment, to achieve good ecological status.

Largely available biomasses and bio-based materials have been applied to bind and retain metals with relative success. However, the potential of living macroalgae and their bioaccumulation capabilities have been little explored. Moreover, most of works are devoted to the removal of a single contaminant in synthetic water, usually at unrealistic experimental conditions.

This work evaluated the uptake of As, Cd, Cr, Cu, Hg, Mn, Ni and Pb by the macroalga, *Ulva lactuca*, from a simulated wastewater, under environmentally realistic concentrations. Different algal dosages (1.5 to 6.0 g L^{-1}, fresh weight) and water salinities (15-35) were studied. Removal efficiencies and bioconcentration factors were calculated, and bioaccumulation kinetics was described using kinetic models.

The simultaneous uptake of 8 metal(oid)s by *Ulva lactuca* points to the possibility of decreasing trace element concentrations in wastewaters, particularly Hg, which legal criteria for drinking water was accomplished. Salinity above 15 had no effect on the removal efficiencies during the short experiments. For all contaminants, a very good agreement between estimated and quantified concentrations of contaminants in *U. lactuca* tissues was observed.

Overal, results highlight the potentiality of macroalgae-based biotechnologies to water remediation and water reuse through environmentally friendly, and cost-effective processes.

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Sistema anaerobio integrado para recuperación de aguas residuales a temperatura ambiente en climas europeos

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Resumen. La tecnología SIAM (Sistema Integrado de reactor Anaerobio metanogénico y biorreactor de Membranas, patente ES 2401445 B2) ha sido desarrollada y validada a escala piloto para el tratamiento de agua residual sintética por el Grupo de Ingeniería Ambiental y Bioprocesos de la Universidad de Santiago de Compostela [1]. El Proyecto LIFE SIAMEC ahonda en la aplicación de esta tecnología en aguas reales, domésticas e industriales, en los climas mediterráneo y atlántico, respectivamente. LIFE SIAMEC pretende superar los principales inconvenientes de tratamientos anaerobios a temperatura ambiente, gases de efecto invernadero y eliminación de nitrógeno, donde el metano disuelto en el efluente será usado como fuente de carbono para desnitrificar [2][3] tanto en un post-tratamiento basado en membranas como no basado en membranas. Este trabajo se va a centrar en el prototipo demostrativo del mediterráneo que ha depurado agua municipal real.

Objetivos. Los objetivos de LIFE SIAMEC son:

- Contribuir a mitigar los problemas de escasez de agua incentivando la recuperación de aguas residuales para reúso.
- Demostrar la viabilidad del tratamiento anaerobio, altamente influenciado por la temperatura, mediante la tecnología SIAM.
- Estudiar de la viabilidad, sostenibilidad y transferibilidad de la tecnología SIAM en otras regiones de la Unión Europea.

Materiales y métodos. El prototipo del mediterráneo consta de los siguientes elementos: tamiz y decantador primarios, con caudal 600 L/h; tanque de laminación 1 (180 L); reactor anaerobio de tipo UASB, con caudal de alimentación de 400 L/h y volumen útil 3’87 m^3 y tanque de laminación 2 (90 L). La salida del reactor UASB se trata en paralelo en dos unidades: Biorreactor de Membranas (BRM) y reactor biológico híbrido con decantador. El BRM de la línea SIAM, con caudal 200 L/h y volumen 2’06 m^3, está compuesto por cámaras anóxica, aerobia y de filtración (con membrana de ultrafiltración). El reactor biológico híbrido con decantador, opera con un caudal de 100 L/h y volumen 2’11 m^3, consta de cámaras anóxica y aerobia, y un decantador lamelar.

Resultados. El prototipo ubicado en clima mediterráneo se ha operado más de 300 días en su etapa anaerobia y más de 200 para las líneas SIAM y convencional. La eliminación de materia orgánica en el sistema UASB ha sido superior al 50%, valor cercano al 60-65% que alcanza un UASB en aguas residuales urbanas. El efluente del sistema UASB se ha tratado en los dos sistemas biológicos dispuestos en paralelo, uno con membrana y otro sin membrana. En ellos se ha observado una alta eliminación de materia orgánica, 90% y 75%, respectivamente. En cuanto a la eliminación de nitrógeno se ha comprobado que el sistema con membranas es capaz de reducir el NT de 70-90 mg/L a menos de 30 mg/L, siendo mucho más robusto y estable que el sistema sin membranas. La eliminación anaerobia de gran parte de la materia orgánica biodegradable permite reducir notablemente la producción de lodo biológico y consumo de energía eléctrica de la planta.

Agradecimientos
Al proyecto LIFE14 ENV/ES/000849, Siamec, así como al personal técnico de la EDAR de Cabezo Beaza en Cartagena, que han hecho posible este estudio.

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Eliminación simultánea de nitrógeno y metano en aguas residuales mediante el empleo de un biorreactor híbrido

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Resumen: El tratamiento anaerobio de aguas residuales domésticas se utiliza ampliamente en países de climas cálidos y templados, debido al menor consumo de energía eléctrica y la baja producción de lodos, pero presenta dos inconvenientes importantes: baja eliminación de nitrógeno total contenido en fase líquida y emisiones de un gas de efecto invernadero, metano, al medio ambiente. En este estudio se propone el empleo del metano disuelto, presente en los efluentes de reactores anaerobios metanogénicos como fuente de carbono para eliminar nitrógeno.

Hasta un 50% del metano producido en los reactores anaerobios puede ser liberado al medio, disuelto en el efluente [1]. El metano tiene un potencial de calentamiento global fuerte, 28 veces superior al CO_2 [2]. Se plantea como objetivo que este metano pueda ser aprovechado para eliminar nitrógeno del agua residual, mediante el uso de microorganismos capaces de llevar a cabo la eliminación conjunta de metano y nitrógeno en las aguas. Para ello es importante analizar la evolución de los microorganismos metanótrofos de lento crecimiento que llevan a cabo dicha reacción.

Materiales y métodos: Para tratar de reducir el impacto de las tecnologías anaerobias más utilizadas, con configuración UASB, se propone la integración de un biorreactor híbrido, con presencia de biomasa adherida y en suspensión, como post-tratamiento. En este estudio se ha operado durante 330 días, a temperatura ambiente, una planta piloto constituida por un reactor UASB de 120 L. El sistema de post-tratamiento híbrido consta de 2 cámaras, la primera anóxica, y la segunda aerobia de 36 y 20 L, respectivamente, así como de un decantador de 10 L. Se ha alimentado al sistema con agua residual sintética (DQO≈500-800 $mg \cdot L^{-1}$ y $N\text{-}NH_4^+ \approx 40\text{-}70\ mg \cdot L^{-1}$). Se ha empleado un caudal de alimentación aproximado de 150 $L \cdot d^{-1}$ y una relación de recirculación (R), entre cámara aerobia y anóxica de 3.

Resultados: En presencia de biomasa en suspensión se han observado los mejores valores tanto en porcentajes de eliminación de CH_4, con valores promedio en la cámara anóxica de 56,6±16%, y de eliminaciones de NT globales de 24,7±5,9 mg $NT \cdot L_{feed}^{-1}$. Pero con el transcurso del tiempo la biomasa en suspensión ha sido lavada del sistema progresivamente, lo que ha propiciado la oportunidad de analizar el papel que desempeña en estos procesos, la biomasa adherida a los soportes, obteniéndose valores de entre un 43,1±14% de CH_4 y de 17,2±5,4 mg $NT \cdot L_{feed}^{-1}$ respectivamente. Es importante mencionar que la eliminación de CH_4 (confirmada por ensayos microbiológicos;FISH) y de nitrógeno no solo tiene lugar en la cámara anóxica sino también en la aerobia.

Agradecimientos

Al Ministerio de Economía y Competitividad de España que financió este estudio a través del Proyecto HOLSIA (CTM2013-46750-R) y a la Xunta de Galicia (GRC 2013-032 cofinanciado por FEDER).

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Avaliação da aplicação de macroalgas vivas na remoção e recuperação de terras raras em água salina

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Documentos recentemente divulgados pela Comissão Europeia classificam os elementos terras raras (REE) como matérias-primas críticas (CRM), devido ao seu elevado valor económico e reduzido número de fontes de matéria-prima. A procura destes elementos tem vindo a aumentar de forma crescente no uso de tecnologias verdes, designadamente carros elétricos, turbinas eólicas e baterias de elevado desempenho [1]. Os processos convencionais para a reciclagem de REE, como a pirometalurgia e hidrometalurgia [2], têm baixa eficiência e apresentam impactos ambientais consideráveis. O presente trabalho pretendeu avaliar a utilização de macroalgas vivas para a remoção e concentração de REE de desperdícios industriais ricos nestes elementos e de águas salinas.

Realizaram-se ensaios de remoção com as macroalgas vivas, *Gracilaria gracilis*, *Fucus vesiculosus* e *Ulva lactuca* em soluções mono e multi-elementares dos REE mais relevantes em termos de procura e risco de fornecimento. Foram usadas pequenas quantidades de macroalga por volume de solução (450 mg L^{-1}, peso seco) e concentrações iniciais dos REE consideradas realísticas. A cinética do processo foi caracterizada através da aplicação de modelos cinéticos reacionais amplamente aceites.

Os resultados apontam para elevadas percentagens de remoção pela macroalga vermelha (>90%), confirmada através de um método de digestão ácida da biomassa. A eficácia, simplicidade e baixo custo do processo de remoção através de macroalgas mostra a sua potencial aplicabilidade e responde ao alerta lançado pela Comissão Europeia.

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Otimização das condições de liquefação da *Cynara cardunculus* L.

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O estudo dos processos de liquefação a baixas pressões e temperaturas tem merecido grande atenção dadas as suas enormes potencialidades. O principal objetivo deste trabalho foi otimizar a percentagem de liquefação *Cynara cardunculus* L. pelo processo de poliálcoois [1]. *Cynara cardunculus* L. é uma planta nativa da região do Mediterrâneo, cultivada desde a antiguidade como um vegetal, utilizando técnicas de manejo intensivo. Hoje em dia C. Cardunculus L. está a ser utilizada para fins industriais, tais como a produção de pasta de papel, extracção farmacológica dos compostos activos, combustível entre outras. A amostra de *Cynara cardunculus* L. foi peneirada em três frações: > 40, 60-80 e < 80 mesh. A sua liquefação foi realizada num reator de camisa dupla aquecido a óleo utilizando-se etilenoglicol (EG) catalisado por ácido sulfúrico (SA) a 3% [2]. A biomassa liquefeita foi dissolvida numa solução metanol e filtrada, determinando-se o resíduo insolúvel gravimetricamente. Por forma, a optimizar as condições de liquefação foram realizados ensaios com diferentes tamanhos, temperaturas (entre 140º e 200º) e tempos (entre 15 e 120 min). Na Figura 1 são apresentados os dados obtidos para a variação da percentagem de liquefacção com a temperatura.

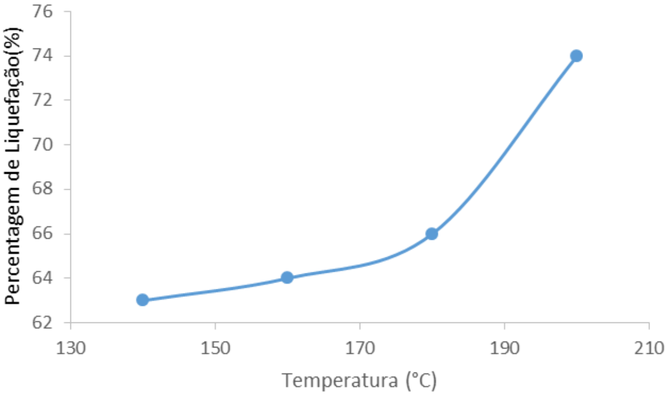

Fig. 1. Variação da percentagem de liquefação com a temperatura.

Os resultados mostram que quanto maior a temperatura, maior a percentagem de liquefação. Estudos relativos ao tempo de liquefação, utilizando uma temperatura de 200ºC, permitem verificar o aumento do rendimento de liquefacção com o tempo, apresentando a cura uma forma logarítmica.

Agradecimentos
Este trabalho é financiado por fundos nacionais através da FCT – Fundação para a Ciência e a Tecnologia, I.P., no âmbito do projeto UID/Multi/04016/2016. Agradecemos adicionalmente ao Instituto Politécnico de Viseu e ao CI&DETS pelo apoio prestado.

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Adsorption of Sudan IV from oily wastewater by using modified activated carbon materials

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A commercial activated carbon (AC: Norit ROX 0.8, D = 0.8 mm) was modified by chemical and thermal processes, following the procedures described elsewhere [1]. The materials were tested as adsorbents for the removal of a lipophilic pollutant, Sudan IV (S-IV), using a biphasic medium (water/cyclohexane) in order to simulate contaminated petroleum mixtures with water [2]. The AC was modified in successive steps considering: (1) grinding and sieving (< 250 µm) and (2) treatment with nitric acid, followed by hydrotreatment with urea and thermal treatment at 800 ºC under inert atmosphere, resulting in the adsorbents PAC and PACNAUT, respectively. Adsorption experiments were performed in a 500 mL batch glass reactor, using 2.5 g of adsorbent per litre of organic phase, 2.5 g/L_{OP}. Fig.1A shows results with different particle size (p_S), initial S-IV concentration ($C_{S\text{-}IV,0}$) and AC modifications. As expected, it can be observed that adsorption is faster when p_S is smaller. However, the powdered activated carbon (PAC) is not able to adsorb all S-IV in high initial concentration (500 mg/L). This target was achieved with PACNAUT (adsorption of S-IV was 90 % at 1 h and 2.5 g/L_{OP} of adsorbent, higher than the removal observed by other authors [2] at the same time and 4 g/L_{OP} of material). The adsorption kinetics was fitted by a pseudo-second-order model to the data obtained with 500 mg/L of $C_{S\text{-}IV,0}$ (Fig. 1B). PACNAUT has higher adsorption capacity (q_e) and rate constant (k_S).

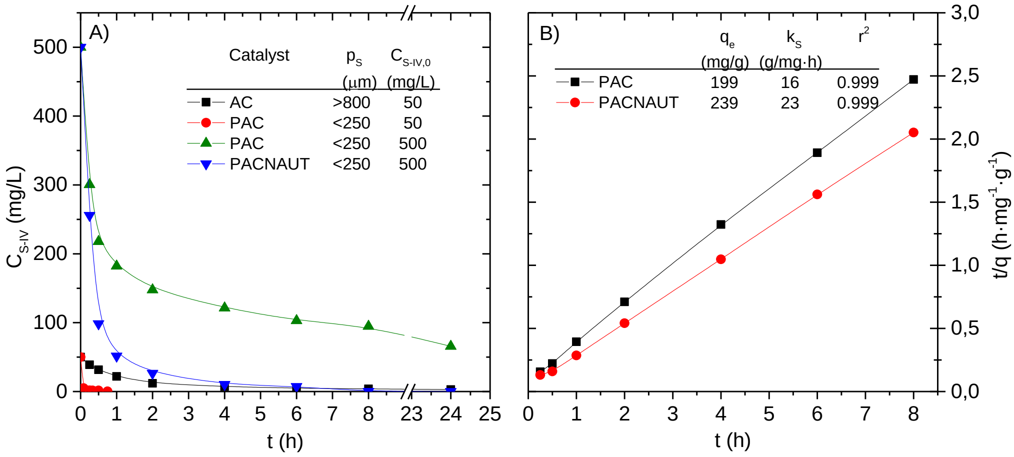

Fig.1. Removal of S-IV in runs performed with different p_S, $C_{S\text{-}IV,0}$ and adsorbents (A) and kinetic model fitted for the experiments carried out with PAC and PACNAUT materials at $C_{S\text{-}IV,0}$ = 500 mg/L (B).

Acknowledgments

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Determination of contaminants of emerging concern in surface water

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Environmental pollution has increased due to the use of a wide range of organic compounds, resulting from anthropogenic activities. The uncontrolled discharge of such substances into the environment originates their accumulation in aquatic compartments and might cause adverse ecological and human health effects, even when present at low concentrations. The growing concern about micropollutants in the environment and their pseudo-persistence trigger the need to develop methodologies for the analysis of organic compounds in environmental matrices.

A sensitive multi-residue analytical method was developed and optimized in this work, based on solid-phase extraction (SPE) followed by liquid chromatography–tandem mass spectrometry (LC-MS/MS) for surface water analysis of 11 contaminants of emerging concern (CECs). These CECs are included in the Watch List of European Commission Decision 2015/495/EU [1,2]. The optimized mobile phase in a Kinetex™ 1.7 µm XB-C18 100 Å column was set as methanol/water at gradient mode with a flow rate of 0.25 mL min^{-1}. The best recoveries for most target analytes were achieved with Oasis® HLB cartridges, using ethanol as conditioning and eluting solvent and 500 mL of water samples at pH 3. The method was validated as recommended by the international guidelines. The method detection limits were between 0.01 and 2.67 ng L^{-1}, whereas the method quantification limits were between 0.03 and 8.08 ng L^{-1}. The identification of the compounds was performed according to European Commission Decision 2002/657/EC, namely by analysing the retention time, two MS/MS transitions for each substance and the ion ratio.

The developed method was applied to 30 surface water samples collected in the spring of 2016, from Sousa and Ave Rivers, both located in Northern Portugal. From the 11 studied compounds, 4 (diclofenac, 2-ethylhexyl 4-methoxycinnamate, clarithromycin and azithromycin) and 7 (diclofenac, 2-ethylhexyl 4-methoxycinnamate, erythromycin, clarithromycin, azithromycin, imidacloprid and thiamethoxam) were detected in Sousa and Ave River samples, respectively. The most frequently found micropollutants were clarithromycin and 2-ethylhexyl 4-methoxycinnamate in the Sousa River and azithromycin in the Ave River. The highest concentrations were detected for diclofenac in the Sousa River (319.8 - 1856 ng L^{-1}) and imidacloprid in the Ave River (up to 136.5 ng L^{-1}). Other physicochemical parameters were measured for both studied rivers.

Acknowledgments
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Peanut shell as biosorbent for gallic acid recovery from aqueous solutions

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Gallic acid has a diverse range of industrial uses, as antioxidants in food, in cosmetics and in the pharmaceutical industry [1]. However, this compound could be considered as a organic contaminant present in several industrial effluents. Therefore, its removal from wastewaters as well as its recovery and isolation is very interesting from environmental and economical points of view, respectively. The peanut shell, an agriculture waste, was studied as a no-cost and readily accessible potential adsorbent for the removal and recovery of gallic acid from aqueous solutions. Thermodynamics studies were carried out based on the evolution of equilibrium isotherms of gallic acid on this biosorbent. For this purpose, three isotherm models (Langmuir, Freundlich and Temkin) were tested to fit the experimental equilibrium data and compared. The Langmuir model provided the best correlation for gallic acid biosorption onto peanut shell.

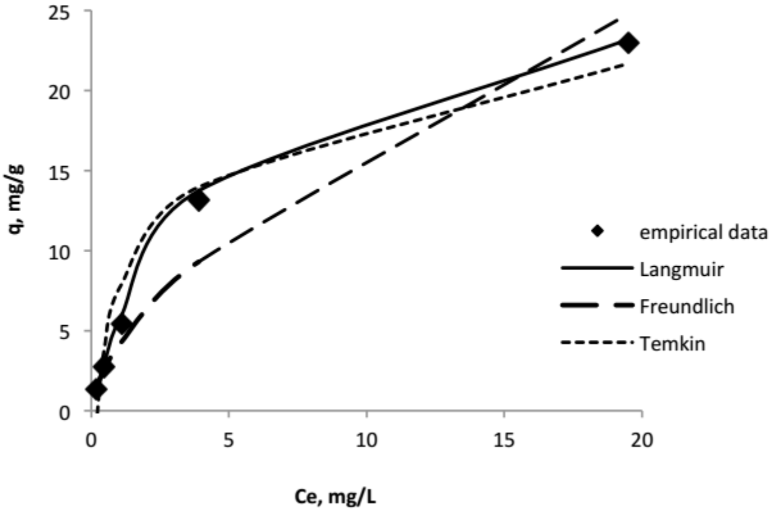

Fig.1. Langmuir, Freundlich and Temkin isotherms.

Finally, the negative values of ΔG indicated that the biosorption process was spontaneous and thermodynamically favorable. Accordingly, the peanut shell was shown to be a very efficient and low cost adsorbent, and a promising alternative for gallic acid recovery from industrial wastewaters.

Acknowledgements
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Importância da monitorização de massas de água em contexto urbano

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A gestão sustentável da água exige o seu uso e tratamento eficiente, estando pois expressa na Directiva Quadro da água da UE (2000/60/EC) a sua proteção e utilização adequada. A presença de lagos ou pequenas massas de água em parques ou jardins inseridos em contexto urbano trazem inúmeros benefícios que incentivam a preservação dessas áreas. A promoção da biodiversidade, o estabelecimento de corredores verdes, a contribuição para o controle de inundações e as dinâmicas socioeconómicas que se geram são apenas alguns exemplos destes benefícios, em que os parques detém um papel crucial. Atualmente tem-se vindo a valorizar e contabilizar os serviços ecossistémicos que eles prestam, posicionando-os como elementos estratégicos das cidades ao nível das infraestruturas verdes e azuis. São também laboratórios vivos que servem de veículo para a execução de atividades de educação ambiental voltadas para a conservação dos recursos hídricos e da própria natureza.

Visto que os lagos ou massas de água dos parques e jardins estão sujeitos a várias agressões de cariz antropogénico, muitas vezes de fontes difusas, em que a gravidade não está identificada assim como as suas repercussões, a avaliação da sua situação ambiental e estrutural com incidência na avaliação da qualidade das águas, é essencial. No presente trabalho pretendeu-se desenvolver uma metodologia para elaboração de um diagnóstico com a identificação dos problemas que afetam estas áreas, para numa fase posterior se elencar ações que visem a sua recuperação e preservação.

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Optimización del tratamiento hidrotémico de *Cantharellus tubaeformis* para la obtención de compuestos bioactivos

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Craterellus tubaeformis, también conocida como *Cantharellus tubaeformis* es un basidomicete ectomicírrico muy común de la familia Cantharellaceae. Esta seta se puede encontrar de forma silvestre, principalmente en el Hemisferio norte [1]. Las setas son consideradas como importantes fuentes de vitaminas, minerales, proteínas e hidratos de carbono [2]. También son reconocidas como alimentos funcionales debido a sus compuestos bioactivos, que ofrecen diversos efectos beneficiosos sobre la salud humana [3].

El principal objetivo del presente trabajo es determinar las condiciones de tratamiento óptimas, para las que se obtenga una fase líquida con un alto contenido en compuestos bioactivos y/o alta capacidad antioxidante. Para ello, la muestra se somete a un proceso de extracción mediante agua caliente presurizada en condiciones no isotermas, y se separa el extracto, que se analiza para evaluar el efecto de la severidad del tratamiento sobre la solubilización de la fracción de polisacáridos. También se determinan proteínas, compuestos fenólicos, capacidad antioxidante equivalente en Trolox y β-glucanos.

Los compuestos mayoritarios determinados en *Cantharellus tubaeformis* fueron carbohidratos y proteínas. En la Figura 1 se muestra la composición de los extractos en función de la temperatura de tratamiento. Se observa que a las temperaturas de 225ºC y 240ºC se obtienen los rendimientos máximos de solubilización de oligosacáridos y de compuestos fenólicos.

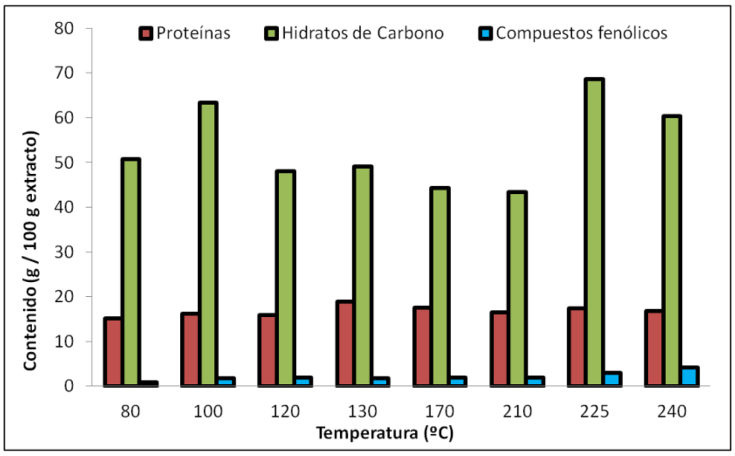

Fig.1. Efectos de la temperatura del tratamiento hidrotérmico sobre la composición de los extractos

Agradecimientos
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Membranas con óxido de grafeno para desalinización de aguas por osmosis directa

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Las reservas hídricas naturales están disminuyendo drásticamente debido a diversos factores como el cambio climático, etc. La búsqueda de nuevas estrategias para la producción de agua limpia a partir de fuentes alternativas es de vital importancia no sólo para la vida humana sino también para el desarrollo industrial. La osmosis directa (FO) es un proceso que ha ganado interés en los últimos años en el área de la desalinización, debido a su baja energía de operación y a la baja desactivación de sus membranas. Sin embargo, las propiedades de las membranas comerciales de FO impiden que el proceso sea competitivo comparado con la osmosis inversa. Los nanotubos de carbono, y más recientemente, el óxido de grafeno (GO) han demostrado tener un enorme potencial para mejorar las propiedades de las membranas de desalinización [1-3]. En este estudio, membranas de polisulfona (PS) con diferentes derivados de grafeno, en concreto GO y GO reducido (rGO), fueron preparadas por el método de inversión de fase, analizando la diferente carga y química superficial del material añadido, así como la composición del baño de coagulación. Estas membranas de PS fueron usadas como soportes de membranas con materiales compuestos de lámina delgada (TFC), cuyo comportamiento fue estudiado en FO de agua salada empleando diferentes configuraciones.

La caracterización física-química de las membranas fue analizada por diferentes técnicas tales como, microscopía electrónica de barrido, medidas de porosidad, FTIR, termogravimetría y determinación del ángulo de contacto. La permeabilidad de las membranas de PS fue determinada por medidas de filtración con agua DI a una presión de 0.5 bar, mientras las membranas de TFC fueron analizadas usando agua DI y una solución acuosa de NaCl (0.6 M) como disoluciones de alimentación y permeado, respectivamente [3].

Las membranas de PS presentaron una estructura asimétrica formada por una capa superior delgada-densa y una sub-capa porosa. La adición de GO favoreció la formación de membranas de PS con una estructura más porosa compuesta por poros alargados, mientras que los macrohuecos fueron principalmente obtenidos en la membrana de PS pura o con rGO. Además de mejorar la estructura de las membranas, el GO permite obtener membranas con menores ángulos de contacto y así, una mayor hidrofilicidad superficial. Por otro lado, las membranas obtenidas con baño agua/isopropanol presentaron una mayor porosidad que aquellas formadas con sólo agua. Las membranas con GO obtuvieron permeabilidades superiores a la membrana de PS pura o con rGO en los ensayos de filtración. Por otro lado, los mayores flujos de agua con las membranas de TFC fueron obtenidos en modo PRO (capa activa de la membrana orientada hacia la disolución de permeado), ya que la concentración de polarización interna es menor en este caso, que cuando se opera en FO (capa activa orientada hacia la alimentación). En general, las membranas con GO permitieron obtener mayores flujos de agua y menores flujos de soluto inverso que la membrana con rGO. Ambas membranas con GO o rGO presentaron mejor comportamiento que la membrana de PS pura, independientemente del tipo de baño de coagulación usado. La membrana de TFC más eficiente fue aquella preparada con un soporte de PS con 0.1 % de GO y formada en un baño agua/isopropanol.

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Valorização da borra de café

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O café é uma bebida apreciada por milhões de pessoas em todo o mundo e cada vez mais são realizados estudos para comprovar os seus benefícios, esta bebida leva porém a produção de um resíduo, a borra de café. A borra de café representa um resíduo biodegradável e com elevada riqueza química que deve ser valorizada. Com este trabalho pretendeu-se estudar a composição química geral da borra do café [1] e isolar a holocelulose deste subproduto, por forma a avaliar o seu potencial para a produção de pastas celulósicas. A borra de café foi sujeita a tratamentos de oxidação por forma a isolar-se a holocelulose [2]. Para a obtenção da holocelulose de café efetuaram-se dois tipos de tratamento oxidativo, o cozimento com peróxido de hidrogénio alcalino (PHA) e o cozimento com ácido peracético (AP). O tratamento com PHA foi realizado num erlenmeyer de 250 mL com controlo de temperatura e equipado com um agitador mecânico. Para a preparação de PHA utilizou-se peróxido de Hidrogénio a 1% (p/v) alcalinizado com hidróxido de sódio 50% (p/v) a pH 11,5±0,1. Para a realização do ensaio colocaram-se 5 gramas de borra dentro do erlenmeyer, às quais se adicionaram 50 mL de PHA. A reacção ocorreu durante 90 minutos. Num erlenmeyer de 250 mL com controlo de temperatura e agitação magnética foram adicionados, para cada ensaio, 10 gramas de borra de café a 50 mL de ácido peracético. Os ensaios foram realizados nas seguintes condições: concentração de AP de 11,69%, tempo de reacção de 90 minutos, temperatura de 80ºC e a um pH de 4. Após o tratamento com AP, as pastas resultantes foram filtradas e lavadas com água destilada e acetona até se atingir o pH neutro. As pastas foram colocadas a secar à temperatura ambiente para serem sujeitas a posteriores análises. As amostras (de borra e pasta de café) foram caracterizadas por FTIR e RMN MAS/PC.

Os resultados obtidos mostraram que a borra de café é constituída por celulose (17,5%), componente mais abundante na sua composição, seguida de hemiceluloses (14,7%) e de lenhina Klason (11,9%). É de salientar, que o valor de lenhina está no entanto sobrevalorizado, visto que nesta análise foi contabilizada a presença de taninos. No que diz respeito aos constituintes de baixo peso molecular, a borra possui na sua composição cinzas com uma percentagem de 1,8 e o teor de extratáveis em acetona ronda os 20,9%. Nos tratamentos oxidativos da borra de café, só com o tratamento com AP é que se verificaram resultados satisfatórios, ou seja, obtenção de uma pasta. Essa pasta foi denominada por holocelulose de café, sendo constituída maioritariamente por celulose e hemiceluloses. Comparando o teor de extratáveis da borra de café antes (20,9%) e após tratamento (27,4%) verifica-se um aumento, justificado pela degradação de componentes como lenhina e taninos, que inflacionam a percentagem dos outros componentes no seu todo.

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White bean as a sorbent for removal of zinc from rainwater at environmentally relevant concentrations and conditions

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The scarcity of fresh water all over the world, and the need for finding alternative water resources conserving public water supplies, highlight the possibility of reusing rainwater as a way to overcome this issue. Although rainwater can be considered in first instance as distilled water, several types of chemical contaminants have been found in harvested rainwater, such as, polycyclic aromatic hydrocarbons and pesticides [1], and heavy metals [2]. Thus, it becomes necessary the removal of contaminants from rainwater to reuse it, for example for domestic purposes, to safeguard human health safety. The search of biomaterials for the removal of contaminants from water becomes essential because they are non-hazardous and readily available from cheap sources.

This study aims to explore the sorption capacity of white beans to remove zinc from rainwater. Batch sorption experiments were carried out to evaluate the influence of several parameters in the process, such as, initial pH of water containing zinc (acid, neutral and basic pH values for rainwater), effect of sorbent amount (three masses), effect of two initial concentrations of metal in water (representing very high and high levels of zinc in rainwater), and effect of contact time between sorbent and water containing zinc. Experiments were performed with a fixed volume of water containing zinc under agitation, and at constant temperature. The variation of zinc concentration in the water was evaluated by atomic absorption spectroscopy, and kinetic sorption studies were also performed. Chemical, structural and morphological features of the white beans experienced along the process of sorption were also evaluated by Fourier transform infrared (FTIR) spectroscopy, by scanning electron microscopy (SEM) and by electron dispersive spectroscopy (EDS).

Acknowledgements
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Caracterización de aguas residuales industriales mediante fluorescencia de matriz excitación-emisión (EEM fluorescence)

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Las técnicas de fluorescencia son una herramienta muy útil para evaluar y monitorizar la presencia de compuestos fluorescentes (sustancias húmicas, proteínas, etc) en aguas (ríos, embalses, aguas subterráneas, aguas marinas) [1,2]. Desde las más sencillas técnicas de fluorescencia usadas al principio (emisión y fluorescencia síncrona) se ha pasado a la más utilizada en la actualidad y más completa fluorescencia de matriz excitación-emisión (*excitation-emission matrix: EEM fluorescence*). La fluorescencia EEM ha sido muy utilizada en el estudio de aguas naturales [3] pero mucho menos en el campo de las aguas residuales, especialmente las aguas residuales industriales.

En la presente comunicación se estudian los espectros EEM para aguas residuales urbanas e industriales de distintos sectores: industrias alimentarias (lácteas, cerveceras, bodegas, fabricación de patatas), fabricación de papel, mataderos, piscifactorías, conserveras de pescado, lixiviados de vertederos urbanos.

El objetivo principal de este trabajo es elaborar una base de datos de espectros EEM de diferentes aguas residuales con el objetivo de investigar en qué casos dichos espectros puedan constituir una auténtica "huella dactilar" que permita identificar el origen de un agua residual (tipo de industria) por su espectro de fluorescencia EEM característico. En la Figura 1 se muestra un ejemplo de espectro EEM para el agua residual de una industria.

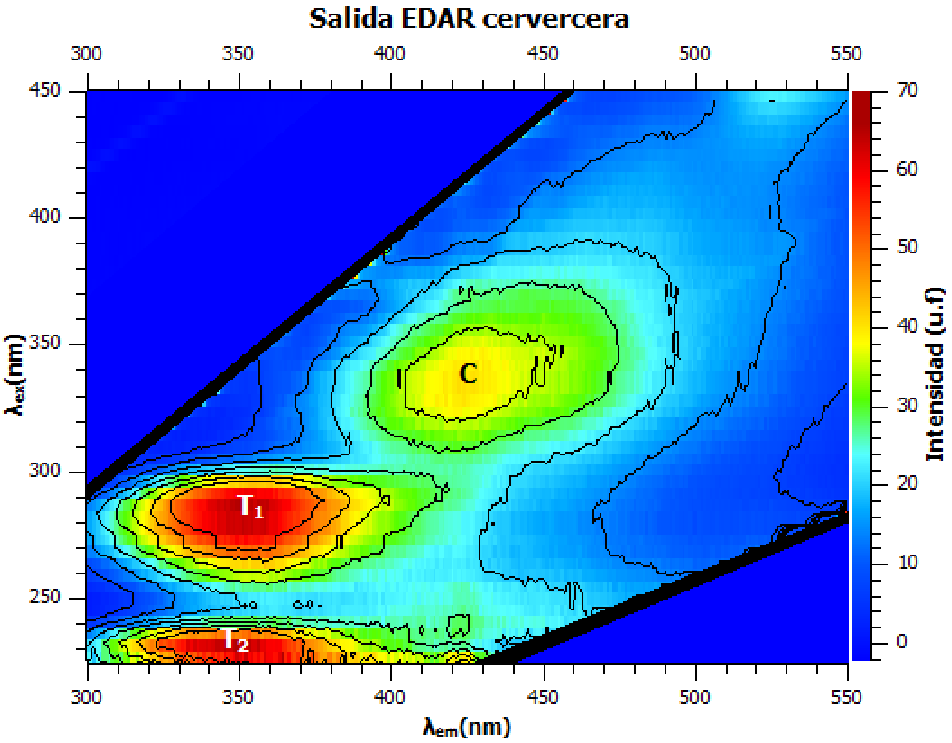

Fig.1. Espectro de fluorescencia EEM de un agua residual de una industria cervecera

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Monopersulfate promoted $LaCoO_3$-TiO_2 photocatalytic oxidation of herbicides. Operational variables and catalyst characterization

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Herbicides are frequently labelled as carcinogens, mutagenic or endocrine disrupters in aqueous ecosystems. Management of organic aqueous pollutants is a matter of concern to water companies that need to develop new and specific technologies for that purpose. Conventional biological treatment seems to be inefficient due to the organic recalcitrant nature of these substances [1]. That is why alternative technologies such as chemical oxidation through Advanced Oxidation Processes are required. Monopersulfate (MPS) is an oxidant which is attracting attention recently. This substance can be used as a promoter of sulfate radicals which present diverse advantages upon hydroxyl radical generation. The use of novel coupled $LaCoO_3$-TiO_2 as photocatalyst with double route of monopersulfate (MPS) activation has been studied. Firstly, as a photocatalyst due to titania; and secondly, through MPS heterogeneous decomposition onto $LaCoO_3$ lattice [2]. Thus, photocatalytic activity was tested for removing a mixture of four herbicides of different recalcitrance (metazachlor, tembotrione, tritosulfuron and ethofumesate).

$LaCoO_3$-TiO_2 with different Co/Ti ratios were made through sequential citrate and sol-gel methods. In the presence of light, MPS is catalytically decomposed, being observed an enhanced herbicide rate removal. 3.5-5 times of increase were appreciated because of UVA light. Although Co/Ti ratio in the range of 0.1-0.5:1 provided the best degradation rates, 0.1:1 was chosen for completing the study of the technology due to economical purposes.

Oxidant concentration, catalyst load, pH and temperature were assessed. Herbicides were completely oxidized depending on the operational variables and their recalcitrant nature. Concentrations up to 10^{-3} M of MPS produce led to an instantaneous removal of herbicides and 55% of TOC conversion in 3 hours. Catalyst load did not show significant influence; however it did improve MPS decomposition rate. Acidic conditions (pH=5) accelerated the process due to homogeneous contribution from leached cobalt (0.8 mg L^{-1} after 3 hours of treatment). Temperature does not seem to have an important influence since the energy of activation of the process is not excessively high.

Phytotoxicity assays, based on *Lactuca Sativa* germination, denoted no inhibition after 180 min of treatment (~80% of initial inhibition). As the reaction exposure increases, phytotoxicity disappears. Hence, the higher the initial MPS amount used, the faster the phytotoxiciy decreases.

Solid properties of Co/Ti=0.1:1 ratio were studied by means of SEM ($LaCoO_3$ aggregates linked to a variety of shapes and sizes of TiO_2), XRF (6.1% of $LaCoO_3$), XPS (superficial Co^{3+}, La^{3+} and Ti^{4+}), XRD (anatase, rutile and rhombohedral $LaCoO_3$) and UV-vis reflectance (visible range absorption and bandgap of 2.88 eV for TiO_2). Recycling uses did not show appreciable deactivation of the solid.

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Decaimento de cloro num sistema de abastecimento de água

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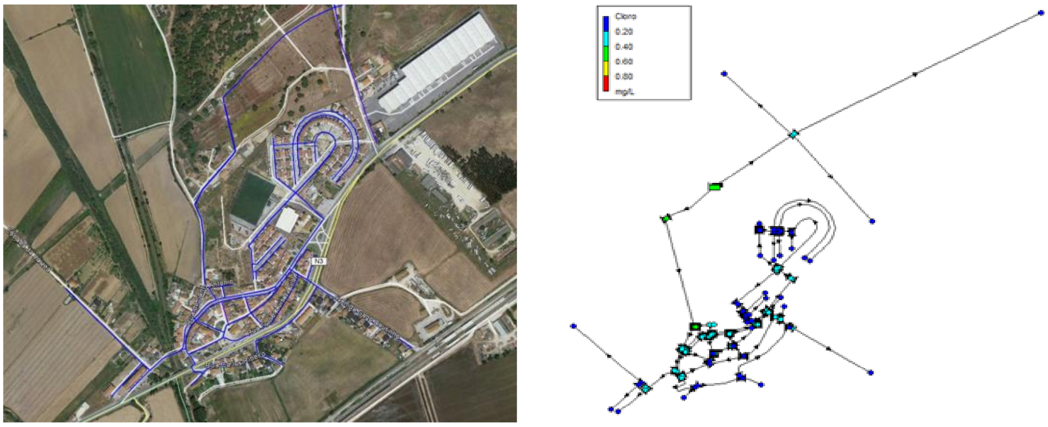
A qualidade da água ao longo dos sistemas de transporte e distribuição é uma das principais preocupações que as entidades distribuidoras de água enfrentam permanentemente [1].

O cloro residual presente na água tratada reage com outros compostos presentes nas paredes das tubagens ou no seio da água, ao longo do sistema de distribuição, levando à diminuição da sua concentração. Esta situação pode conduzir ao total desaparecimento do cloro residual livre, aumentando as probabilidades de contaminação microbiológica [2].

É necessário um adequado modelo geral de decaimento de cloro na água, para apoiar no eficaz planeamento/gestão da desinfeção em sistemas de distribuição [3].

O objetivo do presente trabalho é estudar o decaimento de cloro num sistema de abastecimento de água, com recurso à modelação de cloro residual, através do *software* EPANET 2.0 [4], um programa de utilização livre e gratuita, fiável e bem documentado, desenvolvido pela *United States Environmental Protection Agency* (USEPA) e traduzido para língua portuguesa pelo Laboratório Nacional de Engenharia Civil (LNEC). Para tal foi necessário efetuar o levantamento da rede, construir e calibrar o modelo hidráulico e de qualidade da água do sistema em estudo, levando a cabo campanhas de medição de pressão, caudal e cloro.

A rede de distribuição de água do sistema em estudo, implementada no programa EPANET 2.0 é apresentada na Figura 1.



a) b)

Fig.1. Rede de distribuição a) mapa no Google Earth e b) no *software* EPANET 2.0

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Oxidation of winery wastewaters by sulphate radicals: solar photolytic and catalytic activation

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Winemaking activities such as washing of tanks, filters and facilities generate a huge volume of effluents [1]. Usually, these wastewaters are released in sewer systems, causing important complications to Municipal Wastewater Treatment Plant (MWWTP). The main problem of biological treatments application is the fact of the great variability in the flow and composition discharges. Recently, sulphate radical-based AOPs (SR-AOPs) are gradually attracting attention as in situ chemical oxidation technologies to treat water effluents, instead of hydroxyl radical AOPs (HR-AOPs). Sulphate radicals ($SO_4^{\bullet-}$) present higher reduction potential (2.5-3.1 V) at neutral pH than hydroxyl radicals ($^{\bullet}OH$) (1.8-2.7 V), being more selective for oxidation [2]. Free sulphate radicals are generated by activation of chemical oxidants as persulphate salts [$Na_2S_2O_8$ (SPS) and $K_2S_2O_8$ (KPS)] or peroxymonosulphate salts [$KHSO_5$ (PMS)] [3]. The objective of this study is evaluating the performance of SR-AOPs assisted by natural solar radiation as an alternative treatment process for the degradation of organic matter. In this way, it was assessed the efficiency of three different sulphate salts (PMS, SPS and KPS), by solar photolytic and catalytic activation [using Fe(II) and Co(II) as catalysts] at different pH (4.5 and 7).

Winery wastewater used in this study were simulated from Douro red wine diluted samples. The different treatments carried out in this research were performed in batch mode using different dosages of sulphate salts [PMS, SPS or KPS (1 – 50 mM)] and different transition metals as catalyst [$FeSO_4{\bullet}7H_2O$ or $CoSO_4$].

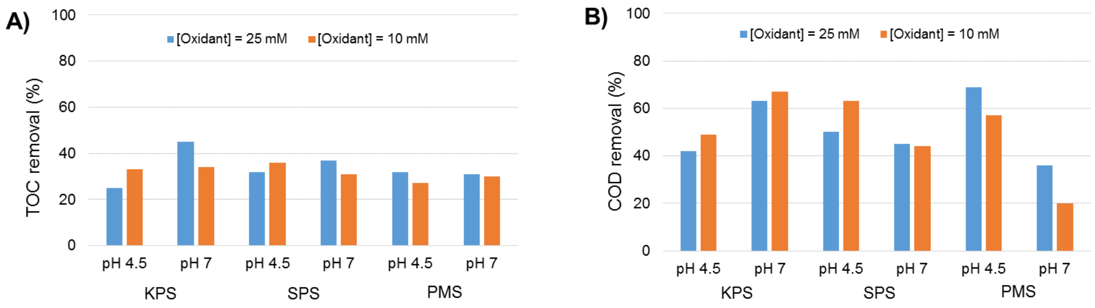

Fig.1. Comparison of a) TOC and b) COD removal efficiencies after 180 minutes of photolytic activation of PMS and PS salts at pH 4.5 and 7.

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Carbon dioxide conversion into value-added chemicals over CdS/reduced graphene oxide composites

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Increasing concerns about the continuous combustion of non-renewable fossil fuels have encouraged the scientific community to explore alternative energy options that can decrease CO_2 emissions. Photocatalytic reduction of CO_2 over semiconductor catalysts could help to decrease the concentration of CO_2 in the atmosphere while at the same time exploiting it as a carbon feedstock for the production of value-added chemicals, such as methanol [1]. However, this remains quite a challenge, because the linear CO_2 molecule is the most stable form of carbon (ΔG_f= -394.36 kJ/mol), and so the activation of CO_2 is the key step in its conversion [2]. Cadmium sulphide (CdS) is probably one of the most studied metal sulfide materials for the photocatalytic reduction of CO_2 because of its relatively narrow band gap (2.4 eV). However, low photocatalytic efficiency due to photocorrosion and fast recombination of the photogenerated charge carriers are the main limitations for the utilization of pure CdS. Graphene derivatives/metal oxide composites have been found to be efficient photocatalysts on account of the vital role of graphene as an electron acceptor/transporter, which reduces the recombination rate of photoexcited electron–hole pairs [3].

In the present work, CdS/reduced graphene oxide (rGO) composites were prepared with different graphene oxide (GO) loadings (3.0, 6.0 and 12.0 wt.%) and with *thermal treatment at 400 ºC* (N_2 atmosphere). The composites were applied in the photocatalytic water reduction of CO_2 into methanol and ethanol. The photocatalytic runs were carried out in a cylindrical glass immersion photo-reactor (250 mL) with a Heraeus TQ 150 medium-pressure mercury vapor lamp located axially in the reactor and held in a quartz immersion tube. The analysis of CO_2 and reaction products was carried out by gas chromatography (Agilent 7890A GC).

The presence of rGO in the composites was found to increase absorption in the visible spectral range, enhancing the CO_2 photoreduction in aqueous phase, with formation of both methanol and ethanol as main products. The photocatalytic activity of the composites exceeded that of bare CdS. The highest CO_2 conversion was obtained with the composite containing 3.0 wt.% GO, which was the most active of the prepared photocatalysts.

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Foto-degradação do florfenicol em sistemas aquáticos

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O florfenicol (FLO) é um antibiótico bacteriostático de largo espectro, permitido para uso em aquacultura marinha e doce [1]. Um grande problema em torno da sua utilização é o tempo que demora a degradar-se no ambiente, estando indicados na literatura tempos de meia vida superiores a 90h, sob a ação da luz [2].

Neste trabalho estudou-se a degradação do FLO em água milliQ e água de aquacultura marinha, sob a ação de luz solar simulada. O simulador de luz solar utilizado é constituído por uma lâmpada de xénon, emitindo radiação na gama de comprimentos de onda de 290 a 800 nm e com uma irradiância de 550 W/m^2. A quantificação do composto foi feita através de HPLC-UV, a 223nm, sendo utilizada uma coluna de fase reversa C18.

Após 120h de irradiação, a velocidade da foto-degradação do composto em água de aquacultura marinha é 3,6 vezes superior à foto-degradação em água milliQ. Neste seguimento, fizeram-se estudos cinéticos de foto-degradação do FLO em água de aquacultura marinha. Os dados foram ajustados não linearmente a uma cinética de pseudo-1ª ordem e o tempo de meia vida determinado foi de cerca de 70h. Fez-se o estudo da influência de dois dos principais constituintes da água de aquacultura na foto-degradação do FLO: os sais marinhos e a matéria orgânica (simulada por ácidos fúlvicos (AF)). Os sais marinhos sintéticos (21 ‰) têm um efeito inibidor na foto-degradação do FLO, enquanto que os AF (20 mg/L) revelaram-se importantes foto-sensibilizadores da degradação. De modo a verificar se o mecanismo de fotossensibilização da reação envolvia o estado tripleto dos AF (^{3}AF*), as soluções de FLO foram borbulhadas com oxigénio ou azoto. Ao pH de 7,3 (pH natural da água de aquacultura marinha), o efeito não parece estar relacionado com o ^{3}AF*, pois a percentagem de degradação na presença de azoto é inferior à da solução borbulhada com O_2.

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Eliminação de micropoluentes orgânicos utilizando leitos de macrófitas e processos avançados de oxidação

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Os processos convencionais utilizados para o tratamento de águas e águas residuais não se revelam comummente eficazes na eliminação de poluentes orgânicos que se encontram em concentrações vestigiais (ng L^{-1} - µg L^{-1}). Estes micropoluentes incluem várias classes de substâncias, nomeadamente as classificadas como prioritárias (PSs - “priority substances”) ou as conhecidas como contaminantes de preocupação emergente (CECs - “contaminants of emerging concern”), dependendo respetivamente da existência ou não de regulamentação. Entre os processos biológicos de tratamento de águas e águas residuais, os leitos de macrófitas (CWs - “constructed wetlands”) têm revelado ser uma opção de baixo custo, de simples operação e manutenção e com eficiência comprovada na remoção de diversos poluentes, como são exemplo o fósforo, azoto, metais e sólidos suspensos totais; contudo, apresentam eficiência limitada na remoção de micropoluentes orgânicos [1]. Por outro lado, os processos avançados de oxidação são muito eficientes na remoção de micropoluentes orgânicos [2], mas envolvem custos mais elevados e encontram limitações na remoção de poluentes inorgânicos. Combinar leitos de macrófitas com processos avançados de oxidação pode assim revelar-se uma boa solução para ultrapassar os problemas encontrados quando os processos são aplicados por separado. No presente trabalho, foram recolhidas amostras de água à entrada e saída de uma exploração de aquacultura de água doce. Após pré-concentração das amostras por extração em fase sólida (SPE), foi utilizada cromatografia líquida acoplada a espectrometria de massa (LC-MS/MS) para determinar 4 PSs (ácido perfluorooctanossulfónico, atrazina, simazina e isoproturão), 11 CECs (diclofenac, eritromicina, claritromicina, azitromicina, metiocarbe, imidaclopride, tiaclopride, tiametoxame, clotianidina, acetamipride e 4-metoxicinamato de 2-etil-hexilo conhecido como EHMC), 2 compostos recalcitrantes em amostras ambientais (carbamazepina e ácido clofíbrico) e 4 fármacos frequentemente administrados em animais (ofloxacina, enrofloxacina, ceftiofur e ivermectina). Do conjunto de 21 micropoluentes orgânicos analisados, apenas 2 PSs (atrazina e simazina) e 2 CECs (EHMC e eritromicina) foram detetados nas amostras, em concentrações na ordem dos ng L^{-1}. Foi ainda estudada a eficiência de um sistema combinando leito de macrófitas com um processo avançado de oxidação (ozonização) para remoção dos micropoluentes orgânicos encontrados nos efluentes da exploração de aquacultura. Realizaram-se também ensaios utilizando a mesma matriz contaminada propositadamente com os 4 micropoluentes detetados (100 ng L^{-1} de cada), incluindo ainda os 4 fármacos veterinários e os 2 compostos recalcitrantes. O sistema biológico demonstrou uma boa eficiência na remoção de todos os compostos em análise, com a exceção do filtro UV orgânico (EHMC) que foi completamente eliminado unicamente quando aplicado o processo avançado de oxidação.

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Identification of major organic contaminants in Estarreja rainwater

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Estarreja region is the second largest chemical complex in the north western coast of Portugal, producing for example aniline and synthetic resins (PVC). Moreover, Estarreja also has a large area dedicated to agricultural activities, such as maize fields. Thus, besides the residential/urban area, Estarreja is strongly affected by anthropogenic activities, namely industrial and agricultural. These activities emit pollutants to the atmosphere, becoming necessary to identify the major contaminants emitted. Thus, as rainwater can remove from the atmosphere pollutants that may be associated with gaseous, liquid and particulate phases, it becomes important to evaluate Estarreja rainwater composition as a first step for screening air quality. Moreover, as rainwater is transported from the atmosphere to the Earth’s surface, the Estarreja rainwater composition affects terrestrial and aquatic ecosystems, and also the quality of freshwater, which may have a significant impact on human health.

This study aims at identifying the major organic contaminants in Estarreja rainwater. For such purpose, samples were collected in two distinct sampling sites of Estarreja: one in the industrial area (industrial); and the other out of the industrial area, and near an agricultural area (industrial background/agricultural). Moreover, the seasonal effect on organic composition of Estarreja rainwater was also evaluated by collecting samples in two sampling periods: in winter (January and February 2016); and in spring (May 2016). The organic compounds were identified by gas chromatography coupled to mass spectrometry (GC-MS).

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Valorização das poeiras de *by-pass* da indústria cimenteira na estabilização de lamas de ETAR

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O presente estudo teve por objecto o apoio técnico e científico no âmbito da valorização de um sub-produto, resultante do *by-pass* da indústria cimenteira, na estabilização de lamas de estações de tratamento de águas residuais, com vista ao cumprimento do disposto no Quadro nº 5, do Anexo nº 1, do Decreto-Lei nº 276/2009, de 2 de outubro.

A produção de cimento Portland é um processo com elevado consumo energético. A energia térmica necessária depende principalmente da utilização de combustíveis fósseis mas, devido ao aumento das preocupações ambientais e ao aumento dos preços dos combustíveis fósseis houve necessidade de se utilizarem combustíveis secundários ou combustíveis alternativos [1]. Esta abordagem originou alguns constrangimentos no processo, levando a alterações processuais das quais surgiram as poeiras de by-pass (PBP). Estas poeiras são reintroduzidas durante o processo de produção de cimento Portland mas, a percentagem de incorporação está limitada às especificações do cimento [2], sendo parte purgada, podendo ser valorizada para diferentes fins [3-7], mas muitas vezes é ainda encaminhada para aterro sanitário.

Com este estudo, pretendeu-se avaliar a aplicação das poeiras de by-pass na estabilização de lamas secundárias, com e sem desidratação. Estudou-se o efeito de três produtos, PBP1, PBP2 e cal com quatro dosagens diferentes: 0; 12; 25; 37 g CaO 100 g-1MS, sobre o pH, temperatura, *Escherichia coli* e *Salmonella* spp. Os resultados revelaram eficácia sobre os parâmetros microbiológicos, ao fim de 24 h de aplicação, em doses iguais ou superiores a 25g CaO 100 g-1MS, em ambas as lamas estudadas. Nestas condições, o pH manteve-se superior a 12. A monitorização realizada ao fim de 3 meses de ensaio não revelou a presença dos microrganismos, mesmo no ensaio controlo. Os resultados obtidos evidenciam a possível reciclagem destes sub-produtos PBP1 e PBP2 como substituintes da cal, na estabilização de lamas de ETAR.

Tabela 1. Efeito das PBP no crescimento de *Salmonella* spp. em lamas de ETAR

	NA	**Cam**	**PBP 1**				**PBP 2**			**Cal**		
			0%	12%	25%	37%	12%	25%	37%	12%	25%	37%
Ensaio 1	+	0	+	0	0	0	0	0	0	0	0	0
Ensaio 2	+	0	+	0	0	0	0	0	0	0	0	0
Ensaio 3	+	0	+	0	0	0	0	0	0	0	0	0

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4-Nitrophenol degradation by photo-assisted Fenton process

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In the last years the presence of nitroaromatic compounds in the environment, namely of 4-nitrophenol (PNP), has required careful attention because this compound is carcinogenic and toxic to humans [1]. Moreover, it is widely used in the petrochemical industry, in coke ovens, in pesticides and herbicides [2] and also in the pharmaceutical industry [3]. The application of Advanced Oxidation Processes (AOP) in the treatment of effluents containing PNP has received increased attention, with promising results, namely through photocatalysis [4] and electrochemical processes [5].

The photo-Fenton process (which makes use of a Fe^{2+}/H_2O_2 mixture in the presence of light) is an AOP that combines the dark Fenton reaction with ultraviolet irradiation, thus maximizing the degradation and mineralization of organic compounds; it was also applied for PNP degradation [6, 7, 8]. However, these studies only evaluate the degradation of PNP and did not quantify the formation of intermediary compounds, as aromatic and carboxylic acids.

In this study the photo-Fenton process was applied for treating a simulated wastewater with 500 mg/L of PNP in a batch reactor. An experimental design approach (Central Composite Design - CCD) was used for evaluating the influence of hydrogen peroxide concentration and irradiance on the PNP degradation (and intermediate compounds formed), on organic compounds mineralization and on the acute toxicity. For that, it was determined the total organic carbon (TOC) removal, it was quantified, by high-performance liquid chromatography - HPLC, the PNP and the main intermediate compounds formed (4-nitrocatechol, benzoquinone and hydroquinone); the acute toxicity tests were made by evaluating the *Vibrio fischeri* inhibition in a Microtox® system.

In the optimized conditions it was reached complete degradation of PNP, 97% of TOC removal and a nontoxic wastewater was generated (the inhibition of *Vibrio fischeri* decreased from 63% to 0.0% for the PNP solution before and after photo-Fenton treatment, respectively). A Lumped Kinect Model (LKM) was applied for the oxidation kinetics under the optimized conditions with a very good fitting to the experimental data.

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XXII Encontro Luso-Galego
Química

COMUNICAÇÕES ORAIS E EM PAINEL

Química e Saúde

Task-specific ionic liquids for pharmaceutical applications

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The suitable combination of Ionic Liquids as a peculiar class of ionic materials with active pharmaceutical ingredients (APIs) can offer innovative platforms in order to improve the therapeutic effect of the solid neutral original drugs [1,2]. According the selection of biocompatible counter-ions, it is possible to tune the properties of several API-ILs in terms of its stability, solubility, permeability and delivery [3]. The discovery of sustainable processes to solve some problems associated to pharmaceutical industry (e.g. polymorphism, low solubility and permeability, reduced bioavailability as well as drug resistance) is one of the biggest challenges for scientific community.

Recent work of our research team involved the development of sustainable synthetic methodologies for combination of pharmaceutical drugs such as anti-inflammatory (ibuprofen); antibiotics (beta-lactam and fluoroquinolones); anti-epileptic (valproate and topiramate), antifungal (amphotericin) and antidepressant (bupropion, fluoxetin) as cations or anions with adequate biocompatible counter-ions [4,5]. Elimination of original polymorphism drug behaviour was observed for ibuprofen based ILs. Additionally, a significant improvement into water and biological fluids solubility as well as permeability have been observed for the majority of new pharmaceutical salts [6]. In general, API-ILs based on antibiotics can reverse the resistance in some clinical strains previously isolated and tested as resistant as well as significant anti-proliferative activity against tumour cell lines [7, 8].

Detailed characterization studies including toxicity, bioavailability, antibacterial and antifungal activities against resistant bacteria and fungi respectively have been performed. Additionally, thermal studies have been also carried out to evaluate the tendency for polymorphism after transformation into pharmaceutical ILs or salts.

Different Task-specific ILs based on active drugs can be useful tools for new therapies and contribute for future pharmaceutical applications.

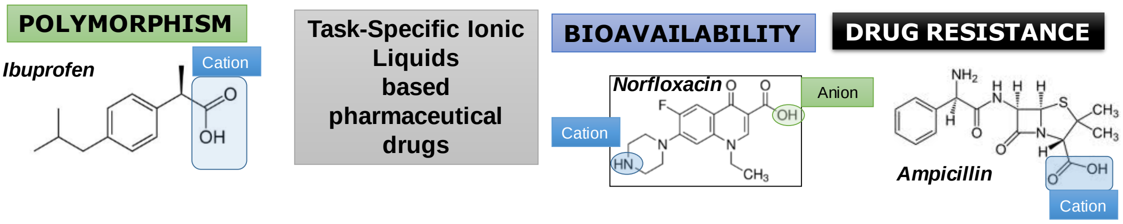

Fig.1. Examples of Task-specific ILs based pharmaceutical drugs

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Synthesis and characterization of pharmaceutical cocrystals of glibenclamide and gliclazide

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New drug development aiming high oral performance and successful delivery of active pharmaceutical ingredients (APIs) requires selection of specific crystal forms. Production of cocrystals is an emerging strategy to improve key solubility issues of drugs [1]. Cocrystals are multicomponent solid crystalline materials composed of two or more different molecules within the same crystal lattice [2]. Pharmaceutical cocrystals are crystalline homogenous molecular complexes different from the precursor compound. They are comprised by one API and one or more coformers held together by noncovalent interactions (generally hydrogen bonds), all solid at room temperature and in a well-defined stoichiometry (e.g. AB, AB2) [3].

In this work, synthesis of glibenclamide (GBL) and gliclazide (GCZ) cocrystals with three different coformers (tromethamine (TRIS), *ρ*-aminobenzoic acid (PABA) and nicotinamide (NICO)) was attempted by solvent evaporation using methanol. Regarding the established Biopharmaceutical Classification System (BCS), GBL and GCZ are considered class IV drug substances, meaning that they have low solubility and low permeability. To assess cocrystallization method efficiency in generating actual cocrystals and their correspondent purity, the obtained compounds were characterized by mid and near infrared spectroscopy, differential scanning calorimetry and X-ray powder diffraction. Results showed that cocrystals of GBL and GCZ were preferentially formed with TRIS, thereby having the best characteristics.

GBL:TRIS and GCZ:TRIS cocrystals were manufactured at a higher scale and further characterized as to purity and scale-up process efficiency. Forthcoming work involves further characterization as to solubility parameters, assisting the definition of the most appropriate dosage. The obtained cocrystals will be used as API in a pharmaceutical formulation (uncoated tablets) replicating existing commercial products in terms of excipients and focusing on dosage equivalency. The resulting solid dosage forms will be further tested according to different methods, especially focusing on dissolution testing.

Acknowledgements

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Non-invasive imaging of solid tumors

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Prevention and treatment of cancer are limited by the non-invasive detection capacity of the diseased tissue. Acoustic and optical techniques are the least expensive and least invasive of the armamentarium of medical imaging. Optical imaging has high sensitivity, high contrast and good spatial resolution but the imaging for deep tissues remains a challenge due to light scattering and strong attenuation in these tissues. The induced fluorescence endoscopy (IFE) has a higher sensibility than conventional endoscopy to identify precancerous and cancerous lesions of the larynx (95% vs. 73% [1]) but insufficient specificity. Photoacoustic tomography (PAT) combines the contrast of optical techniques with the penetration depth and spatial resolution of acoustic techniques.

Progress in this field depends on the availability of biocompatible contrast agents that absorb light in the phototherapeutic window (700-900 nm, where tissues are more transparent and have minimal auto-fluorescence) and accumulate in tumors. Additionally, IFE probes must have high fluorescence quantum yields and large Stokes shifts between absorption and fluorescence, whereas PAT contrast agents must have ultrafast radiationless deactivations and positive structural volume changes.

Diamagnetic metal complexes of phthalocyanines with n-butoxyl groups in all the α-benzo positions of the macrocycle skeleton, $MPc(OBu)_8$, have strong near-infrared absorptions and intense fluorescences that are Stokes shifted by more than 15 nm. Interestingly, the silicon complex $Si(OH)_2Pc(OBu)_8$ is also remarkably photostable and non-toxic. The use of $Si(OH)_2Pc(OBu)_8$ in the fluorescence imaging of BALB/c mice bearing a 4T1-luc2 tumor in the mammary fat pad unambiguously revealed the presence of the tumor when it had only 1 mm in diameter and was not visible with the naked eye. Compound $Si(OH)_2Pc(OBu)_8$ has an intrinsic ability to accumulate in the tumor, adequate spectroscopic properties and excellent stability to function as a NIR fluorescent label in the early detection of tumors [3].

At this time are being conducted studies with functionalized carbon nanotube to achieve excellent contrast agents for photoacoustic tomography taking advantage of the excellent characteristics of this material.

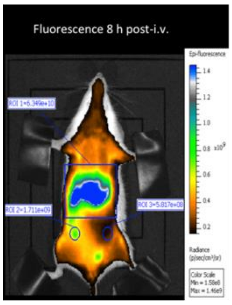

Fig.1. Whole-body fluorescence imaging of BALB/c mice bearing a tumor in the right abdominal fat pad collected 8 hours after the i.v. administration of the Pc dye with excitation at 745 nm and fluorescence emission at 810-875 nm

Acknowledgements
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Potencial antitumoral de cogumelos silvestres: um caso de estudo com espécies *Leccinum*

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Além de constituírem uma excelente opção como alimento devido ao seu valor nutricional, os cogumelos (silvestres e/ou comerciais) têm sido descritos como matrizes naturais com inúmeras propriedades bioativas, incluindo potencial antitumoral [1,2].

No presente trabalho foi estudado um extrato fenólico, obtido da espécie *Leccinum vulpinum* Watling, que revelou ser rico essencialmente em ácidos hidroxibenzóicos (nomeadamente ácido gálico, ácido protocatéquico e ácido *p*-hidroxibenzóico). Foi efetuado um *screening* inicial, testando o referido extrato contra um painel de linhas celulares tumorais humanas (MCF-7: adenocarcinoma de mama; NCI-H460: carcinoma de pulmão; HCT-15: adenocarcinoma colorectal; e AGS: adenocarcinoma gástrico), de forma a verificar o seu efeito no crescimento celular das linhas em estudo.

Uma vez que a proliferação celular foi inibida em todas as linhas testadas, e dada a evidência de uma relação inversa entre o consumo de cogumelos e a redução do risco de incidência do cancro da mama [3], foi efetuado um estudo detalhado na linha celular MCF-7. Para tal, foram realizados alguns ensaios funcionais, de modo a verificar os efeitos do extrato na proliferação celular, no perfil de ciclo celular e apoptose. O potencial do extrato como indutor de danos ao nível do ADN foi também avaliado.

De uma forma geral, o extrato fenólico da espécie *L. vulpinum* diminuiu a proliferação celular, sendo que o tratamento celular com uma concentração de extrato correspondente ao GI_{75} reduziu significativamente a percentagem de células na fase S do ciclo celular. Adicionalmente, o extrato induziu apoptose, sendo que o tratamento celular com uma concentração de extrato correspondente ao GI_{50} e ao GI_{75} aumentou a percentagem de células em apoptose para 13,4% e para 27%, respectivamente, enquanto os valores controlo de apoptose foram de 6 - 9%. Os resultados obtidos sugerem também que o extrato em estudo causou danos ao nível do ADN celular, uma vez que proteínas envolvidas na reparação de danos no ADN, nomeadamente PARP, ficaram sobre-expressas nas células tratadas com o extrato. Isto foi confirmado pelo Ensaio Cometa (*Alkaline Comet Assay*), tendo sido verificado um aumento significativo da percentagem de ADN na “cauda” do Cometa, após tratamento celular com 250 mg/mL de extrato.

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Arylxanthones with anti-inflammatory potential in cellular systems

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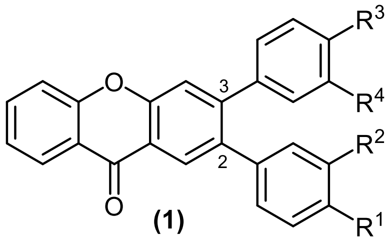
Xanthones are a family of naturally-occurring oxygenated heterocyclic compounds. A wide range of natural and synthetic analogues are known to possess diverse biological activities including antifungal, antimalarial, antioxidant and antitumor, among others [1]. There are only a few publications related to arylxanthones [2], most of them focused on arylxanthones synthetic strategies and their biomedical potential, mainly highlighting them as effective scavengers of reactive oxygen species (ROS) and reactive nitrogen species (RNS) [3,4]. As far as we know, the anti-inflammatory potential of xanthones bearing an aryl group has not been studied so far. With this idea in mind, our purpose was to evaluate the putative anti-inflammatory effects of several arylxanthones bearing hydroxyl groups in certain positions of their main core, namely through their ability to inhibit 5-lipoxygenase (5-LOX) and cyclooxygenase 1 (COX-1) and 2 (COX-2), both enzymes involved in the arachidonic acid metabolism [5,6].

Preliminary results showed that some of the studied arylxanthones were able to prevent leukotriene B_4 production in human neutrophils, the xanthone with a catechol group at position 2 being the most active one. The inhibition of prostaglandin E_2 production was assessed in human whole blood and the majority of the tested compounds were able to inhibit COX-1 while being completely ineffective in COX-2.



(1)

R^1, R^2, R^3, R^4 = H, OH

Fig.1. General structure of the 2,3-diarylxanthones studied.

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Optimization of flat sheet polysulfone membrane developed for biomolecules separation

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Polysulfone (PSF) membranes are used in various fields of industries to separate broad spectrum of molecules. Nowadays one of the main application of PSF membranes is hemodialysis. The advantage of using this polymer for blood purification is the higher biocompatibility and the greater ability to remove a wide range of uremic toxins, in comparison with formerly used cellulose based membranes. However PSF membrane removal ability for middle size uremic toxins, such as β2-microglobulin is so far insufficient. Due to the natural hydrophobic character, the PSF membrane is prone to fouling of proteins on its surface, which may negatively influence its molecular removal efficiency. The hydrophilic character can be modified by adding of polymeric additives such as polyethylene glycol (PEG) or polyvinylpyrrolidone (PVP) to the casting solution [1,2]. Moreover, the removal efficiency is also crucially dependent on the membrane structure and morphology. These characteristics are fundamentally affected by the type and quantity of polymer; solvents; additives as well by conditions during the phase inversion and membrane precipitation [3].

In the present work, the mini-scale hemodialysis system was developed to evaluate different PSF membranes permeability for biomolecules. These membranes were prepared with different type and quantity of additives and underwent different conditions during preparation. The effect of additive PEG (MW= 6000; 20000; 35000 g/mol) and PVP (MW=40000 g/mol) on the PSF membrane structure and biomolecules removal characteristics were then evaluated.

The thin flat sheet membrane was obtained by phase inversion technique; the casting solution was composed of PSF, N-methylene-2-pyrrolidone as solvent and PEG/PVP as additive. The solution containing PVP was homogenized using Turrax and ultrasonicator. The polymer dope solution was then casted on silicon wafer using a spin coater. Ultrapure water was used as non-solvent in coagulation bath. To mimic the conditions of hemodialysis, the mini-module was fabricated from polydimethylsiloxane as a channel network and subsequently treated with plasma in order to increase wettability. Two closed circuits were separated by PSF membrane and the device was connected to a peristaltic pump by PVC tubing. Then, evaluation of the solutes removal rate by PSF membrane was performed, at room temperature, by permeation study using urea (MW~60 Da), lysozyme (MW~14 kDa) and bovine serum albumin (MW~66 kDa), during at least 4 hours.

The membrane prepared with PVP showed better results concerning to removal of urea and lysozyme (47,53% and 48,83%, respectively) when compared to PEG (3,67% and 2,25%, respectively), however the bovine serum albumin loss was observed lower by membrane containing PEG. Thus, the passage of albumin through the membrane has to be further optimized. In conclusion, the type of additive in dope solution significantly influence the biomolecules permeability adequate for hemodialysis.

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UHPLC-MS analysis and in vitro biological activity of *Calendula* L. species growing in continental Portugal

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Calendula L. (Asteraceae) is a valuable but uncharted genus regarding its diverse medicinal and nutritional applications. Its potential in the treatment of numerous infections have been highlighted through several studies in *C. officinalis* [1,2]. Nevertheless, little is known about the antimicrobial activity of *C. arvensis* and even less regarding *C. suffruticosa* subspecies [3,4]. Therefore, the present study aims the assessment of the phenolic composition, antibacterial and antifungal activity of *C. arvensis* L., *C. suffruticosa* Vahl subsp. *algarbiensis* (Boiss.) Nyman and *C. suffruticosa* Vahl subsp. *lusitanica* (Boiss.) Ohle growing in Portugal.

The methanol extracts were analyzed by UHPLC-ESI-DAD-MS^n allowing the identification of 42 compounds, of which 6 were detected for the first time in the *Calendula* genus. The biological activity (MIC and MLC) was evaluated against gram-positive and gram-negative bacteria, yeasts, dermatophytes and *Aspergillus* sp. strains by broth macrodilution method. The results showed that the extracts were very active against dermatophytes dissimilar to the results against *Aspergillus* sp., yeasts and bacteria strains. *C. suffruticosa* subsp. *algarbiensis* showed the best results especially against two strains of *Microsporum* sp. with antidermatophytic activity superior to the one exhibited by the control, the clinically used fluconazol.

Concluding, this study allowed an in-depth knowledge about the phenolic composition of *Calendula* genus through the detection of 6 compounds for the first time and the first description of the phenolic composition of *C. suffruticosa* subspecies. Additionally, a better understanding of the bioactivities of these extracts was achieved. The results showed that *C. suffruticosa* subsp. *algarbiensis* possesses a noteworthy antidermatophytic activity, especially against *Microsporum* strains with MIC and MLC values inferior to the ones presented by the control fluconazol. Therefore, *C. suffruticosa* subsp. *algarbiensis*'s extracts could be an alternative source to this synthetic drug, decreasing their side effects. Additionally, through the accomplished findings, including a PCA, a differentiation among the *taxa* was possible. Yet, an analysis with more samples is required for accurate results.

Acknowledgements

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Enhanced cytotoxicity against human tumour cells using prenylated chalcones through disruption of the p53-MDM2 interaction

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The p53 inactivation by interaction with MDM2 is a common event in human cancers. The restoration of the p53 activity through abolishment of the p53-MDM2 interaction represents an efficient and selective therapeutic strategy against tumours retaining wild-type p53. Chalcones have been reported to inhibit the p53-MDM2 interaction, although with modest activity. Recently, a marked growth inhibitory effect against wild-type p53-expressing tumour cells was described for the *O*-prenyl derivative (2) of 2'-hydroxy-3,4,4',5,6'-pentamethoxychalcone (1) [1]. Herein, the molecular mechanism underlying the improved cytotoxic activity of prenylchalcone 2 was investigated [2]. Using a yeast-based p53-MDM2 interaction assay, it was shown that prenylchalcone 2 inhibited the p53-MDM2 interaction with enhanced activity compared to compound 1. These results were supported using human colon adenocarcinoma HCT116 cells with wild-type p53 (HCT116 p53$^{+/+}$) and its p53-null isogenic derivative (HCT116 p53$^{-/-}$). We showed that the potent *in vitro* growth inhibitory activity of prenylchalcone 2 was associated with the activation of a p53-dependent pathway involving cell cycle arrest and a mitochondrial-dependent apoptotic pathway, through disruption of the p53-MDM2 interaction. Our findings show that prenylation is a determinant factor for the enhancement of chalcones tumour cytotoxicity by improving their ability to disrupt the p53–MDM2 interaction. Prenylchalcone 2 may open the way to more potent and selective p53-MDM2 interaction inhibitors with improved antitumor properties.

Acknowledgments

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2-Benzylchromones: synthesis of a novel series of chromone derivatives as potential anti-inflammatory agents

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The quest for new and safer anti-inflammatory drugs is still the focus of several medicinal chemistry programs. Chromones (4*H*-chromen-4-ones) are a group of naturally occurring compounds ubiquitous in plants. [1] This singular ring system has proven to be a privileged scaffold in medicinal chemistry, due to its unique structural features and diverse biological activities. [2]

Our project was therefore intended to highlight the potential of chromones as anti-inflammatory agents, specifically as inhibitors of nitric oxide (NO) production. To do so, numerous 2-benzyl-chromones, with distinct substitution patterns, were synthesized through a Baker-Venkataraman rearrangement, using 2'-hydroxyacetophenones and ethyl 2-phenylacetates as starting materials, allowing to understand the influence of different substituents in the efficacy of the synthetic method applied. Moreover, this novel series of chromone derivatives was evaluated towards its cytotoxicity and capacity to inhibit nitric oxide production in a standard *in vitro* inflammation model consisting of LPS-activated RAW 264.7 macrophages.

The results of both synthetic procedures and anti-inflammatory assays will then be presented and discussed in order to conclude about the anti-inflammatory potential of this particular type of compounds. Furthermore, these conclusions will also be supported by other inhibition assays, performed to the most promising compounds, providing a deeper understanding about their molecular mechanism of action.

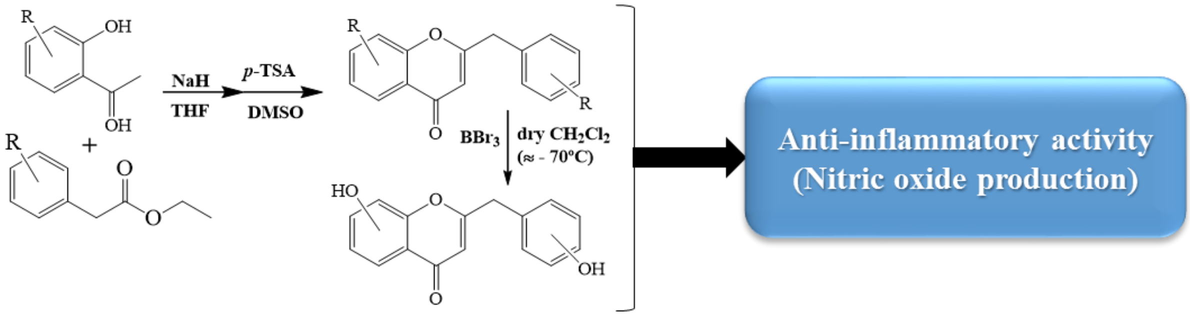

Fig.1. Synthesis of novel 2-benzylchromones and anti-inflammatory activity evaluation.

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Supercritical CO_2 assisted process for the production of nano-hydroxyapatite/chitosan scaffolds

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Hydroxyapatite/chitosan (HAp/CS) hybrids are suitable materials for non-load-bearing bone graft applications but their productive process still faces important challenges. In this work, a simple 3-step process to produce n-HAp/CS hybrid scaffolds was developed, in which supercritical carbon dioxide ($scCO_2$) extraction was used and proven to be a viable technique for simultaneous purification and potential sterilization. The advantages of this method were studied over other currently used procedures, often based on neutralization steps. The obtained scaffolds were characterized in what concerns morphology, porosity and pore size distribution, swelling capacity, and mechanical properties. A microbiological test was performed in order to evaluate if the scaffolds were sterilized, and biological assays were also carried out in order to assess cytotoxicity of the produced scaffolds.

Based on the results obtained from this study it was shown that, opposed to the other purification procedures used, it was possible to preserve the structure fixed by the first freeze-drying step, and the salt impurities derived from the neutralization procedures with NaOH were avoided using the $scCO_2$ extraction. Also, the final freeze-drying step required with the alternative neutralization procedures was, in this case, eliminated. Sterilization conditions were tested and, with an extraction yield of 80%, it was determined that the best achieved $scCO_2$ extraction conditions are two 2-hour cycles in static mode at temperature 75 ºC and pressure 8.0 MPa (scaffolds labelled as "n-HApCS-$scCO_2$-75/75"). The produced scaffolds presented a storage modulus of (20.5 ± 2.9) kPa at 1 Hz frequency and elastic properties. Moreover, the scaffolds contained highly pure nanocrystalline HAp, and mimic the structure and composition of bone extracellular matrix, exhibited adequate micro- and macroporosity, interconnected structure, and fast swelling, which are highly desirable features for bone regeneration.

Furthermore, even though additional studies are necessary to validate the used $scCO_2$ extraction conditions for the sterilization of the scaffolds, preliminary results presented in this work are promising. Results from the microbiological assay showed no microbial growth, evidencing that the produced n-HApCS-$scCO_2$-75/75 scaffolds were sterile, enabling the adhesion and proliferation of osteoblastic cells. The biomaterial allowed cellular proliferation, which increased gradually along the experimental period. Moreover, cells with normal morphology, a tendency for pores colonization and the existence of organized cell groups, increasing in extension along the culture period, were observed. Therefore, sterile n-HAp/CS scaffolds, with desirable properties for the treatment of small, non-load-bearing bone defects, were successfully produced by a simple 3-step process, consisting of: (1) preparation of homogeneous and stable n-HAp/CS dispersion by fast stirring; (2) freeze-drying for the elimination of the solvent and fixation of the microstructure; and (3) purification, with potential sterilization capacity, of the scaffolds using supercritical CO2 (scCO2) extraction.

Acknowledgements

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Searching for new reactivators of mutant p53 as promising anticancer agents

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Mutant p53 forms are highly prevalent in human tumors and their expression is restricted to tumor cells, which makes the pharmacological reactivation of mutant p53, through reestablishment of the wild-type p53 activity, an effective and selective anticancer therapeutic approach [1]. Additionally, the expression of mutant p53 in human tumors strongly correlates with highly aggressive tumor phenotypes due to increased resistance to conventional chemotherapy and metastasis formation. Recently, our group identified the compound SLMP53-1 as the first reactivator of mutant p53R280K, using a yeast-based screening strategy [2,3]. Its antitumor activity and molecular mechanism were validated in human tumor cell lines and human xenograft mouse models [2].

In this work, the yeast assay, previously validated to search for reactivators of mutant p53 forms [2], was extended to other highly prevalent mutant p53 forms. The analysis of a new library of synthetic derivatives of SLMP53-1, using the yeast approach, led to the identification of a new potential reactivator of mutant p53Y220C. Human tumor cell lines expressing mutant p53Y220C have been used to ascertain the tumor growth inhibitory activity and to validate the molecular mechanism of this compound, namely the reestablishment of wild-type-like DNA-binding ability to mutant p53Y220C.

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Estudio de las propiedades físicas de mezclas de arcillas, algas y agua de mar para aplicaciones en talasoterapia.

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El término talasoterapia (del griego Thalassa = mar y Therapeia = curación) fue acuñado por el Dr. La Bonnardière en 1865 en Francia. Los centros de talasoterapia son establecimientos en donde se usa el agua de mar y otros recursos marinos (como el clima, la arena, el sol o las algas) con fines terapéuticos y preventivos. Cada vez más se usa el agua de mar con fines de bienestar y puesta en forma, ya que esta agua, junto con el clima marino, ejerce un efecto estimulante general del organismo y de todas las funciones orgánicas.

Los limos marinos son productos constituidos por la mezcla de una fase sólida (arcilla, turba, sedimentos, etc.) y agua de mar. Pueden ser naturales, cuando se forman en los estuarios de los ríos en su confluencia con el mar, o en las orillas de mares lagos salados o mares interiores (como el Mar Muerto o el Mar Negro). Pero generalmente son artificiales, y se preparan en el momento de su uso o mediante un proceso de maduración (contacto del agua de mar con el sustrato sólido). Para este proceso de maduración se usan tanques de acero de diferentes capacidades según el volumen que se quiere elaborar. También se usan mezcladores de diferentes materiales para preparar o agitar las mezclas antes de usarlas y calentarlas.

Para su aplicación se pueden utilizar técnicas como: las envolturas y los emplastos. Para alteraciones reumatológicas, rehabilitación, etc., los limos marinos se aplican en caliente y para ello deben ser calentados en equipos habilitados a tal efecto o a baño María. Para alteraciones dermatológicas o áreas inflamadas se aplican en frío.

El objetivo de esta investigación es el estudio de la densidad, calor específico, conductividad térmica y la viscosidad de mezclas de arcillas, algas y agua de mar usadas en centros de talaso.

La medida de la densidad se ha llevado a cabo mediante el uso de un picnómetro (Álamo, 25ml)[1], para la conductividad térmica se ha utilizado un analizador térmico KD2 Pro Decagon Devices Inc., [2] y el calor específico experimental se midió usando un microcalorímetro Calvet[3].

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The effect of 2-deoxyglucose in photodynamic therapy with redaporfin

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The selectivity of the treatments used in cancer therapies has become an essential feature to improve the ability to kill cancer cells while sparing normal cells. The combination of different drugs is one way of potentiating the efficacy and selectivity of a treatment, opening the possibility of using lower doses, thereby minimizing adverse effects but still increasing the efficacy of treatment. It is known that tumor cells have an alteration in glucose metabolism, characterized by an increase in glycolysis, even in environments with normal oxygen concentration (Warburg Effect) [1]. This modification has been explored, including in clinical trials, with the expectations that the inhibition of glycolysis should alter especially the metabolism of tumor cells. This is the case of trials with 2-deoxyglucose (2DG), a glycolysis inhibitor [2]. Photodynamic therapy (PDT) uses a photosensitizer (which is innocuous in the dark) and light with an appropriate wavelength, that activates the photosensitizer in the presence of oxygen to produce reactive oxygen species [3]. 2DG is phosphorylated to 2-deoxy-D-glucose-6-phosphate which is not metabolized and accumulates in the cell, inhibiting glycolysis. The privation of glucose increases oxidative stress due to an increased production of hydrogen peroxide and superoxide ion, which may reduce viability of tumor cells by antagonizing the Warburg effect while enhancing oxidative stress produced by PDT.

In vitro combination studies employed A549 (human adenocarcinoma) and COS -7 (monkey kidney fibroblasts). We investigated cell viability after PDT with redaporfin – a photosensitizer developed in our laboratories – combined with 2DG in concentrations of 500 nM, 1 mM and 2 mM), in order to examine whether combination of both was more effective than the individual effects.

For the A549 cell line, the combination of redaporfin-PDT with 2mM 2DG led to a cell viability that was significantly lower than redaporfin-PDT alone. In the case of the COS -7 cell line, there was a decrease in cell viability with 2DG alone in the same concentration range, which was not observed in A549. There was also a significant decrease in cell viability at the concentrations of 1 mM and 2 mM of 2DG in combination with PDT compared to PDT alone.

The results suggest that PDT can be more effective in cancer cell lines compared to non-cancerous cell lines. Furthermore, the treatment is more effective when combined with 2DG. The presented results motivate further studies, currently taking place, aiming at the transfer of this combination to *in vivo* studies.

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Synthesis and characterization of a soluble bacteriochlorin for cancer treatment

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Photodynamic therapy (PDT) is a therapeutic strategy that combines the administration of a drug – the photosensitizer (PS) molecule – followed by the irradiation of the target tissue using light with an appropriate wavelength. The combination of light with PS in the presence of molecular oxygen leads to the formation of reactive oxygen species (ROS) which lead to the selective destruction of target tissue [1].

The bacteriochlorins have been increasingly used as photosensitizers due to some of their characteristics such as the affinity for tumors [1], and the intense absorption band in the phototherapeutic window (650 - 800 nm), which is the range of wavelengths in which the laser light has a higher tissue penetration depth [2,3].

In this work, a sulfonated and fluorinated bacteriochlorin (LUZ10) was synthesized and characterized with chemical, photochemical and *in vitro* studies. The chemical and photochemical characterization covered properties such as the solubility in aqueous medium, the infrared electronic absorption spectrum, triplet state lifetime, and singlet oxygen and fluorescence quantum yields. The *in vitro* studies used the CT26 (mouse colon carcinoma) cell line, where the toxicity of LUZ10 was studied in terms of the lethal dose in the presence and absence of excitation light.

This study revealed that LUZ10 has good properties as a photosensitizer for use in oncology. In particular, LUZ10 is soluble in aqueous media, which reduces the burden to the organism compared with other molecules of the same class. Solubilizers are needed to administer most photosensitizers, and are often associated with unwanted side effects that can be avoided with a water-soluble photosensitizer such as LUZ10.

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New anthocyanin derivatives for technological applications in the cosmetic industry

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There is a growing market demand for the incorporation of plant-derived ingredients in new products of the cosmetic industry. The ability to prevent oxidative damages has led to the incorporation of natural bioactives in lotions and facial creams to prevent skin diseases and premature ageing [1]. Anthocyanins are polyphenols arising from plant secondary metabolism that have been shown to display many bioactive properties such as free radical scavenging, metal-chelating, antimicrobial, wound healing, chemopreventive activities [2,3]. On the other hand, they present a lower stability in aqueous solution towards pH, light and temperature and a low solubility in lipophilic media, which compromises their effective application in lipophilic systems and cosmetic formulations.

This work aims to recycle anthocyanins from industrial wastes, to use them as genuine forms and to perform their enzymatic lipophilization by addition of selected chain fatty acids using different experimental conditions (Figure 1) [4].
Also the development of a new skin barrier (SB) model to assay the absorption of bioactives at the skin level using keratinocytes living cells inoculated in a culture well was performed. Around 24h after inoculation is possible to observe the formation of a confluent monolayer. A microelectrode-based biosensor device, referred to as the Electric Cell-substrate Impedance Sensing (ECIS), was used as a continuous data acquisition system [5]. This new system allowed a simple, fast and reliable screening of the capacity of the new lipophilized anthocyanins in comparison with the native ones to cross the skin barrier and at the same time to monitor cell morphology and perform cell-based assays including wound healing assays, towards skin care.

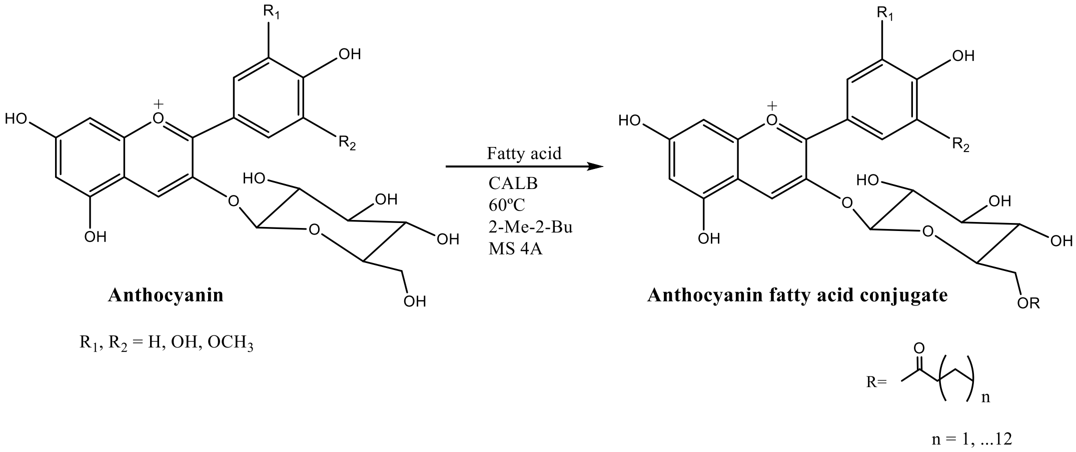

Fig.1. Enzymatic lipophilization of anthocyanins with selected chain fatty acids.

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Chemical composition and potential anti-proliferative in cells lines from extracts of *Citrus reticulata* Blanco peel

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Citrus reticulata Blanco are cultivated worldwide, as is the case of Mediterranean countries, with a large economic and environmental impact [1]. The industrial transformation of citrus fruit produces every year millions of tons of wastes. These wastes or by-products can be potential sources for other industries, for the bioethanol production, cosmetics industries as well as phytopharmaceutical industries [1]. Several bioactivities such as antioxidant, antimicrobial, anti-inflammatory had been attributed to the *C. reticulata* peel [2].
The objective of this study was to extract bioactive compounds from *C. reticulata* fresh peels, to perform its chemical characterization and to evaluate its anti-proliferative potential on BT-474 (human breast carcinoma), Caco-2 (colorectal adenocarcinoma) and HepG2 (hepatocellular carcinoma) cells lines using AlamarBlue assay. The hidro-ethanolic (HE) crude extract had a yield of 3.3% (w/w), with a total polyphenol content of 12.23 ± 4.20 mg GAE/g of sample and an antioxidant activity of 322.12 mmol TE/kg of sample. After SPE fractionation, the methanolic fraction (Fr.HE) had a yield of 7.79% (w/w), showed an increase in total polyphenol content and in the antioxidant activity (56.43 ± 1.613 mg GAE/g of sample and 1638.12 mmol TE/kg of sample, respectively). After 48 hours the exposure of cells to different concentration produced an IC_{50} in BT-474 cells of 349.3±13.2 µg/ml for the HE extract and 174.5±5.8 µg/ml for the Fr.HE, >>500 µg/ml and 391.9±15 µg/ml (HE extract and Fr.HE, respectively) in the Caco-2 cells and for HepG2 cell the values of IC_{50} of >>500 µg/ml and >500 µg/ml (HE extract and Fr.HE, respectively). The results indicate that this extract has a therapeutic and preventive potential.

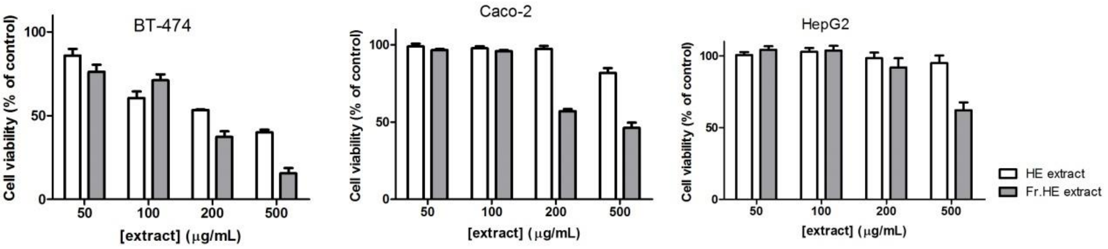

Fig.1. Cell viability and anti-prolifertaive activity of BT-474, Caco-2 and HepG2 cells exposed at 48 hour to hidro-ethanolic crude extract (HE, white bars) and its methanolic fraction (Fr.HE, grey bars). Data are expressed as percentage of control, untreated cells, as mean ± SD.

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Urinary levels of monohydroxyl PAH metabolites in Portuguese firefighters: background levels and impact of tobacco smoke

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Firefighting occupational exposure is classified as possible carcinogen to humans by the International Agency for Research on Cancer and the US National Institute for Occupational Safety and Health [1,2]. Full monitoring of firefighters' exposure to PAHs via all exposure routes should be performed through the quantification of their internal dose. The consumption of tobacco is responsible for the exposure to many smoke components including more than sixty known carcinogens, including polycyclic aromatic hydrocarbons (PAHs) [3]. PAHs are ubiquitous compounds formed during pyrolysis or incomplete combustion of organic matter, being well known for their toxic, mutagenic, and carcinogenic properties to humans [4,5]. So far, the impact of tobacco smoke on firefighters' total exposure to PAHs is very limited.

The present work assesses the background total PAHs internal dose of healthy smoking and non-smoking firefighters serving at Bragança (North of Portugal) fire station. Five of the most predominant PAH metabolites, namely 1-hydroxynaphthalene (1OHNaph), 1-hydroxyacenaphthene (1OHAce), 2-hydroxyfluorene (2OHFlu), 1-hydroxyphenanthrene (1OHPhen), and 1-hydroxypyrene (1OHPy) were detected in all firefighters. Urinary 3-hydroxybenzo[a]pyrene, the PAH biomarker of carcinogenicity, was not detected. Globally, total urinary concentrations (∑OH-PAHs) ranged between 0.491 to 1.02 µmol/mol creatinine and from 0.053 to 0.472 µmol/mol creatinine, respectively for smoking and no-smoking firefighters. The urinary levels of OH-PAHs were 1.3 (2OHFlu) to 2.7 (1OHPy) times higher in smoking than in no-smoking firefighters. Urinary 1OHNaph and 1OHAce were by far the most abundant compounds (>90% of ∑OH-PAHs), being followed by 2OHFlu (2.7-5.4%), 1OHPy (2.1-4.1%), and 1OHPhen (2.2%). Urinary OH-PAH levels will be discussed taking in consideration the existent preliminary guidelines for occupational exposure to PAHs.

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Metabolomics of Age-related Macular Degeneration (AMD): a Nuclear Magnetic Resonance (NMR) study of plasma

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Metabolomics is defined as the qualitative and quantitative analysis of metabolites present within organism, cell, or tissue [1]. Age-related Macular Degeneration (AMD) is the leading cause of irreversible vision loss in elderly in developed countries; it is a multifactorial disease, combining phenotypic, environmental, and genetic risk factors [2]. Metabolomics can help in the detection and possible identification of biomarkers of this disease as well as measuring its impact on plasma metabolome.

Blood samples were collected for a Portuguese cohort with 201 AMD patients, comprising 3 stages of the disease – 45 early stage (aged 70±5.3 years), 124 intermediate stage (aged 75±7.5 years) and 32 late stage patients (aged 80±7.2 years), and 42 controls subjects without any vitreoretinal disease (aged 68±4.9 years). Plasma samples were analyzed by Nuclear Magnetic Resonance (NMR) spectroscopy. For each sample, three 1D experiments were acquired: standard ^{1}H spectrum; T_2-edited (Carr-Purcell-Meiboom-Gill, CPMG) ^{1}H spectrum to allow better visualization of low molecular weight metabolites and diffusion-edited ^{1}H spectrum to select signals of bound or large molecules.

Partial Least Squares-Discriminant analysis (PLS-DA) of the ^{1}H NMR CPMG spectra pointed to a probable separation (Q^2=0.296) between controls and late stage AMD patients. Late stage patients showed higher levels of *dimethylsulfone, acetate and pyruvate and lower levels of HC=CH lipids* compared with control subjects.

As late stage patients are older than controls subjects, the covariance effect between the studied stages and age could not be discarded. In order to investigate this confounder on the metabolome a group of patients in an intermediate stage of the disease was considered, as it is characterized by a wide range of ages. It was found that ~16% of total variability present in NMR spectra could be related to the age contribution; in fact, older people had higher levels of *acetoacetate*, *citrate*, *dimethylsulfone* and *β-hydroxybutyrate*.

Taking this into account, we propose that *acetate*, *pyruvate*, and *HC=CH lipids* may potentially be part of a metabolic signature of AMD, potentially useful in distinguishing late stage patients from subjects without any vitreoretinal disease.

Acknowledgments
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Kinetic of adsorption of pharmaceuticals compounds from aqueous solutions onto activated carbons

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Introduction

Activated carbons (AC) can be used as an antidote to different intoxications[1] and as sustainable adsorbents for the removal of pharmaceutical compounds[2]. This work presents the "in vitro" kinetic of the adsorption of three pharmaceuticals compounds onto different types of ACs. The objective of this work is the obtaining and the interpretation of the breakthrough curves of each adsorbing-adsorbent system as well as the analysis of their therapeutic application.

Experimental

Adsorbents was texturally characterised from their N_2 adsorption-desorption isotherms at -196ºC. The breakthrough curves were obtained with the "in flow" analysis of the adsorption process by using a ¼ inch O.D. and 8.0 cm in length adsorption chamber introduced into a thermostatic bath at 37ºC, where a known amount of the adsorbent forming a packed bed was introduced. Filter sheets had ends that allowed the passage of the liquid stream and prevented the adsorbent itself to leave inside. The solution of the adsorbate, stored in a reservoir, was ran through the bed, with a constant flow of 2.0cm^3 min^{-1}, using an HPLC pump model Shimadzu LC-10AS long enough to saturate the adsorbent. The quantitative analysis of the pharmaceutical compounds in the effluent were analyzed by the UV-1603 Shimadzu spectrophotometer in continual.

Results and Discussion

The breakthrough curves (*cf.* Fig. 1) were interpreted following a model[3] based on the hypothesis that the surface of the adsorbent is formed by different regions and each one of them consist of different adsorbent-adsorbate energy adsorption sites. Since each region behave as a homogeneous surface, assuming that there is no interaction between such regions, it is possible to describe it by applying the Thomas model[4] to each region. Quantitative parameters of the model were analyzed starting from the influence of the textural characteristics of ACs and molecular structure of the pharmaceuticals compounds.

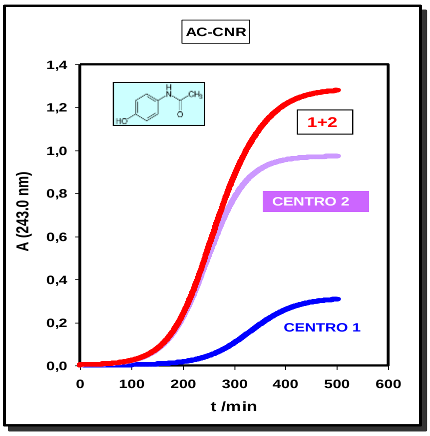

Fig. 1. Breakthrough curve for the two-centres adsorption model

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Síntese e avaliação farmacológica de peptidomiméticos do PLG

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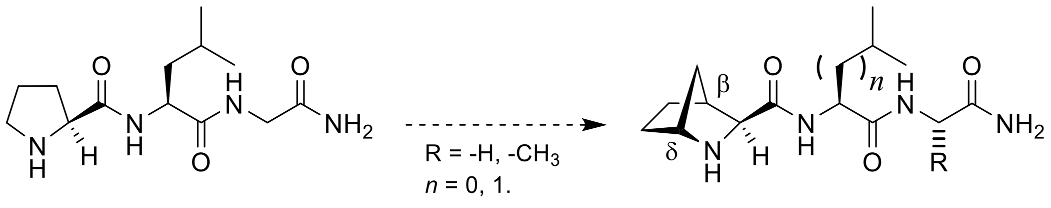
O neuropéptido L-prolil-L-leucilglicinamida (**PLG**, Fig.1) resulta da clivagem proteolítica da hormona oxitocina e possui um papel importante ao nível do sistema nervoso central. Estudos farmacológicos apontam que as suas funções biológicas estão intimamente ligadas à modulação dos recetores dopaminérgicos D_2, convertendo-os num estado de alta afinidade para a dopamina, atuando assim como um modulador alostérico positivo. [1,2]

Neste contexto, o PLG tem por isso demonstrado um papel importante na doença de Parkinson uma vez que esta última está relacionada a um deficit do neurotransmissor dopamina, afigurando-se assim como uma nova abordagem para a descoberta de novos fármacos para esta doença e outras relacionadas.[1]

Os aminoácidos estruturalmente constringidos, tal como as pseudoprolinas rígidas, podem ser importantes para elucidar a conformação bioativa de péptidos contendo prolina, pela estabilização de elementos de estrutura secundária.[3]

O sistema bicíclico ácido *exo*-2-azanorbornano-3-carboxílico é um exemplo de uma estrutura rígida usada na química peptídica como um análogo de prolina *trans*-β,δ-substituído,[2] em permanente conformação envelope Cγ-*endo*.

Neste trabalho estudamos a influência da restrição da conformação espacial do resíduo de prolina na sequência do PLG através do design, síntese e avaliação farmacológica de prolinomiméticos β,δ-constringidos do PLG (Fig.1).



PLG

Análogos do PLG β,δ-constringidos

Fig.1. Estrutura do PLG e dos respetivos análogos sintetizados.

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From α-glucosidases to cholinesterases inhibition – synthesis, SAR STD and docking studies

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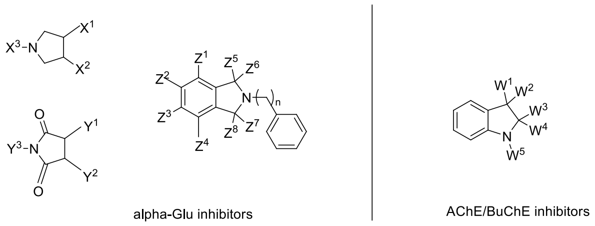
The design and synthesis of pyrrolidine-based iminosugars for evaluation of α-glucosidase inhibition has been reported[1-4]. Further inhibition and toxicity assays, as well as docking studies including homology modelling for *S.cerevisae*'s and Rat (intestinal) α-glucosidases afforded important insights about structural features from both the enzymes and the ligands[3,4]. An interesting structural relation was noted between phtalimide and indolinone derivatives[5], the latter being both acetylcholinesterase and butyrylcholinesterase inhibitors, therefore of strong clinical interest, leading to indolone analogue synthesis, inhibition assays, STD and docking studies, already reported[6,7]. Our current developments will be shown here.



alpha-Glu inhibitors

AChE/BuChE inhibitors

Fig. 1. Structural relations between α-glucosidases and cholinesterases inhibitors

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Acknowledgements

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XXII Encontro Luso-Galego
Química

COMUNICAÇÕES ORAIS E EM PAINEL

Química-Física

Crosslinked polymer network for polymer dispersed liquid crystal devices with permanent memory effect

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Controllable light scattering in liquid crystal (LC) composites by applying electric field could be a promising method to develop optical memory devices. From LC composites, polymer dispersed liquid crystal (PDLC) are possible candidates. They are polymer films with three-dimensional distribution of LC domains suspended in to them normally sandwiched between two conductive glass slides. PDLCs can change transmittance from a totally opaque state to totally transparent state during the application of an external electric field. Typically, the opaque appearance returns to the PDLC when electric field is switched off [1]. However in this work we produce PDLC that use the electric field to create an initial alignment direction that can be frozen even when electric field is switched off giving rise to a permanently alignment state of LC molecules. This property is called permanent memory effect (PME). In the future, based on this feature we can develop an array of optical elements (pixels) by using PDLC technology where write, read and erase information can be modulated by applying an electric field to each pixel. We are concerned first to understand the properties of permanent memory effect for later applying it in the fabrication of digital memory devices.

More than one mechanism for permanent memory effect may be responsible. In this way a correlation between the polymer glass transition temperature and crosslinking of the polymer are competitive effects in determinate the permanent memory effect. In our previously studies [2,3] we found a stronger association between PDLCs produced from higher functional monomers and permanent memory effect. The main problem found was the heavily crosslinked networks even only partial polymerization of the systems. With this high degree of crosslinked polymer networks the LC molecules remain trapped in polymer matrix and are unable to respond to an applied field. In this way, although the excellent result for permanent memory effect (100%) the use of multi-functional pre-polymers in preparation of PDLC with permanent memory effect could encounter problems as higher crosslinked density by high temperatures. Based on these studies and in view of the above problems, the present work aims to be an improvement comparing with previous results obtained for cross-linking polymer matrix. We have seen that crosslinked oligomers with linear polymeric arms significantly lower glass transition temperature (lower than room temperature) than comparable with multi-functional pre-polymers analogues, keeping the permanent memory effect unaffected in the time range from one- to two- hours of thermal polymer curing at 74ºC, enhancement thermal stability. We report the synthesis and characterization of multi-arm oligomers with linear polymeric arms extending radially from a central core with reactive end groups. The end groups are the carbon-carbon double bond where crosslinking occurs. Thus, the alcohol end of corresponding triols and tetraols have been functionalized by a nucleophilic substitution with (meth) or acryloyl chloride, resulting in crosslinkable oligomers. In the second part of the research the resulting multi-armed oligomers end-functionalized were then tested in preparation of PDLCs with permanent memory effect. For a noticeable of this effect a gradient of polymer network density it was obtain by a proper time of polymerization and it was also achieved by incorporation of a weakly crosslinked co-oligomer.

Acknowledgments

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Choline chloride-based ionic liquids as templating agents towards mesoporous biopolymer/sol-gel composites

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Mesoporous materials have attracted much attention of chemists and material scientists for a long time due to commercial interest in their application in chemical separations and heterogeneous catalysis and due to scientific interest in the challenges posed by their synthesis, processing, and characterization. In recent years, It has been reported the use of deep eutectic solvents as template to monolithic mesoporous silica with wormhole framework via the nanocasting technique [1].

In this context, a method already described in the literature for the reticulation of Chondroitin Sulfate (CS), a linear acidic polysaccharide composed of repeating disaccharide units and modified with sulfate residues, via a sol-gel process [2], was revisited with the aim of exploring for the first time two different ionic liquids based on choline chloride as mesoporosity precursors. The originally described materials presented characteristics of microporosity (pore size <2 nm), low BET superficial area (range of 4-6 m^2 / g), but showed significant retention capacity of different metal cations The purpose of preparing mesoporous sorptive materials for metal cations such as Pb(II), and Cd(II) was the increase of the loading capacity and improvement of kinetic features. Simultaneously controls, corresponding to adsorbents without CS, were performed. All sorbents were structurally characterized and its efficiency in sorption of the cations under study was assessed by determination of adsorption isotherms and kinetics.

The developed sorbents presented mesoporosity, with a distribution of pores in the meso range (average diameter approx. 4 nm) and high surface areas (range of 140 - 210 m^2/g). The retention capacity, of these new materials, increased for all cations studied (q_{max}Pb(II) approx. 60 mg/g and q_{max}Cd(II) approx. 50 mg/g), compared to the materials already described in the literature (q_{max}Pb(II) approx. 24 mg/g and q_{max}Cd(II) aprox. 21 mg/g). Moreover, the mesoporous materials showed faster kinetics with higher values of k_2 (approx. 1.4 g/mg min^-1) compared to microporous materials (approx. 1.1 g/mg min^{-1}).

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Oddities in the inner-valence shell charge distribution of scandium, titanium and vanadium in MO_nX_m (X=F, Cl) complexes

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First-row transition metal complexes play an important role in the development of novel catalysts, and also serve as surrogate models of enzymatic active sites. Their structural diversity presents also a challenging ground on which novel theoretical insights on the electronic structure of atoms and molecules may be gathered. One such example is the arrangement of the Inner-Valence Shell Charge Concentrations (iVSCC) in first-row transition metal complexes, which were first described by Gillespie and co-workers [1]. According to Gillespie's observations[1,2], the iVSCC should be located in the region occupied by the *3d* orbitals; equal in number to the coordination number of the metal centre; and located opposite to each of the ligands [1,2]. Recently, non-gillespiean arrangements of the iVSCC were described in vanadium-acetate complexes[3]. It was further demonstrated that violations to the gillespiean rules have a negative impact on the stability of the metal centre. In the case of vanadium-acetate complexes, such destabilization was compensated by an additional stabilization of the acetate ligand(s) [3].

In this work, a more complete survey of scandium, titanium and vanadium complexes with general formula MO_nX_m (M= Sc, Ti, V; X= F, Cl) were studied using Density Functional Theory (DFT, at the TPSS/Def2-TZVP level), and the topology of the electronic density of these complexes at different stable geometries was analysed under the formalism of Bader's Quantum Theory of Atoms in Molecules (QTAIM). The results show a diverse set of complexes at different geometries with different arrangements of the iVSCC in their metal centre and different relative stability. What is more, a linear relationship between each complex stability and their adherence to Gillespie's rules was not observed. Instead, a more complex set of relationships between the arrangement of the ligands and that of the iVSCC has been observed, the most relevant of which are discussed in this presentation.

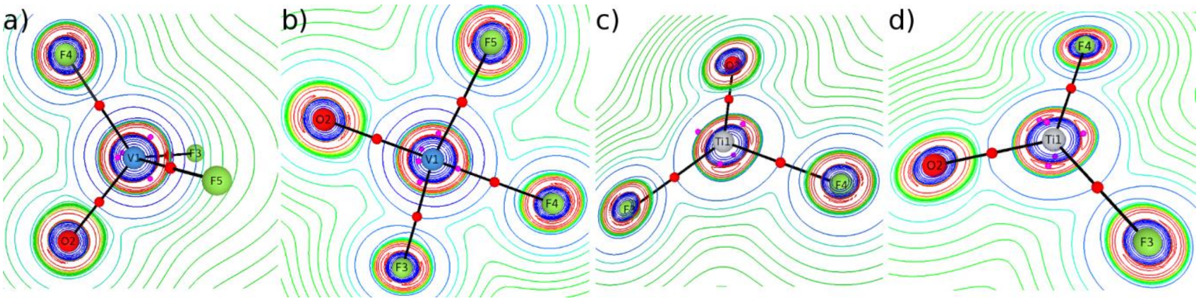

Fig.1. Molecular graphs of VOF_3 (a and b) and $TiOF_3$ (c and d) at their most stable (a and c) and metastable conformations (b and d), superposed with the contour plot and minima of $\nabla^2\rho(\mathbf{r})$ (pink spheres). While in VOF_3 the Gillespie-complying arrangement renders the most stable of the two forms (a); in the case of $TiOF_3$, the most stable form (c) deviates the most from Gillespie's rules.

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Light-induced conformational changes in matrix-isolated molecules: the case of 6-methoxyindole

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Trapping biologically relevant molecules in low-temperature matrixes of inert gases and using infrared spectroscopy as probing technique is a very powerful methodology for identifying and characterizing experimentally the conformational structure of isolated species. In turn, this knowledge is of fundamental importance for better understanding their biological activity. Moreover, the possibility of changing the conformational distribution of matrix-isolated species, either by thermal excitation or by subjecting the samples to narrowband or broadband radiation of the UV or IR spectral regions, opens a window for exploiting conformer-specific reactivity.

In this communication, we will present recent advances in the study of light-induced conformational changes in matrix-isolated molecules (xenon and argon were used as matrix host gases). As model system we choose 6-methoxyindole. The conformational space of this molecule is characterized by two rotamers: *syn* and *anti* (see Fig. 1), whose energy difference falls between 1.8 and 3.2 kJ mol^{-1} in favour of the *syn* form (values calculated at different levels of theory) [1].

After identifying the spectral signatures of the two conformers in a freshly deposited cryogenic matrix, monochromatic near-infrared (NIR) laser radiation tuned at the frequency characteristic of the first NH stretching overtone (2νNH) of each conformer was applied. This procedure led to selective and large-scale population shift between the two conformers (Fig.1). Such remarkable finding constitutes the unique case known so far of an internal rotation of a bulky fragment (including a carbon atom) in a low-temperature rigid matrix induced by NIR excitation of a group (in this case NH) located in a remote position [1].

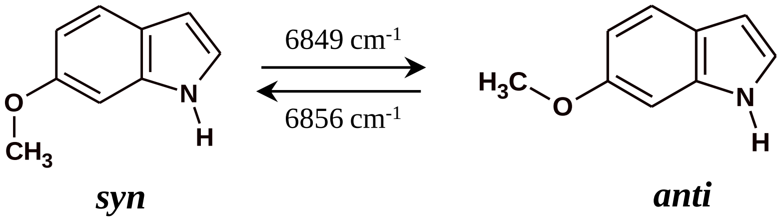

Fig.1. Conformers of 6-methoxyindole and their NIR-induced interconversion. The numbers next to the arrows are the experimental wavenumbers corresponding to the 2νNH overtone transitions for the *syn* (top) and *anti* (bottom) conformers in a xenon matrix (30 K) that were used in the NIR irradiations.

Additionally, we have found that the conformational populations of 6-methoxyindole trapped both in xenon and argon matrixes can also be controlled by broadband infrared excitation, monochromatic UV-light, and thermally. These results will also be presented.

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Physical vapor deposition of thin films for organic electronics

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Physical vapor deposition (PVD) is one of the most used and efficient methods to fabricate thin films. In PVD, the vapor source is a solid or liquid material, and this method implies only physical processes such as high-temperature vacuum sublimation/vaporization with consequent condensation onto a substrate surface.

We present a high vacuum thin film deposition apparatus, ThinFilmVD, for physical vapor deposition of semiconductor materials with electronic applications. [1] The thin films are prepared from the mass flow of effusing vapor from the Knudsen cell, which is maintained at phase equilibrium conditions. The ThinFilmVD allows accurate vapor pressure measurements as well as a high versatility in the deposition of thin films, as-grown crystals, composites, and hybrid micro- and nanostructured materials (Fig. 1).

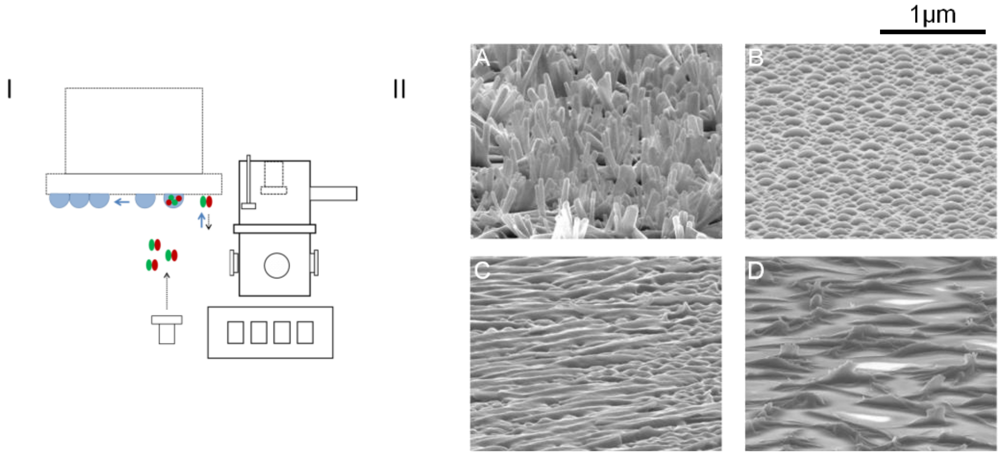

Fig.1. I – ThinFilmVD methodology; II – Micrographs of thin films of organic materials prepared by PVD (A – as-grown crystals; B – amorphous materials; C – nanocomposites; D – hybrid materials).

From this methodology, thin films of several classes of organic semiconductor materials (OSCs) [2,3], ionic liquids (droplets and thin films) [4] and more recently perovskites were prepared on the surface of transparent conductive oxides (TCOs). The structural and morphological characterization of the nanostructures were evaluated by high-resolution scanning electron microscopy (SEM) and X-ray powder diffraction (XRD). Our results evidence that thin films prepared by PVD have higher coverage and uniformity when compared with the solution coating methodology.

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Pseudocapacitive electrochemical storage mechanisms in non-stoichiometric cerium oxide/multiwalled carbon nanotube composites: a square wave voltammetry study in different aqueous electrolytes

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Hybrid supercapacitors have been widely explored during the last decades since they bridge the gap between electric double layer capacitors (high power density) and conventional batteries (high energy density). Electrodes combining physical (capacitive) and chemical (pseudocapacitive) charge storage can be prepared by supporting redox-active species on a porous/conductive surface. In this regard, cerium oxide/carbon nanotube composites are interesting materials, as transition metal oxides present a high redox activity while carbon nanotubes present outstanding electron conduction. Besides the electrode properties, the electrolyte also determines the faradaic reactions that take place at the electrode/electrolyte interface. In general, the existing reports on hybrid supercapacitors have been focused on the exploration of novel electrode materials to achieve high energy densities. Nevertheless, a shortage of detailed research to fully understand the charge storage phenomena occurring at the surface of the electrodes is more than noticeable. Our group has recently developed a promising electrochemical method to identify the charge storage mechanisms at the surface of carbon-derived electrodes [1]. This novel method, based on the deconvolution analysis of Square Wave Voltammetry (SWV) curves, was used in the present work to study the influence of the electrolyte on the electrochemical activity of different cerium oxide/carbon nanotube composites.

With this purpose, two cerium oxide/carbon nanotube composites were prepared by sol-gel deposition of cerium oxide on the carbon nanotubes surface. One of the composites was prepared in a strong basic medium to promote the hydrolysis of the cerium precursor. The second one was prepared in the absence of catalyst in order to decrease the rate of hydrolysis. The modification of the deposition conditions led to materials with different morphology, texture and surface chemistry, causing significant changes on their electrochemical performance. The charge storage mechanisms occurring on the surface of both composites were thoroughly studied in order to understand such different behavior. A combination of sweep wave voltammetry and deconvolution analysis in acid (1M H_2SO_4), basic (1M NaOH) and neutral (1M Na_2SO_4) electrolytes was carried out. It was observed that slow hydrolysis rates of cerium oxide lead to the formation of nanosized and well distributed ceria particles. This particular morphology enhances the dispersion of Ce^{+3} centers and facilitates the appearance of defects and amorphous oxide structures. All these circumstances promote the redox/intercalation phenomena and improve the electronic/ionic transport within the bulk of the electrode.

Acknowledgements
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Adsorption of phenol onto activated carbon fiber

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Introduction

Phenol and its derivatives are common contaminants in wastewater and they are characterized by a high resistance to degradation. It is therefore used as a model in research to develop new technologies for remove or waste recovery, which would be a step forward in environmental and economical terms. Activated carbon fibers (ACFs) are essentially microporous carbonaceous materials whose high internal surface confers them exceptional adsorptive properties. The aim of this work is the study of the phenol adsorption onto ACF, especially the influence of experimental variables on the breakthrough curves.

Experimental

The ACF was texturally characterised from the N_2 adsorption-desorption isotherms at -196ºC. The adsorption isotherms were obtained at 37ºC, keeping the adsorbing and the adsorbent in agitation in order to reach the equilibrium. The breakthrough curves were obtained by an "in flow" analysis of the adsorption process by using a ¼ inch O.D. and 8.0cm in length chamber introduced into a thermostatic bath, where a known amount of adsorbent forming a packed bed was introduced. Filter sheets had ends that allowed the passage of the liquid stream and prevented the adsorbent itself to leave inside. The solution of the adsorbate, stored in a reservoir, was ran through the bed using an HPLC pump model Shimadzu LC-10AS long enough to saturate the adsorbent. The quantitative analysis of the phenol adsorption was monitored by the UV-1603 Shimadzu spectrophotometer in continual.

Results and Discussion

The adsorption isotherms and the breakthrough curves were interpreted following a model[3] based on the hypothesis that the surface of the adsorbent is formed by different regions and each one of them consist of different adsorbent-adsorbate energy adsorption sites (*cf.* Fig.1). Since each region behaves as a homogeneous surface, assuming that there is no interaction between such regions, it is possible to describe it by applying the Langmuir equation for the isotherms and the Thomas model[4] for the breakthrough curves for each region. The experimental results and the quantitative thermodynamic and kinetic parameters of the model were analyzed to interpret the adsorption process and the influence of the experimental variables in the kinetic process.

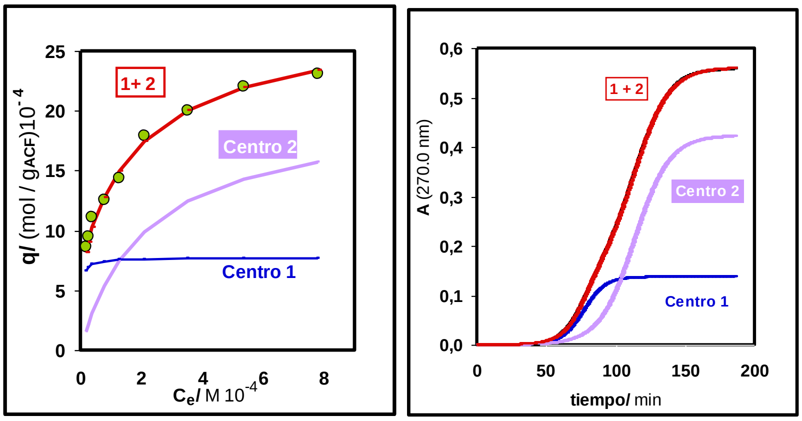

Fig. 2. Two-centres model for isotherm and breakthrough curve for phenol-ACF system

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Influence of ^{13}C enrichment on the luminescence of C_{70} fullerene

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Fullerenes C_{60}, C_{70} and some of their derivatives exhibit a strong thermally activated delayed fluorescence (TADF).[1-2] In the TADF mechanism, after excitation and once attained S_1, intersystem crossing (ISC) to the triplet manifold occurs, followed by a second ISC from T_1 back to S_1, and then by fluorescence emission.[3, 4] The S_1-T_1-S_1 cycle may repeat itself a number of times before fluorescence finally takes place, however this mechanism is operative in the absence or presence, in very low concentrations, of molecular oxygen, otherwise the triplet state is quenched.[4] For this reason, fullerenes, namely C_{70}, can be used in very sensitive oxygen sensors.[5]

The major effect of ^{13}C enrichment on the TADF of both C_{60} and C_{70}[6,7] and respective oxygen sensing properties[5] was already reported for the extreme cases, but a detailed understanding of this unique isotope effect is still lacking.

In this work, we report and discuss in detail, how the progressive ^{13}C enrichment affects the delayed fluorescence and phosphorescence of C_{70} fullerene.

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Water solubility of terpenes and terpenoids

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Terpenes and terpenoids represent an enormous and wide class of natural products where the vast majority are found only in plants. They are components of essential oils, flavours, spices and fragrances, and became a very important subject due to their biological sources and industrial importance [1,2]. Many of them are considered as GRAS (Generally Recognized As Safe) and their importance is related with their use in the pharmaceutical and chemical industries [3]. With the increasing importance of their practical applications in the fragrance and flavours, process-relevant physico-chemical data of terpenes and terpenoids have been retrieved over time. Meanwhile, with an emerging perception of terpenes and terpenoids impact on the environment, right through to implications on a global scale, those data are proving to be insufficient.

In this work, the water solubility of carvacrol, thymol, eugenol, geraniol, linalool, DL-citronellol, (1R)-(−)-Fenchone, (1R)-(+)-camphor, eucalyptol, (R)-(+)-limonene, (S)-(+)-carvone, (−)-menthone, and (−)-isopulegol are reported, in the temperature range from (298.15 to 323.15) K. Due to the very low solubility values, a special approach has been followed for the solubility measurements; a saturated aqueous solution was generated within a dialysis tubing, followed by careful sampling and dilution in methanol. The process was speeded up using an ultrasonic bath with temperature control before the equilibrium step. The main advantage of the present technique is to avoid sampling of solute not dissolved, but present in micro-emulsions, a common experimental error, which often leads to overestimated solubility values. UV spectroscopy was used for quantitative analysis.

Results show that the applied experimental method provides accurate aqueous solubility data for these slightly soluble compounds.

Acknowledgments
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Efeito do solvente na interação de xantona com DNA

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As propriedades farmacológicas da xantona e de compostos estruturalmente semelhantes têm sido objeto de estudo no desenvolvimento de novos fármacos. As potencialidades anti-tumorais que estes compostos exibem para finalidade terapêutica têm sido estudadas no segmento da farmacopeia oncológica, como possíveis precursores de compostos bioativos para o tratamento deste tipo de doença. A compreensão do mecanismo de interação que se estabelece entre a xantona e a molécula de DNA, de cadeia dupla, possível alvo biológico neste tratamento oncológico, permite avaliar novas possibilidades de formulação de compostos que exponenciem o seu efeito bioativo. Deste modo, a compreensão do mecanismo de interação entre a xantona e a molécula de DNA pode dar uma contribuição fulcral para otimização de estratégias de formulação de compostos com fins terapêuticos.

Nesta comunicação, apresentam-se os resultados do estudo da interação de xantona com DNA de cadeia dupla, em diferentes solventes. Utilizando espetroscopia de UV-vis, foram registados espetros e efetuadas experiências de desnaturação térmica de soluções de DNA e xantona com diferentes concentrações. Todas as experiências foram efetuadas em soluções aquosas e em soluções em água/etanol, mantendo constante o pH e a força iónica de todas as soluções. A partir dos espetros UV foram obtidas constantes de ligação DNA-xantona a 293.15 K. A partir das curvas de desnaturação obteve-se a variação da fração de DNA desnaturado com a temperatura para cada concentração de xantona, assim como a temperatura de desnaturação e o hipercromismo.

Os resultados indicam uma interação acentuada de xantona com DNA, que afeta a estabilidade da dupla hélice, e sugerem que a ligação de xantona a DNA ocorre essencialmente por intercalação entre os pares de bases da molécula de DNA. O efeito do solvente é discutido em termos das características da ligação de xantona a DNA.

Pretende-se, com este estudo, dar um contributo para a compreensão do mecanismo de interação entre xantona e DNA, importante para o desenvolvimento de fármacos estruturalmente semelhantes a xantona, com efeitos anti-tumurais pela interação com DNA.

Análise físico-química para determinação da estabilidade de duas formulações de aplicação tópica com produtos apícolas

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Um dos passos determinantes do desenvolvimento de formulações cosméticas é a elaboração de estudos de estabilidade, cujo objetivo é a prever possíveis alterações físico-químicas, químicas e microbianas que sejam possíveis de ocorrer no intervalo de tempo entre a produção do cosmético e o dia no qual este expira. A elaboração destes estudos contribui para a escolha da embalagem na qual o cosmético será embalado, assim como para o desenvolvimento da formulação, fornecendo informações relevantes acerca de incompatibilidade entre os ingredientes e/ou instabilidade do cosmético. Adicionalmente, os estudos de estabilidade permitem a avaliação da segurança, eficácia e atuação do cosmético.

Com este trabalho pretendeu-se desenvolver duas formulações cosméticas para aplicação tópica que combinem diferentes produtos apícolas e óleos essenciais de plantas medicinais com efeitos conservantes. Foi testado o efeito de dois produtos apícolas diferentes (extrato hidroalcoólico de própolis e dois méis de *Lavandula spp.* com diferentes proveniências) e de óleos essenciais de duas espécies diferentes (*Thymus Zygis L. subsp.* Zygis e *Mentha pulegium L.*). Para tal elaboraram-se várias preparações às quais foi adicionado um dos óleos essenciais (o.e) e um produto apícola.

Foi ainda elaboradas, para cada tipo de formulação, uma preparação com óleo essencial e sem a incorporação de nenhum produto apícola e uma preparação sem a adição de óleo essencial nem de qualquer produto apícola, tendo estas sido utilizadas como referência. Relativamente aos produtos apícolas o mel de *Lavandula* spp. foi utilizado na proporção de 1:50 (v/m) e de 1:20 (v/m) e o extrato hidraalcoólico de própolis foi adicionado numa concentração de 5% (m/v). A concentração de óleo essencial utilizada foi de 7,86x10^{-4} g/g o.e/emulsão.

Cada uma das preparações obtidas foi subtida a diferentes testes físico-químicos, com o objetivo de avaliar a estabilidade das emulsões. A variação do pH foi analisado ao longo de 15 dias, tendo sido medida de 4 em 4 dias, a viscosidade foi analisada no tempo zero e após 15 dias utilizando diferentes velocidades de rotação por minuto. Procedeu-se ainda à elaboração de testes de vibração, nos quais as amostras foram colocadas num vortex durante 10 segundos e a testes de luminosidade, tendo as amostras sido acondicionadas em caixas de plástico transparentes, com recurso a uma lâmpada dayligth, durante 15 dias, encontrando-se a lâmpada 16 horas ligada e 8 horas desligada, com o objetivo de detetar sinais de instabilidade à exposição à luz. Adicionalmente foi medida a densidade de cada uma das formulações.

De todas as amostras analisadas não foi verificada qualquer alteração no aspeto das emulsões quando submetidas ao teste de vibração, o que indica que estas são estáveis e que a utilização dos produtos apícolas não afeta o comportamento das emulsões. Relativamente aos testes de luminosidade, apenas uma das preparações não apresentou alterações na cor, tendo-se verificado no entanto uma diminuição do pH de 4,7 para 3,6. Em relação às restantes amostras todas apresentaram uma alteração na cor de bege para branco, pelo que se pode concluir que estas amostras são fotossensíveis e que devem ser guardadas num local escuro ou em alternativa numa embalagem opaca. O valor da densidade de todas as amostras situou-se no intervalo entre 0,5-0,6.

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Entalpias de solução de tetrafluorborato de 1-hexil-3-metilimidazólio: estudo do efeito de solvente

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Os líquidos iónicos são uma classe de compostos químicos que tem sido extensivamente estudada nos últimos trinta anos [1]. Estes estudos incluem, para além da síntese, a sua utilização como solventes em diferentes reacções. Também a caracterização físico-química e a aquisição de parâmetros termodinâmicos deste tipo de compostos tem sido levada a cabo ao longo dos últimos anos. Apesar do conjunto vasto de resultados disponíveis na literatura, a larga maioria dos estudos aborda os líquidos iónicos unicamente do ponto de vista de solvente e não como possível soluto.

No seguimento de estudos anteriormente realizados no âmbito do Grupo de Estrutura e Reatividade da FCUL [2], o objectivo deste estudo é identificar de que forma o tetrafluorborato de 1-hexil-3-metilimidazólio interactua com solventes de diferentes polaridades e propriedades ácido-base, recorrendo a uma metodologia baseada em relações quantitativas estrutura-propriedade [3].

Na realização deste trabalho as entalpias de solução do tetrafluorborato de 1-hexil-3-metilimidazólio (c ≈ 0.01 mol dm^{-3}) foram medidas em 14 solventes com diferentes funcionalidades. As equações modelo obtidas, permitiram identificar e quantificar as interações soluto-solvente dominantes. Os resultados mostram o papel relevante e positivo da acidez de Lewis/dipolaridade do solvente, traduzidas pelo termo E_T^N de Dimroth e Reichardt [3] no processo de solução e o efeito contrário da dipolaridade/polarizabilidade.

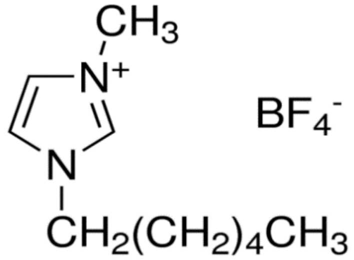

Fig.1. Tetrafluorborato de 1-hexil-3-metilimidazólio

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Polymorphism of 2-phenylbutiric acid

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Polymorphism, the ability of molecules to give rise to more than one arrangement in the solid state, has great implications in a variety of domains, for instance in pharmaceutical performance and solid state reactivity. 2-Phenylbutyric acid is structurally closely related to several nonsteroidal anti-inflammatory drugs. Moreover, although co-crystals of racemic 2-phenylbutyric acid and of its enantiomers with isonicotinamide have been published [1], as far as we know no solid state investigation of the pure compounds has been performed.

In this communication an investigation on the polymorphism of 2-phenylbutiric acid is undertaken. A multidisciplinary investigation using differential scanning calorimetry, polarized light thermal microscopy, infrared spectroscopy and X-ray diffraction analysis was performed.

For the racemic compound two polymorphic forms could be identified, often concomitantly obtained by melt cooling. A solid-solid transition from the lower melting form, $T_{\text{fus,II}}$ = (26 ± 0,2) ºC to the higher melting one, T_{fus} = (41 ± 0,2) ºC, was observed by thermomicroscopy.

The pure enantiomers, liquids at room temperature, give rise to glasses on cooling in all experimental conditions accessed.

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Estudio teórico experimental de la viscosidad dinámica de mezclas n-octano + 1-heptanol a diferentes temperaturas

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En los últimos años se han realizado numerosos estudios de la viscosidad dinámica de mezclas de n-alcanos + 1-alcoholes. En este trabajo se estudia el comportamiento de la viscosidad de mezclas binarias n-alcano + 1 alcohol a diferentes temperaturas y a presión atmosférica.

La densidad se midió utilizando un densímetro tubo vibrante Anton Paar DMA 4500. Los detalles sobre el procedimiento experimental, calibración, control de temperatura se pueden encontrar en Lago et al [1]. Usando este método, la densidad se determina con una incertidumbre de 10^{-4} g cm^{-3} en todo el rango de temperaturas.

Las medidas de viscosidad se realizaron con un viscosímetro Anton Paar AMV 200, conectado a un baño de circulación de fluido PolyScience que controla la temperatura con una incertidumbre de 10^{-2} K. Este dispositivo determina la viscosidad del fluido a través de la medición del tiempo de caída de una bola de acero de laminación en el interior de un capilar de vidrio lleno con la muestra [2].

La viscosidad dinámica de las mezclas n-octano + 1-heptanol disminuye al aumentar la concentración de n-octanol y la temperatura. El incremento de la viscosidad disminuye con la temperatura, por otra parte presenta una asimetría encontrándose los máximo a fracciones molares ricas en 1-heptanol.

En la bibliografía existen numerosa ecuaciones de predicción de la viscosidad de mezclas de líquidos como: Grunberg-Nissan [15], McAllister [16], Auslander [17], Teja-Rice [18], Tamura-Kurata [19], Dolezalek-Schulze [20], McAllister-Laddha [21], Heric-Brewer [22], Dimitrov-Kamenski [23], Focke-Du Plessis [24]. En este trabajo se analiza la capacidad predictiva de la viscosidad dinámica de distintas ecuaciones.

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Strategies to tailor the properties of hydrothermally synthesized glucose derived carbon/carbon nanotube hybrids

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Interest in hydrothermal conversion of biomass has increased sharply in recent years due to its low cost and mild synthesis conditions, making the process more affordable and environmentally friendly than conventional methods [1]. However, one of the main limiting factors hindering the applicability of the as-prepared hydrothermal carbons is that they usually exhibit limited porosity [2]. In order to overcome this drawback, different strategies, such as carbonization and activation, have been addressed to introduce micro-mesoporosity and to modify their surface chemistry [3]. Tailoring the properties of hydrothermal carbons is of great importance for most applications, and so more research is needed in this field.

In the present study, glucose-derived carbon/carbon nanotube hybrids were prepared by hydrothermal carbonization (HTC) of glucose in the presence of nanotubes (CNT) and oxidized nanotubes (CNT_{ox}). The as-prepared hybrids were subjected to different thermal post-treatments: i) carbonization (at 700ºC under N_2 flow), ii) chemical activation (with KOH 50 w/w. % at 700ºC under N_2 flow) and iii) physical activation (at 1000ºC under CO_2 flow). The applied thermal post-treatments promote modifications in the porous and chemical properties of the synthesized materials. Carbons obtained from glucose are exclusively microporous, and their surface areas increase in the following order: carbonization (460 m^2/g) < chemical activation (660 m^2/g) < physical activation (2300 m^2/g). In addition, physical activation of samples in which small amounts of CNT_{ox} were added into the precursor solution (0.25 wt. %), leads to materials with larger surface area (2600 m^2/g) and also promotes the formation of mesoporosity (V_{meso} = 0.15 cm^3/g). Concerning chemical properties, it was found that chemical activation gives rise to materials with higher percentage of oxygen (6.4 wt. %) than carbonization (1.1 wt. %) or physical activation (up to 0.3 wt. %).

The potential of the hybrid carbon materials towards their use in electrochemical applications was also studied by means of cyclic voltammetry in a three-electrode cell. Physical activation increases the specific capacitance of the glucose-derived carbon from 12 to 126 F/g. Noteworthy, the capacitance enhancement is even more pronounced (178 F/g) for physically activated samples when CNT_{ox} are added to the precursor solution. Additional electrochemical characterization reveals that the latter hybrid material not only offers higher molecular diffusion due to the presence of mesoporosity, but also higher faradaic activity due to the larger amount of accessible redox active oxygen-functionalities.

In conclusion, this work highlights the synthesis of materials with well-developed porosity along with appropriate surface chemistry, offering high potential as electrodes for electrochemical systems.

Acknowledgements

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Monomer-excimer spectral phasors and mixed fluorescence decays in the phasor space

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Phasor plots (plots of the Fourier sine transform vs. the Fourier cosine transform, for one or several angular frequencies) of both the fluorescence intensity decay [1-3] and of the fluorescence spectrum (spectral phasor plot) are being increasingly used in studies of homogeneous and heterogeneous systems. In this work, the phasor approach is applied to monomer-excimer systems with a focus on mixed decays and spectra, i.e. containing a contribution from both monomer and excimer. The phasors of mixed decays fall on a straight line delimited by the excimer and monomer phasors. With a fixed concentration, and by continuously increasing the emission wavelength, the phasor moves from pure monomer to pure excimer. At a certain intermediate wavelength, which is concentration dependent, the phasor crosses the universal semicircle and the decay becomes single exponential. This is an interesting case of an exponential decay not corresponding to a single fluorescent species. Monomer-excimer steady-state fluorescence spectra are also studied. A new method for obtaining and displaying the isostilbic point is presented. Spectral phasors are discussed in the context of monomer-excimer analysis. All results are demonstrated experimentally with pyrene in methylcyclohexane at room temperature, for which a full phasor picture emerges, combining in a single diagram monomer, excimer and mixed decays measured at several concentrations.

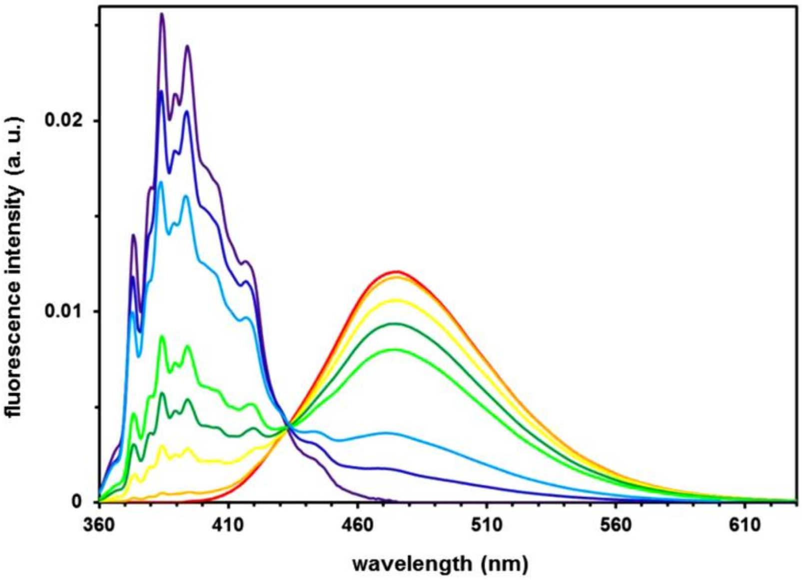

Fig.1. Area normalized fluorescence spectra of pyrene in MCH at 25 ºC as a function of concentration. Monomer (violet), 5.1×10^{-6} M (indigo), 1.0×10^{-4} M (blue), 4.9×10^{-4} M (light green), 9.7×10^{-4} M (dark green), 2.4×10^{-3} M (yellow), 0.019 M (orange), and excimer (red). The isostilbic point at 433 nm is clearly seen

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Solid state investigation of supramolecular interactions between pyridinecarboxamides

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The design and synthesis of stable solid-state structures based on noncovalent interactions is included in the field of supramolecular chemistry. [1] The construction of a variety of organized frameworks, allows tuning of physical-chemical properties, and is one of the goals of crystal engineering. [2]

Pyridinecarboxamide isomers, nicotinamide (NA), isonicotinamide (INA) and picolinamide (PA), Figure 1, have been used as co-formers in several pharmaceutical cocrystal systems, although interactions between themselves have never been studied, to our knowledge. Each of these compounds has been investigated for formulation of drugs used against Alzheimer's disease, age-related loss of thinking skills, and depression. [3] Nicotinamide (Vitamin B3), possesses special relevance because it is generally regarded as safe (GRAS) by FDA (Food and Drug Administration).

In this work a solid state investigation of NA+INA, NA+PA and INA+PA mixtures was undertaken. Mixtures were prepared in different proportions by liquid (ethanol) assisted mecanochemistry.

The solids obtained were characterized by thermal methods - differential scanning calorimetry (DSC) and polarized light thermomicroscopy (PLTM), infrared spectroscopy (FTIR/ATR) and X-ray powder diffraction (XRPD).

Binary solid-liquid phase diagrams were determined. The system NA+INA gives rise to a cocrystal NA:INA in a 1:1 molar ratio and presents polymorphism. The NA+PA and INA+PA mixtures give rise to simple binary solid–liquid phase diagram with an eutectic point, well described by the Schröder-van Laar equation.

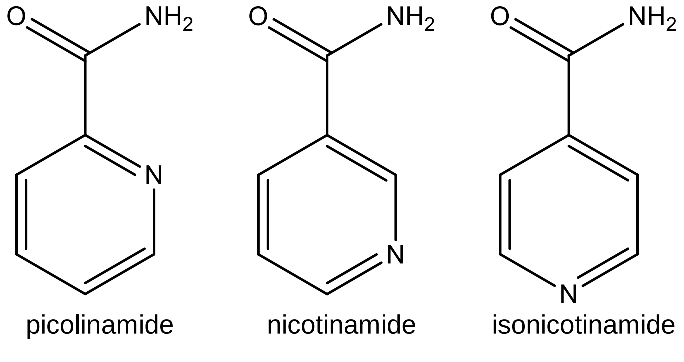

Fig.1. Pyridinecarboxamides isomers

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Caraterização da química superficial de nanotubos de carbono oxidados por meio de técnicas analíticas complementares

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A relevância que os materiais de carbono têm assumido nas últimas décadas em diferentes tecnologias de proteção ambiental e processos de conversão/armazenamento de energia encontra-se intrinsecamente relacionada com a possibilidade de afinar as suas propriedades químicas superficiais em função da aplicação requerida, mediante tratamentos térmicos e químicos adequados [1]. Não obstante, o aparecimento e a disponibilidade de novas técnicas de caracterização revelaram-se fulcrais por permitirem uma melhor compreensão das modificações introduzidas nos materiais por via desses tratamentos. Todavia, algumas técnicas não permitem uma análise quantitativa, outras requerem grandes quantidades de amostra, outras são demoradas ou difíceis de implementar. Em alguns casos, a interpretação dos dados é também muito subjetiva [2-4].

No presente trabalho, a química superficial de nanotubos de carbono modificados foi estudada combinando distintas técnicas analíticas relativamente acessíveis, nas quais se incluem a análise e interpretação dos perfis de CO e CO_2 dessorvidos em ensaios de TPD, e a interpretação dos espectros de XPS relevantes. Para o efeito, nanotubos de carbono comerciais foram oxidados com ácido nítrico e posteriormente tratados termicamente a diferentes temperaturas com o objetivo de remover seletivamente os grupos oxigenados incorporados (Fig.1).

O estudo sistemático envolvendo a identificação e quantificação de tais grupos permite uma interpretação menos ambígua dos dados, e uma melhor caracterização da química superficial dos materiais.

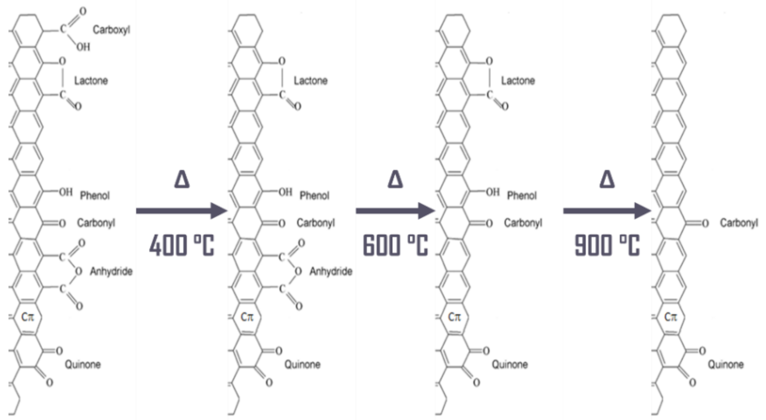

Fig.1. Grupos oxigenados identificados na superfície das amostras de nanotubos de carbono

Agradecimentos
Este trabalho foi desenvolvido no âmbito do projeto “AIProcMat@N2020 - Advanced Industrial Processes and Materials for a Sustainable Northern Region of Portugal 2020”, com referência NORTE-01-0145-FEDER-000006, cofinanciado pelo Programa Operacional Regional do Norte (NORTE 2020), através do Portugal 2020 e do Fundo Europeu de Desenvolvimento Regional (FEDER) e do Projeto POCI-01-0145-FEDER-006984 - Laboratório Associado LSRE-LCM - financiado FEDER, através do COMPETE2020 – Programa Operacional Competitividade e Internacionalização (POCI) e por fundos nacionais através da Fundação para a Ciência e a Tecnologia I.P. R.P. Rocha agradece a bolsa SFRH/BD/95411/2013.

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Cyclohexane oxidation using an iron catalyst heterogeneized on hierarchical Y prepared by crystal rearrangement method

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The aim of this work is the development of hierarchical Y zeolites to act as an efficient support for the immobilization of a C-scorpionate iron (II) complex, the [$FeCl_2(HCpz_3)$] (pz = pyrazolyl) [1], to be used as heterogeneous catalysts in the transformation of cyclohexane to cyclohexanol and cyclohexanone in environmentally friendly reaction conditions.

The hierarchical supports were prepared through the crystal rearrangement method proposed by Garcia-Martinez *et al.* [2] using NaOH, TPAOH or NH_4OH as alkaline agents in the presence of CTAB surfactant, under autogeneous pressure. The structural, textural and morphological properties of the supports were characterized by X-ray powder diffraction, N_2 adsorption isotherms and electronic microscopy (TEM and SEM). The complex was immobilized in the supports by the incipient wetness impregnation method using water as solvent.

Upon the optimization of the reaction parameters, the recycling of the catalysts was investigated. Figure 1 shows the product yields evolution during 3 consecutive cycles.

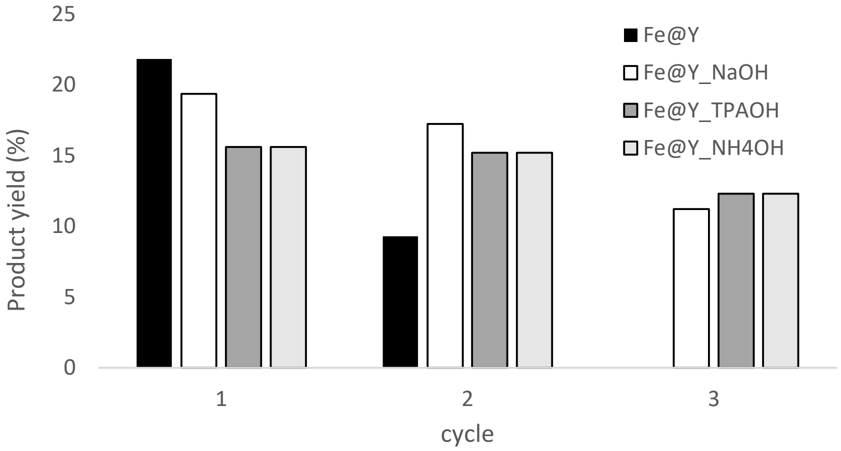

Fig.1. Evolution of product yields with the number of catalytic cycles

Hierarchical zeolites behave as more efficient supports, when compared with parent Y zeolite, with a higher possibility of reusing without significant decrease of product yield.

Acknowledgements
Support for this work was provided by FCT through PEst UID/MULTI/00612/2013, UID/QUI/00100/2013, PTDC/QEQ-ERQ/1648/2014 and PTDC/QEQ-QIN/3967/2014 projects.

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Study of solid-liquid phase diagrams of methyl stearate and hexadecane by differential scanning calorimetry

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The availability of energy is essential for the humanity and nowadays a key factor of progress and sustainability. The use and availability of energy at relatively low cost and abundance, are dependent of alternative sources and types of energy. Biodiesel is an important alternative to mineral sources of energy, but some challenges have to be overcome in order to optimize their production, usability, sustainability and to decrease their environmental impact.

The study of low temperature behaviour of biodiesel and Blends, namely the study of the effect of the composition in the crystallization on Blends of diesel with Biodiesel

In this work was explored different mixtures with molar fractions between 0 and 1 to create solid-liquid phase diagrams of methyl stearate with hexadecane to understand the crystallization behaviour of one of the main compounds in Biodiesel with an alkane present in the Diesel fuel.

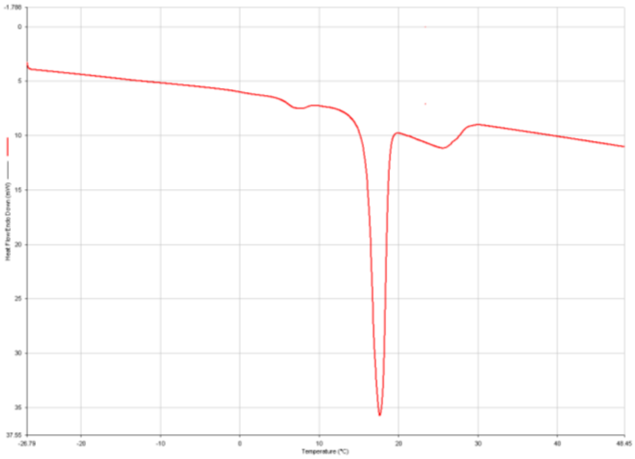

Fig.1. DSC of a mixture of 30 %(mol/mol) of methyl stearate and 70 %(mol/mol) of Hexadecane

Acknowledgments
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Energetic effects of substitution of the hydrogen's amino group on morpholine molecule by alkylamino groups

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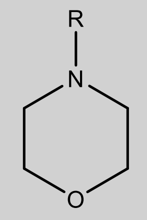
Experimental studies were performed in order to evaluate and understand the energetic effect inherent to the substitution of the hydrogen of the amino group of the morpholine scaffold by bulky substituents (ethylamino and propylamino), according the structure depicted in figure 1. This goal has been performed studying the compounds *N*-(2-ethylamino)morpholine and *N*-(3-propylamino)morpholine and comparing the corresponding results with those previously obtained for morpholine [1].

This work reports the enthalpies of vaporization and the massic energies of combustion of the *N*-(2-ethylamino)morpholine and *N*-(3-propylamino)morpholine, obtained respectively by Calvet microcalorimetry and static combustion calorimetry measurements. These properties were used to derive the enthalpy of formation of the two morpholine derivatives, in the liquid and gaseous phases, at *T*=298.15 K.

The values derived of the gas-phase enthalpies of formation for *N*-(2-ethylamino)morpholine and *N*-(3-propylamino)morpholine are discussed and compared with those determined for other related derivatives.

The optimized structures of the molecules were performed computationally using the B3LYP//6-31G(*d*) DFT method.

The structural changes and the inherent energetic effects, associated with the substitution of the hydrogen's amino group by the ethylamino and the propylamino substituents will be analyzed.



R = H, morpholine
R = $C_2H_4NH_2$, *N*-(2-ethylamino)morpholine
R = $C_3H_6NH_2$, *N*-(3-propylamino)morpholine

Fig.1. General structural formulae for morpholine derivatives.

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Termoquímica de derivados metilados do benzoxazole: uma abordagem calorimétrica e computacional

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Os derivados do benzoxazole são compostos heterocíclicos com um largo espetro de atividades biológicas, sendo muito utilizados na área farmacológica devido às suas propriedades terapêuticas [1,2]. Por outro lado, exibem propriedades óticas podendo ser utlizados no desenvolvimento de sensores [3], díodos orgânicos emissores de luz (OLED´s) [4], entre outras aplicações.

O conhecimento das propriedades termodinâmicas destes compostos heterocíclicos, em particular as energias de Gibbs e entalpias de formação, nos estados condensado e gasoso, permite uma melhor compreensão do seu comportamento químico, contribuindo para o desenvolvimento de novas aplicações. Continuando o nosso recente trabalho sobre a termodinâmica de benzoxazoles alquil substituídos [5,6], cuja fórmula estrutural é apresentada na Fig. 1, este trabalho apresenta um estudo termoquímico complementar, experimental e computacional, do 5-metilbenzoxazole.

O valor da entalpia molar de combustão padrão (p^o = 0.1 MPa) deste composto foi obtido por calorimetria de combustão, em bomba estática, a T = 298.15 K e, a partir deste, calculou-se o valor da entalpia molar de formação padrão, no estado condensado, à mesma temperatura. O valor da entalpia molar de sublimação padrão, a T = 298.15 K, foi determinado por microcalorimetria Calvet, de altas temperaturas. A conjugação destes resultados permitiu calcular a entalpia molar de formação padrão, no estado gasoso. Este último parâmetro foi também determinado computacionalmente, usando o método G3(MP2)//B3LYP. Os resultados obtidos são discutidos, conjuntamente com os descritos na literatura, com o intuito de se desenvolverem correlações entre a estrutura e a energética destas espécies.

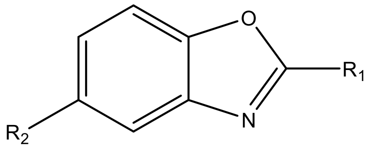

Fig.1. Fórmula de estrutura dos derivados do benzoxazole estudados (R$_1$, R$_2$ = H, CH$_3$)

Agradecimentos
Agradece-se à Fundação para a Ciência e Tecnologia (FCT), Lisboa, Portugal, o financiamento concedido ao CIQUP (Projeto UID/QUI/0081/2013) e ao FEDER pelo financiamento no Projeto POCI-01-0145-FEDER-006980 e no Projeto "Sustained Advanced Materials", ref. NORTE-01-0145-FEDER-000028 (FCUP), através do Programa NORTE2020. Ana L.R. Silva agradece à FCT (Portugal) a bolsa de doutoramento (SFRH/BD/69606/2010).

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XXII Encontro Luso-Galego
Química

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Química Industrial e Engenharia

p-Nitrophenol degradation by Fenton reaction in a bubble column reactor

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p-Nitrophenol is one of the hazardous compounds most commonly found in the effluents generated by several industries and its destruction and mineralization by conventional methods is quite difficult due to its high chemical stability, toxicity and solubility in water. The advanced oxidation processes (AOPs) are among the most effective methods for treating pollutants with high chemical stability and/or low biodegradability. AOPs generate hydroxyl radicals, species with high oxidation potential (2.8 eV [1]) that are able of degrading most organic compounds. In the Fenton's reaction the hydroxyl radical is generated by decomposition of hydrogen peroxide catalysed by ferrous irons in acid medium [1,2].

In this work it was studied the oxidation of *p*-nitrophenol in a bubble column reactor (see Figure 1) using the Fenton process. Up to the author's knowledge, there are no studies in the literature about the use of bubble columns for the degradation of *p*-nitrophenol by this oxidation process, and the performances achieved with the developed strategy are above those reported for the Fenton process in a batch reactor. Moreover, after process optimization the concept can be extended for simultaneously treating gas and liquid streams.

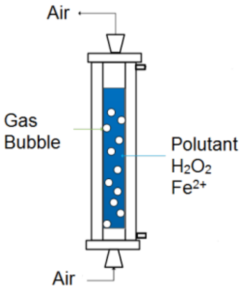

Fig.1. Scheme of the bubble column reactor.

In the operation of this unit and along this work the gas stream was composed of only air, and the pollutant had been dissolved in the liquid phase. Thus, the use of the gas stream aimed to promote the mixture in the liquid phase, which was experimentally checked to be reached, without any concentration gradients along the column (i.e., in the axial direction).

Firstly, a parametric study was carried out for evaluating the effect of the H_2O_2 concentration, of the catalyst (Fe^{2+}) dose and also of pH on the removal and mineralization of a solution containing 500 mg/L of *p*-nitrophenol. It was found that, under the best operating conditions found (pH= 3.0, $[H_2O_2]$ = 1.6 g/L, $[Fe^{2+}]$ = 80 mg/L and T = 22-24 ºC), it was possible to obtain a nontoxic effluent, a total reduction of *p*-nitrophenol and a mineralization of 49.2±2.4% with an efficiency of oxidant used (ratio between TOC conversion and percentage of H_2O_2 consumption – X_{TOC}/X_{H2O2}) of 0.54±0.03.

In the second part of this work, some strategies were applied, namely the divided addition of the optimum H_2O_2 dosage and/or the pH adjustment during the reaction, for improving the mineralization rate. It was found that the addition of H_2O_2 every 5 minutes allow reaching a much higher TOC removal and efficiency of oxidant used, namely 68.8±2.9% and 0.92±0.07, respectively.

Acknowledgements
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Improved hydrotalcites for CO_2 capture

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The in-situ capture of CO_2 from the reaction medium with the aim of shifting the thermodynamic equilibrium of reversible reactions where it is formed is being widely considered since it would allow improving conversion in such reactions or, alternatively, the use of lower process temperatures (e.g. 300-400 ºC for sorption enhanced of either steam reforming processes or water gas shift). At these temperatures, hydrotalcites are the best option for CO_2 capture. Hydrotalcites are anionic clays with a layered double-hydroxide structure derived from brucite and general formula $[M^{II}_xM^{III}_{(1-x)}(OH)_2][A^{n-}]_{x/n}\cdot mH_2O$, where M^{II} and M^{III} are di- and trivalent metal cations inside the brucite-like layers and A^{n-} is a charge compensating anion [1].

In this work, different hydrotalcites were prepared via co-precipitation followed by impregnation with potassium (a well known important promoter). The base material is an Mg-Al hydrotalcite with CO_3^{2-} as the charge compensating anion (HTC). The other materials consist of HTC impregnated with approximately 20 wt.% of potassium (K-HTC), HTC submitted to microwave irradiation and impregnated with the same amount of potassium (K-HTC MW) and HTC partially substituted with Ga, impregnated with 20 wt.% of potassium and with microwave treatment (K-HTC-Ga MW). The CO_2 sorption isotherms of these materials were obtained under dry conditions. The results obtained so far are very promising, with outstanding capacities as compared to literature values, especially for K-HTC-Ga MW where a sorption equilibrium value of 2.09 mol/kg at 3.10 bar of CO_2 was obtained (Fig.1). Properties of these materials were related with their detailed physico-chemical characterization data by several techniques (nitrogen adsorption, XRD, FTIR, SEM and TG/DTG). Finally, breakthrough experiments with K-HTC-Ga MW under dry and wet conditions are being performed so that the effect of steam on the sorption capacity can be assessed. Moreover, the effect of temperature, pressure and CO_2 concentration is being analyzed as well. Ultimately, sorption/desorption cycles will be done so that the stability and working capacity of K-HTC-Ga MW are assessed.

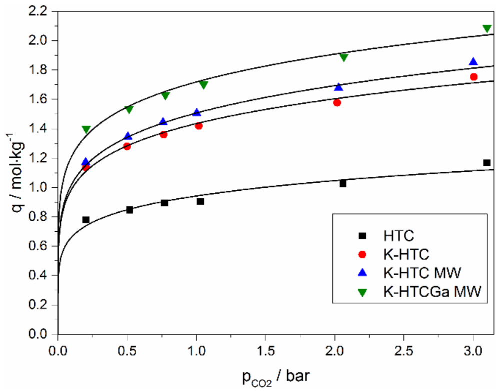

Fig.2. CO_2 sorption equilibrium isotherm at 573 K for the prepared materials

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Separation of nadolol stereoisomers using different simulated moving bed strategies

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Nadolol is a pharmaceutical drug marketed as a mixture of four stereoisomers, used to treat cardiovascular diseases. However, its prescription is also related with some severe risks such as heart failure. It is well known that pure enantiomer separation is important to control chiral drugs safety. Recently, our research group reported the pseudo-binary separation of nadolol by simulated moving bed (SMB) technology using both coated Chiralpak AD and immobilized Chiralpak IA chiral stationary phases (CSP) [1,2].

The introduction of a wide range of new and more powerful preparative stationary phases allied to the development of new and more versatile strategies and modes of SMB operation are now a reality. Several configurations have been proposed in order to extend the SMB technology to the separation of multicomponent mixtures by using a cascade of SMBs in series or other complex SMB related techniques like multi-zone SMB, intermittent SMB and JO processes. The JO technology allows the separation of ternary mixtures through a cyclic process constituted by two discrete steps [3,4].

In this work, different strategies for the complete separation of the nadolol quaternary mixture are presented, by using different solvent compositions, CSP and SMB related techniques. Experimental and simulation results will be presented including: (i) The use of Chiralpak IA CSP that, comparing to Chiralpak AD, allows the use of a wider range of solvents and therefore better separation performances; (ii) The use of the JO process to achieve a final ternary separation, applied to the mixture of the three stereoisomers co-eluted in the raffinate in the previous separation; and (iii) The separation of the two pairs of nadolol enantiomers using an achiral C18 material, followed by two parallel SMB binary chiral enantioseparation steps.

The application of these different approaches represents possible SMB strategies for the complete separation of the quaternary nadolol chiral mixture and will be compared in terms of system productivity and solvent consumption.

Acknowledgements
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Influencia ejercida sobre la velocidad de absorción debido a la adición de metanol en un proceso de captura de CO_2 mediante disoluciones acuosas de N-metildietanolamina (MDEA)

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En el presente trabajo se recogen los resultados del estudio de un proceso de captura de CO_2, empleando como absorbente el sistema (N-metildietanolamina + agua + metanol). La absorción se llevó a cabo en un reactor tipo tanque agitado, operando a presión atmosférica y a una temperatura de 30 ºC. Se ha evaluado la influencia sobre la velocidad de absorción de CO_2 ejercida tanto por la cantidad de amina (0; 5; 15; 30; 40 y 50 % en peso), como por la fracción de metanol (0; 0,4; 0,7 y 1) presente en el disolvente.

El análisis de los resultados permite deducir que, con independencia del disolvente utilizado, la velocidad de absorción aumenta a medida que lo hace la concentración de alcanolamina presente en la disolución, siendo este incremento más acusado cuando el disolvente está constituido en su totalidad por agua [1]. Por otra parte, el aumento de la fracción de metanol en el disolvente se traduce en una reducción de la velocidad de absorción, siendo esta disminución más acusada cuanto mayor es la cantidad de MDEA presente. Sin embargo, también se observa que para concentraciones de amina reducidas, el incremento de la fracción de metanol implica un aumento de la velocidad de absorción.

Se concluye que la adición de metanol mejora la transferencia de materia del proceso en disoluciones orgánico-acuosas de MDEA con una concentración comprendida en el intervalo (0 - 5 % en peso), para una proporción de metanol en el disolvente superior al 40%.

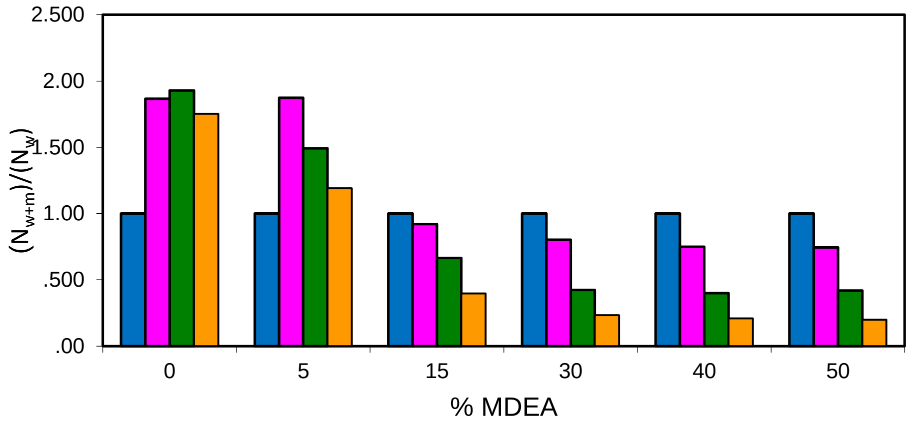

Fig.1. Variación de N en función del porcentaje de metanol presente en el disolvente:
🟦 0 % metanol; 🟪 40 % metanol; 🟩 70 % metanol; 🟧 100 % metanol

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Utilização da espectrometria de absorção molecular na região do ultravioleta para avaliação da estabilidade oxidativa de óleos vegetais

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A estabilidade oxidativa dos óleos vegetais é uma propriedade que pode afetar o aroma, sabor e textura, além de estar relacionado com a qualidade do biodiesel a ser produzido. Altos teores de ácidos graxos insaturados presentes nos óleos, utilizados como matéria-prima do biodiesel, diminuem a estabilidade deste, comprometendo seu rendimento e podendo causar danos nos motores a longo prazo [1]. Atualmente, utiliza-se como padrão para avaliar a estabilidade oxidativa o Período de Indução (PI) determinado pelo método Rancimat (EN 14112) [2]. O presente trabalho utilizou a espectrometria de absorção molecular na região do ultravioleta (230 nm), para obtenção do PI e posterior avaliação da estabilidade oxidativa de óleos de girassol e de soja. Para tal avaliação, um sistema alternativo ao Rancimat, utilizando equipamentos comuns de laboratório, foi proposto. O sistema (Fig. 1) foi baseado nos critérios estabelecidos na norma EN 14112. O processo de oxidação foi acelerado utilizando aquecimento a 110 ºC e fluxo de ar de 13 $L.h^{-1}$. Os compostos voláteis, liberados durante a indução dos processos oxidativos foram coletados em água ultrapura, sendo monitorados por condutividade e medidas de absorvância em 230 nm, em intervalos de 10 minutos. Os resultados de PI obtidos foram comparados com a metodologia oficial, utilizando o Rancimat. As curvas de absorvância *versus* tempo de aquecimento obtidas por meio da espectrometria de absorção molecular na região do ultravioleta foram semelhantes às curvas de condutividade *versus* tempo de aquecimento. Consequentemente, os PI obtidos para as amostras de óleo de girassol e soja, utilizando as duas técnicas foram semelhantes, os valores também indicaram uma boa correlação com os resultados obtidos pelo método Rancimat (Tabela1). O sistema proposto mostrou-se eficiente para o monitoramento da estabilidade oxidativa de óleos vegetais, e a utilização da espectrometria de absorção molecular pode ser uma alternativa para a determinação do PI de amostras de óleos vegetais.

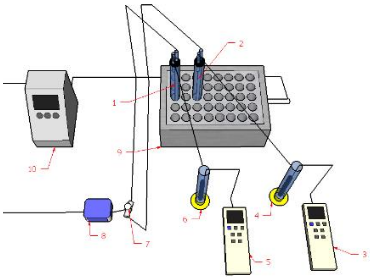

Fig.1. Sistema proposto para avaliar a estabilidade oxidativa medindo a condutividade por meio da formação de voláteis

Tabela 1. Comparação considerando Intervalo de confiança de 95%

	Condutividade	**Absorvância**	**Rancimat**
	PI ± µ (horas)	PI ± µ (horas)	PI ± µ (horas)
Girassol	4,85 ± 0,16	4,75 ± 0,33	5,49 ± 0,47
Soja	5,98 ± 0,38	5,63 ± 1,08	6,65 ± 0,22

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Preparation of amino resins and their impact on the production of wood-based panels

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In the last decades, the industry of wood products is going through a great evolution thanks to companies like Sonae Arauco, which focus has been on developing more and better wood-based products. In 2015 Portugal produced 1 million and three hundred thousand m^3 and exported 278 million euros of wood-based panels [1]. Among these products, the best known are the commercially available particleboard (PB), medium density fibreboard (MDF), oriented strand board (OSB) and plywood (PW). For all these types of panels the use of a synthetic adhesive is required. Among the wide range of adhesives/resins employed in the wood industry, the most important are the amino resins which include urea-formaldehyde (UF) resins, melamine-formaldehyde (MF) resins and melamine-urea-formaldehyde (MUF) resins.

The aim of this work is to optimize the amino resins (UF and MUF) synthesis process by assessing the impact on the final characteristics of wood-based panels (PB and MDF). To understand how the operating conditions influence the final product properties, different tests will be performed. Tools for design of experiments (DoE) will be used for planning experiments and data processing. The purpose is to correlate the conditions of the laboratorial reactor and the main properties of resins (molecular weight distribution, degree of branching, condensing structures and reactivity) and thereafter with some of the final product properties (physical-mechanical performance and formaldehyde emissions). In a second step, using the most promising formulations, other factors related to the sizing process (wood moisture content, resin content) and pressing (temperature, pressing cycle) will also be considered.

At an early stage, different variables related to resins synthesis were studied, trying to better understand their impact on wood-based panels properties, in particular particleboards. In an initial approach, an industrial UF resin was synthesized at different values of pH, temperature, and final viscosity. The resins were characterized using empirical quality control methods and advanced physicochemical characterization techniques. The panels produced were characterized using standard tests. The results are being analysed using the JMP Statistical Software.

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Methane production from water electrolysis using graphite electrodes

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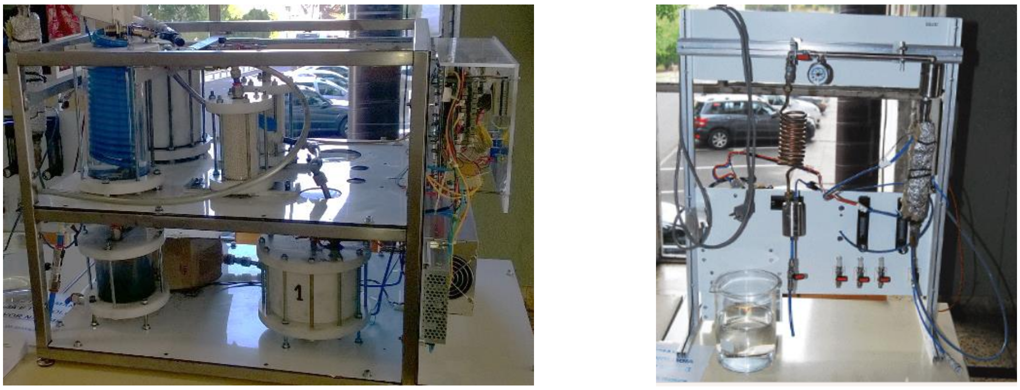
Since the Second Industrial Revolution, the world energy demand has always been increasing, leading humanity to gradually focus on the sustainability of its activities [1]. The aim of this work is the production of synthetic fuels such as methane and methanol, cleaner than fossil fuels and coal, to be used as an energy carrier in one of the most promising systems to produce electric energy: fuel cells. The work, currently in development, is targeted on methane production, which has been achieved from synthesis gas, produced in a one-step innovative 1 kW prototype (Figure 1 a) of alkaline water electrolysis (patented) using graphite electrodes and without separation of gases (containing CO, CO_2, H_2 and small amounts of O_2) [2].

Firstly, the behavior of the syngas composition has been studied through the optimization of operational parameters such as temperature, pressure and voltage; afterwards, the synthesis gas obtained has been sent to a catalytic reactor (filled with a Ni/CaO-Al_2O_3 catalyst) for preliminary tests at 1 bar and different temperatures, in order to produce methane.

The best results, in terms of conversion, have been recorded at 125 °C, reaching a carbon dioxide conversion to methane of 45 % and a methane selectivity of 97 %, with a gas flow of 45 L/h.

The preliminary tests performed, varying syngas composition, pressure and temperature inside the catalytic reactor, have shown the high potential of this innovative and sustainable water electrolysis system (especially in view of the use of renewables as an energy source) in order to produce synthetic fuels for subsequent production of electric energy via fuel cells, having several possible applications, such as in rural electrification.



a) **b)**

Fig. 1. Propotypes a) electrolyser and b) catalytic reactor

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Produção do gás de síntese através da eletrólise da água, usando o conceito *electrocracking*

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A procura mundial de energia tem vindo a aumentar nas últimas décadas. A produção de gás de síntese tem uma importância histórica nos períodos de escassez energética, principalmente durante a Segunda Guerra Mundial. É atualmente, considerada como uma alternativa aos combustíveis fósseis, a fim de assegurar a sustentabilidade energética.

O presente trabalho de investigação consiste na produção de gás de síntese através do eletrólise da água, recorrendo ao uso de energia elétrica renovável, e ainda, de biomassa liquefeita (designada de "liquefeito") como fonte de carbono necessária à obtenção de monóxido e dióxido de carbono. O trabalho foi dividido em duas fases: realização de ensaios a céu aberto, e no protótipo laboratorial de 100 W, usando quatro eletrolisadores diferentes (A, B, C e D), onde a principal diferença entre eles, está no material do que é feito e no tipo de elétrodos utilizados (conforme a Tabela 1).

Tabela 2. As caraterísticas dos eletrolisadores utilizado, neste trabalho

	Eletrolisador	Material	Caraterísticas
Protótipo laboratorial	Eletrolisador A	Teflon	4 elétrodos de aço (3 células), com 25 cm^2 de área cada um;
	Eletrolisador B	Aço inox	7 elétrodos de aço (6 células), com área igual a 20 cm^2 cada elétrodo
	Eletrolisador C	Aço inox	7 elétrodos da rede de níquel, com área igual a 20 cm^2 cada elétrodo
	Eletrolisador D	Aço inox	9 elétrodos de aço (8 células) com área igual a 20 cm^2 cada elétrodo

Foram estudadas as influências da concentração do eletrólito, da temperatura e da pressão nas principais saídas do processo, tais como: o caudal dos gases produzido, os teores de monóxido de carbono, dióxido de carbono e oxigénio, bem como a energia consumida no processo. Tendo em conta os resultados obtidos no eletrolisador D nos ensaios de optimização, as condições ótimas obtidas foram: eletrólito NaOH 1,2 M misturado com 20 % de liquefeito, pressão de 1 bar, temperatura de 70 ºC e densidade corrente igual a 0,100 A/cm^2. Deste modo, obtiveram-se teores de monóxido, dióxido de carbono e oxigénio iguais a 25,32, 0,00 e 8,01%, (percentagens volumétricas) respectivamente. Por sua vez, o caudal total da mistura gasosa produzida e a energia consumida foram, respectivamente, iguais a 8,31 L/h e 7,75 Wh/L. Esse gás, dependendo das condições operacionais, pode ser convertido em combustíveis sintéticos renováveis, tais como metano, metanol, dimetil éter, diesel, etc., que possam ser utilizados em transporte rodoviário.

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Preparative separation of nadolol racemates using reversed-phase liquid chromatography

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Nadolol is a nonselective beta-adrenergic receptor antagonist (β-blocker) pharmaceutical drug, widely used in the treatment of cardiovascular diseases, such as hypertension, ischemic heart disease (angina pectoris), congestive heart failure, and certain arrhythmias. Its chemical structure has three stereogenic centers which allows for eight possible stereoisomers. However, the two hydroxyl substituents on the cyclohexane ring are fixed in the cis-configuration, which precludes four stereoisomers; in fact, two pairs of enantiomers. Nadolol is presently marketed as an equal mixture of the four stereoisomers, designated as the diastereoisomers, “racemate A” and “racemate B” [1].

There are still few published works concerning the separation of nadolol stereoisomers. Most of these works refer the resolution at analytical scale and few refer the separation at preparative scale using the simulated moving bed (SMB) technology [2-4]. This technology is generally based on the use of chiral adsorbents which must have enough recognition for all the chiral species.

In this work it is proposed an alternative strategy, implementing a first achiral separation step, to be followed by two subsequent parallel chiral separation steps. In this first achiral step, C18 columns are used to perform the separation of the two pairs of nadolol enantiomers (“racemate A” from “racemate B”) under reversed-phase mode.

Extensive experimental and simulation results will be presented including solvent screening, measurement of equilibrium and kinetic data, and both fixed-bed and SMB preparative separations. These different separation strategies will be compared in terms of system productivity and solvent consumption.

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Removal of methylene blue and malachite green by adsorption on chestnut shell (*Castanea sativa*)

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A great concern has persisted over the years due to the high pollution of waste waters caused by the discharge of large amounts of synthetic dyes from various industries such as textile industries, cosmetics, pharmaceuticals, etc. In particular, it has been estimated that about 20% of water pollution is caused by the treatment and dyeing of textiles in which more than 8000 chemicals are used [1]. Cationic dyes such as methylene blue (MB) and malachite green (MG) have a high degree of toxicity and have some adverse effects on human health and environment. Their complex molecular structure and synthetic origin makes them extremely stable and difficult to eliminate by conventional methods. Adsorption on activated carbons is one of the most efficient methods for removing dyes from wastewaters. However, the interest is now centered on substituting expensive activated carbons for efficient and low-cost adsorbents based on natural waste materials [2].

The aim of this study was to evaluate the potential of chestnut shell (*Castanea sativa),* a waste product from the food industry, for the removal of MB and MG from aqueous solutions. Chestnut shell was prepared by grinding, sieving, water washing and drying at room temperature. Surface morphological and physico-chemical characteristics of the shell were analysed before and after adsorption, using scanning electron microscopy (SEM), optical microscopy (Fig. 1) and Fourier transformed infrared spectroscopy (FTIR). Furthermore, the point of zero charge (PZC) was determined; a value of 3.7 was obtained. The wavelength for the maximum absorbance and the stability with time of MB and MG aqueous solutions depending on pH were also determined.

Adsorption experiments were carried out in batch mode at 25ºC and at the natural pH of the dye solutions to study the influence of contact time, initial dye concentration and adsorbent dose on dye removal percentage and adsorption capacity. The amount of dye adsorbed increased with increasing contact time. Equilibrium time was highly dependent on initial dye concentration and varied between 2 min (for 5 mg/L) and 90 min (for 200 mg/L). Equilibrium removal percentages close to 99% were reached at all initial concentrations essayed (5-200 mg/L). Adsorption rate decreased significantly when adsorbent dose was reduced from 10 to 2.5 mg/L; an adsorbent dose of 5 g/L was selected as the optimal. Kinetic data for the removal of MB and MG by chestnut shell were best fitted by the pseudo-second-order kinetic model. Equilibrium data for both dyes were best fitted with the Langmuir model. Maximum adsorption capacities (q_{max}) of 42.37 and 53.19 mg/g were obtained for MB and MG, respectively. The results obtained demonstrate that chestnut shell is a potential low cost adsorbent for the removal of methylene blue and malachite green from waste waters.

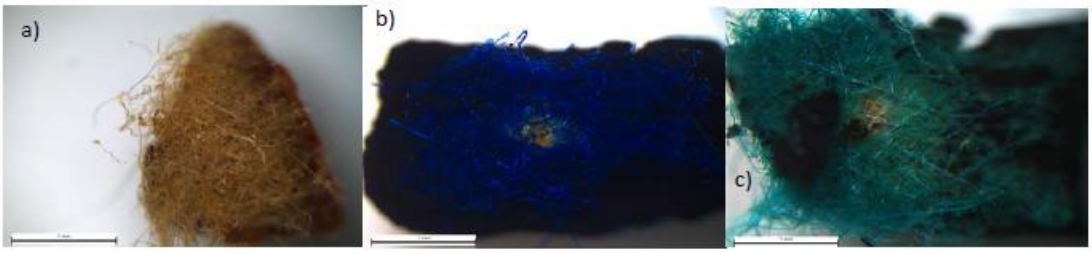

Fig.1. Optical microscopy images of chestnut shell before (a) and after adsorption of methylene blue (b) and malachite green (c)

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Aqueous two phase extraction and antioxidant activity of phenolic compounds from *Eucalyptus grandis* sawdust

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In Uruguay, forestry activity has been rising in a sustained way over the last 20 years [1]. Therefore, a remarkable amount of wood residues are generated, that are mainly used to produce energy. In this project, an alternative way of exploiting one of these materials, *Eucalyptus grandis* sawdust, is proposed. In particular, the extraction of antioxidant compounds prior to combustion in order to valorize the residue. At present, much attention is being paid to develop alternative ways of extraction and purification of biological products. Therefore, more efficient separation and purification processes are necessary to attain major efficiency and lower production costs [2]. In this direction, Aqueous Two-Phase Systems (ATPS) have been used in bio-separations for nearly fifty years. It is an important emerging green technique that has numerous advantages over conventional extraction, being in particular more environmentally friendly [3].

The aim of the present work was to study the extraction and the partition behavior of phenolic compounds from eucalyptus sawdust using to two different types of ATPS: polyethylene glycol (PEG)-$(NH_4)_2SO_4$ and ethanol-$(NH_4)_2SO_4$. The objectives were to analyze their application for the recovery of phenolic compounds with antioxidant activity and to determine the effect of system parameters on extraction efficiency.

For PEG-$(NH_4)_2SO_4$ ATPS the influence of the tie line length (TLL) and polymer molecular weight (MW) was evaluated. Three polymers, PEG 1000, PEG 2000 and PEG 4000 were selected and for each one different TLL were tested at a constant volume ratio (V_R = 1). Experiments were performed at 25ºC for 90 min at a solid/liquid ratio (S/L) of 1/10 (w/w) and natural pH. Regarding the ethanol-$(NH_4)_2SO_4$ ATPS, extractions were performed for 90 min at the natural pH and the influence of TLL (44.9-56.7% (w/w), V_R (1-2.8), S/L (0.25:10-1:10 w/w) and extraction temperature (25-65ºC) was studied. The selection of the variables and their variation ranges were based on previous studies [4,5]. For both types of ATPS, the total phenolics recovery yield (Folin-Ciocalteu method) and the FRAP antioxidant capacity of the extracts were determined.

Phenolic compounds concentrated preferentially in the PEG-rich and ethanol-rich top phases for PEG and ethanol based ATPS, respectively. For PEG based ATPS phenolics recovery varied from 0.403 to 0.702 mg GAE/100 mg wood dry basis (db) and the FRAP antioxidant activity from 2533 to 3943 mmol AAE/100 mg wood db. System based on PEG 1000 at the highest TLL essayed led to best results. Phenolics recovery increased significantly for the ethanol based ATPS (0.75-1.30 mg GAE/100 mg wood db) and also the FRAP antioxidant activity of the extracts (3604-14486 mmol AAE/100 mg wood db).The maximum phenolics recovery yield and extract antioxidant activity were obtained for the ethanol-$(NH_4)_2SO_4$ system based on 40.6% ethanol, 12.4% $(NH_4)_2SO_4$ and 47% H_2O at 65ºC using a Vr =2.8 and S/L of 1/10 (w/w). The results of the present work confirm the capacity of the ATPS essayed for the extraction and partial fractionation of phenolic compounds as an alternative to traditional organic solvents.

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Wastewater sludge treatment by wet air oxidation technology

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In the treatment of sewage sludge, oxidation is brought about by continuously pumping the sludge and a proportionate amount of oxygen (both sludge and oxygen at elevated temperatures and pressures) into a reactor vessel. Combustion occurs as the oxygen in the compressed air combines with the organic matter in the sludge to form CO_2, N_2, and steam, while the ash remains in the residual water. The reactor, and the whole process system, is automatically maintained at a constant pressure and the products of the combustion are continuously removed from the reactor [1].

The composition of sewage sludge can vary greatly depending on its origin, but the main components are carbohydrates, proteins and lipids. The first stage in the WAO of sludge involves a large proportion of the insoluble organic content being converted into simpler soluble organic compounds (sugars, amino acids, fatty acids, etc.). The smaller molecules are then oxidized into easily biodegradable and oxygenated products (carbon dioxide, inorganic salts and water). These reactions are propagated by an organic radical obtained through oxidation of C-H bonds. The organic compounds are gradually decomposed into more stable intermediates which are finally oxidized to carbon dioxide and water. The overall reaction rate slows down as the easily oxidized compounds are gradually removed and acetic acid and other stable intermediates are formed.

In this work, the effects of several parameters as temperature, pressure and gas (oxygen or air) on the activated sludge oxidation were analyzed. As an example, Fig. 1 shows the TC removal at several temperature and pressure conditions.

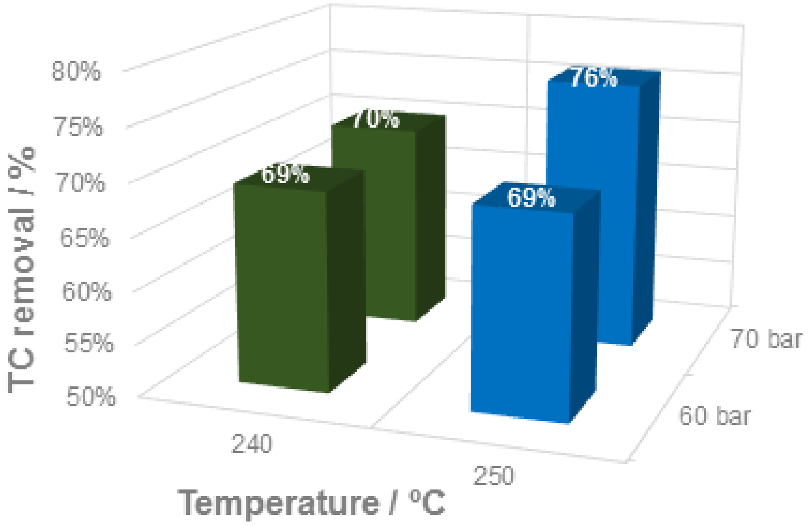

Fig.1. TC removal of sludge at different temperature and pressure conditions

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Impacto del biodiesel sobre la volatilidad del gasóleo

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La necesidad de proteger el medio ambiente ha llevado a la búsqueda de nuevos combustibles de automoción y a la modificación de las características de los ya existentes. Uno de los caminos elegidos ha sido incluir biocombustibles en la formulación de los combustibles de automoción convencionales dada su gran capacidad para mezclarse con éstos [1].

Incorporar biodiesel (FAME) al gasóleo, supone apostar por un futuro energético más sostenible e implica un mayor esfuerzo de I+D; ya que es necesario estudiar cómo se modifican las características del combustible tras la mezcla para que su comportamiento sea óptimo en los motores de cualquier automóvil [2]. Como norma general, según especificaciones internacionales, el gasóleo se puede combinar con biodiesel hasta un máximo del 7% en volumen sin necesidad de informar al consumidor al respecto. Existen también taxis o autobuses urbanos que utilizan una mezcla de gasóleo y biodiesel en una proporción de 70 a 30% en volumen [3].

Entre las características a tener en cuenta a la hora de establecer la calidad de un combustible utilizado en automoción destaca la volatilidad, característica relacionada directamente con las prestaciones del motor y las emisiones contaminantes que este produce [4]. La volatilidad no es una magnitud física que pueda medirse directamente, se requiere definir métodos de evaluación de la misma. Uno de los métodos universalmente empleados para determinar la volatilidad de un combustible es el ensayo de destilación [5] que nos ofrece distinta información de acuerdo al tipo de combustible ensayado.

En este trabajo, se realiza el ensayo y se obtiene la curva de destilación a 24 muestras de gasóleo con distintos porcentajes de biodiesel (FAME), entre un 0,0 y un 30% V/V. Los resultados obtenidos muestran una clara disminución de volatilidad en las mezclas, consecuencia de las propias características del biodiesel: alto punto de ebullición y baja volatilidad.

Agradecimientos
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Variación de la volatilidad de la gasolina por adición de bioetanol

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Incorporar bioetanol a la gasolina hace necesario estudiar cómo se modifican las características del combustible tras la mezcla para que su comportamiento sea óptimo en los motores en que vaya a ser empleado [1]. Como norma general, según especificaciones internacionales, la gasolina se puede combinar con bioetanol en un porcentaje no superior al 10% en volumen sin necesidad de informar al consumidor al respecto [2].

La volatilidad junto al poder antidetonante son las dos características principales de la gasolina. La volatilidad está directamente relacionada con las prestaciones del motor y las emisiones contaminantes que este produce [3]. Uno de los métodos universalmente empleados para determinar la volatilidad de un combustible es el ensayo de destilación [4].

En este trabajo, para determinar la volatilidad se realiza la curva de destilación a 24 muestras de gasolina con un porcentaje en bioetanol comprendido entre un 0,0 y un 10,0% V/V. La comparación entre las curvas de destilación obtenidas para el combustible sin adición de bioetanol y las muestras de combustible con distintos porcentajes en volumen de bioetanol nos permite comprobar las variaciones producidas en la volatilidad del producto como consecuencia de la presencia de bioetanol en su composición.

El estudio de los dos primeros tramos de la curva (IBP-E20; E20-E70), de los tres en que se dividió la curva de destilación de las muestras de gasolina en este estudio, muestra que el porcentaje evaporado es mayor en las mezclas, lo que demuestra que en el intervalo de temperatura que oscila entre 30°C y 90°C, intervalo que va desde el IBP hasta el punto medio de destilación, la volatilidad de las gasolinas aumenta por adición de bioetanol. En el tramo final, las curvas de destilación de las muestras son prácticamente coincidentes, no se observan cambios significativos, como cabía esperar conociendo el punto de ebullición del bioetanol.

Agradecimientos
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Caracterización térmica de materiales de cambio de fase (PCM) en elementos constructivos

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Actualmente, el consumo de energía primaria en edificios se corresponde con el 40% de la demanda energética total. Por ello, la Directiva Europea 2010/31/UE de Eficiencia Energética en los Edificios tiene como objetivo claro la definición del edificio de consumo "*casi nulo*". Una de las alternativas en el campo de la edificación es el almacenamiento pasivo de energía, en el que el ahorro energético es un componente fundamental, permitiendo adaptar los períodos de suministro a la demanda energética.

En este estudio se presenta una alternativa para contribuir a la mejora de la eficiencia energética mediante el empleo de materiales de cambio de fase (PCM) integrados en elementos constructivos. Estos materiales permiten almacenar el calor latente de cambio de estado a una determinada temperatura y liberarlo cuando las condiciones ambientales lo requieran, alcanzando de este modo un mayor confort térmico para las personas y una mejora energética en el edificio.

Para analizar el comportamiento térmico del material de cambio de fase seleccionado y su incorporación en elementos constructivos, se han llevado a cabo experimentos en el laboratorio a partir de dos placas de yeso, incorporando en una de ellas un 20 % de PCM. El material de cambio de fase seleccionado ha sido una parafina micro-encapsulada [1] en un material polimérico (Micronal DS-5040-X,de BASF), que cambia de fase dentro del rango de temperaturas de confort humano, concretamente 23ºC. Entre las técnicas de caracterización utilizadas se encuentran la Difracción de Rayos X, el Análisis Termogravimétrico, la Calorimetría Diferencial de Barrido, la Microscopía electrónica de barrido (SEM), la Termografía Infrarroja (Fig. 1) y la determinación de la transmitancia térmica.

Se ha comprobado que las parafinas presentan condiciones óptimas para ser empleadas en edificación en función a su nivel térmico y a su elevado calor latente de fusión. Con este estudio experimental se ha demostrado que las placas de yeso que incorporan PCM en su interior han mejorado las condiciones térmicas respecto al yeso convencional.

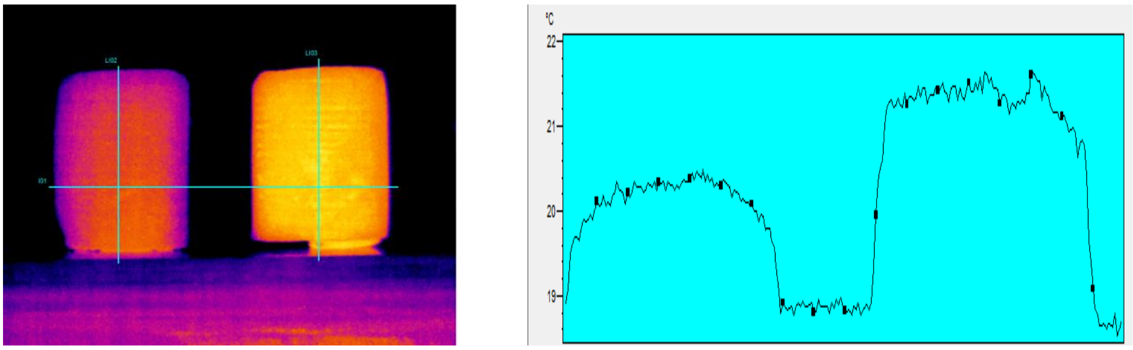

Fig.1. a) Imagen térmica del enfriamiento de las dos placas ensayas (yeso, izquierda, y yeso+ PCM, derecha); b) Isoterma horizontal mostrando una diferencia de temperatura próxima a los 2 ºC

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Al Departamento de Ingeniería de los materiales, Mecánica aplicada y Construcción, y en particular a Antonio Collazo Fernández, por su colaboración en la realización de ensayos de caracterización del PCM. A la empresa BASF, y en especial a Kresimir Cule, por proporcionar una muestra gratuita del PCM ensayado.

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XXII Encontro Luso-Galego
Química

COMUNICAÇÕES ORAIS E EM PAINEL

Química Inorgânica

Incremento da actividade peroxidasa de complexos de Mn(III) mediante o uso de ligandos ONNO que facilitan xeometrías con distorsión tetragonal

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As peroxidasas son un grupo de enzimas da familia das oxidorredutasas que utilizan peróxido de hidróxeno como substrato en combinación cunha fonte endóxena que proporciona os equivalentes redutores; entre elas están as peroxidasas de manganeso naturais. A síntese de modelos biomiméticos destas enzimas ten interese pola súa potencial aplicabilidade na etapa de branqueamento da polpa de madeira (degradación da lignina) ou no tratamento de residuos acuosos.

No seo do grupo de investigación temos caracterizado diferentes modelos sintéticos con actividade peroxidasa [1-2] utilizando bases de Schiff tetradentadas tipo ONNO como ligandos do ión metálico. Nesta comunicación presentamos catro complexos $Mn_2L^1_2(H_2O)_2(DCA)_2$ (**1**), $MnL^2(H_2O)_2(ClO_4)$ (**2**) $Mn_2L^3_2(H_2O)_2(DCA)_2$ (**3**), $MnL^3(H_2O)_2(ClO_4)$ (**4**), caracterizados mediante análise elemental, espectroscopia IR, EPR e de ^{1}H RMN paramagnético, espectrometría de masas ESI, medidas de momento magnético e de condutividade, e, o complexo **1** por difracción de raios X de monocristal.

A actividade peroxidasa medida, utilizando ABTS como indicador, é elevada para os complexos **1** e **2**, que son aqueles complexos que incorporan ligandos cun espaciador curto entre os aneis aromáticos, o cal constriñe o anel quelato cando os nitróxenos se enlazan ao ión metálico, provocando xeometrías con distorsión tetragonal identificadas mediante espectroscopia EPR (Figura 1).

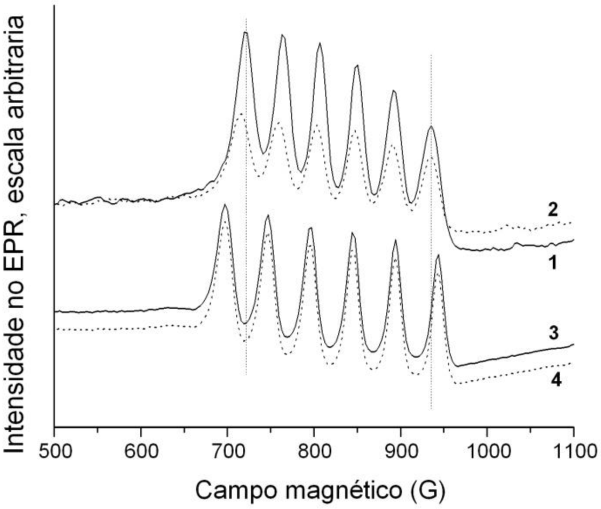

Fig.1. EPR en modo paralelo para os complexos **1**-**4** en disolución de tolueno:dmf:EtOH (2:1:pinga). Condicións: frecuencia 9.37 GHz, T= 9K

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Synthesis and characterization of new metal complexes of 2-oxoacenaphthylen-1(2H)-ylidene nicotinohydrazide

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Acylhydrazones are a group of compounds of general formula R−C(=O)−NH−N=C−R′ that have aroused great interest from the point of view coordinative and for its various applications which highlights its use in fields such as catalysis, photochemistry, agriculture and medicine. In the latter, they show important properties such as antibacterial, antifungal, antiviral, antitumor, antioxidant, analgesic, anti-inflammatory and vasodilator [1].

For this and continuing our research program regarding new metallic compounds with biological activity [2], we have recently synthesized and characterized a new compound, the 2-oxoacenaphthylen-1(2H)-ylidene nicotinohydrazide (HL) [3]. In order to explore the antitumor activity previously studied in thiosemicarbazones [4], we have explored its reaction with Cu(II), Ni(II) and Co(II) acetates and chlorides which leads to the formation of a series of novel complexes following the general procedure shown in Figure 1.

The complexes obtained were characterized by elemental analysis, conductivity measurements, Fourier Transformed Infrared Spectroscopy (FTIR), magnetic moment measurements, mass spectroscopy and UV-Vis spectroscopy. This allows us to propose the general formulas, $[M(L)_2]$ for the complexes obtained from metal acetates and $[MCl(L)]$ to those obtained from metal chlorides. Moreover, our results suggested that the ligand (HL) might be acting as tridentate.

Biological studies are in progress to obtain information about the cytotoxic activity of both ligand and complexes.

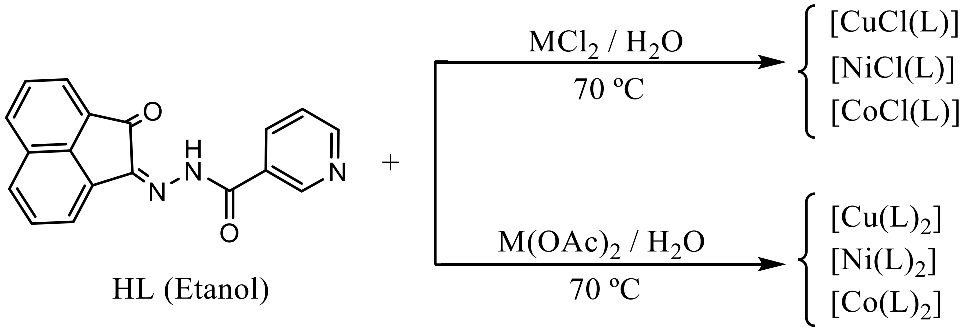

Fig.1. Reaction scheme

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Estudo do proceso de auto-ensamblaxe dun mesocato de Zn(II) cun ligando *tris*tiosemicarbazona

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O estudo do proceso de auto-ensamblaxe de arquitecturas metalosupramoleculares segue a ser un campo de intensa actividade científica na actualidade.[1] O noso grupo de investigación é pioneiro no emprego da síntese electroquímica como ruta eficiente para a preparación de helicatos e mesocatos metalosupramoleculares a partir de ligandos tipo hidrazona e tiosemicarbazona.[2,3]

Neste contexto, presentamos nesta comunicación os resultados obtidos na ensamblaxe dun ligando *tris*tiosemicabazona potencialmente hexadentado [N_3S_3] e trianiónico con ións Zn(II). A síntese electroquímica conduce á formación dun composto neutro do tipo [Zn_2L_2], no que cada átomo metálico se coordina a un átomo de nitróxeno imínico e a un átomo de xofre tioamídico de dúas ramas desprotonadas pertencentes a dúas unidades de ligando diferentes. Cando se produce a coordinación do ligando aos centros metálicos as moléculas de ligando non se cruzan, polo que o complexo presenta unha estrutura supramolecular tipo mesocato (Fig. 1). A rama de ligando protonada non intervén na coordinación aos ións metálicos, polo que esta *tris*tiosemicarbazona se comporta como os seus homólogos de dúas ramas *bis*tiosemicabazonas con espaciador fenilo.

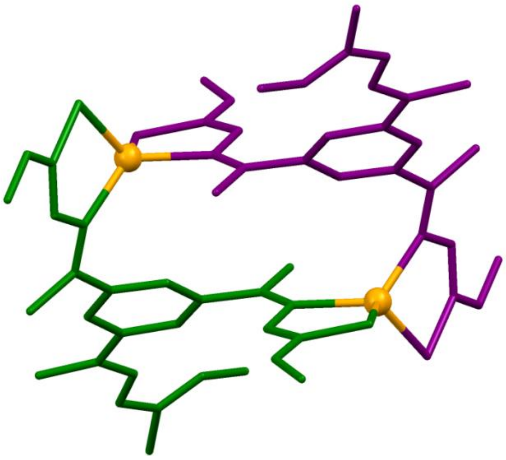

Fig.1. Representación *ball and sticks* do mesocato Zn_2L_2

Agradecementos
Os autores agradecen o apoio económico para a realización da investigación por parte da Xunta de Galicia (EM2014/018, GRC2014/025, R2014/004) e do Ministerio de Economía y Competitividad (CTQ2015-70371-REDT MetDrugs e CTQ2015-71211-REDT MetalBIO).

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Ionic liquids at MOF composite materials: synthesis and catalytic performance

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Ionic liquids (ILs) have originated a green revolution in chemistry, physics, and materials science in the past two decades. ILs are usually constituted of large organic cations and weakly coordinating inorganic or organic anions. Compared to molecular compounds, they are characterized by peculiar and tuneable properties, such as high ionic conductivity, negligible vapour pressure, and high electrochemical and thermal stability [1], as well as a significant ability to solubilise organic, inorganic, and polymeric materials.

Metal-Organic Frameworks (MOFs) are a type of porous materials that consist of metal centres connected with each other 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 [2]. Another course of the exploration of the combined advantages of both ionic liquids and metal-organic frameworks is the incorporation of ILs into the MOFs' porous networks.

At the moment, two routes are being evaluated in order to assess the more efficient method of incorporating an IL into the porous framework of MOF materials. Accordingly, the present work pursues the direct contact method, where the solid MOF support is suspended in a solution containing the IL and a solvent (for decrease of viscosity purposes only), and a ship in the bottle method (SIP) where the IL is synthesized IN SITU in the pores of the networked structure of the MOFs. Following our previous works in MOF materials, MIL-101(Cr) was utilized as the support MOF material and two different 1-alkyl-3-methylimidazolium bromides constitute the ILs being incorporated. The characterization of the composite materials was carried out by Powder X-ray diffraction and FT-IR techniques. The isolated materials were tested as heterogeneous catalysts under sustainable environments for styrene oxidation.

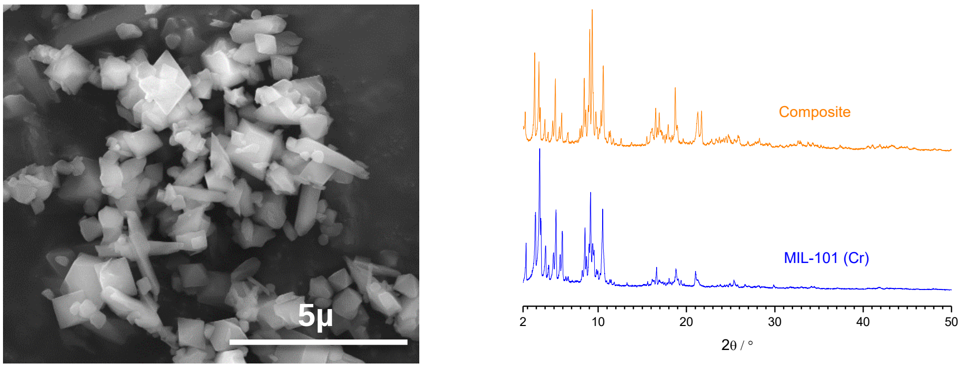

Fig.1. SEM image (left) and PXRD pattern (right) of R-MIM@MIL-101(Cr) composite material

Aknowledgements
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XXII Encontro Luso-Galego
Química

COMUNICAÇÕES ORAIS E EM PAINEL

Química Orgânica

GC-MS profile *of Calendula* L. species: a comparative analysis

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Calendula L. (Asteraceae) is an unexplored genus on a chemical level since studies concerning this subject were only carried out in *C. officinalis* and *C. arvensis* species [1-3]. The present study focus on 4 *taxa* of this genus growing in Portugal: *Calendula officinalis*, *C. arvensis*, *C. suffruticosa* subsp. *algarbiensis* and *C. suffruticosa* subsp. *lusitanica*. The hexane extracts were analysed by gas chromatography/mass spectrometry (GC-MS) leading to the identification of 63 compounds. Pyrrolizidine alkaloids (33.7%), terpenes (19.9%) and carboxylic acids derivatives (18.8%) were the most abundant families in *C. officinalis*. Regarding *C. arvensis* extract, carbohydrates (30.3%), terpenes (28.8%) and carboxylic acids derivatives (26.8%) supremacy was observed. In *C. suffruticosa* subsp. *lusitanica*, pyrrolizidine alkaloids (42.4%), terpenes (20.0%) and carboxylic acids (18.8%) were the principal chemical families whereas in the case of *C. suffruticosa* subsp. *algarbiensis*, terpenes (23.9%), pyrrolizidine alkaloids (22.4%) and carbohydrates (20.4%) dominated the extract. The lipophilic characterization of the two *C. suffruticosa* subspecies are been reported for the first time. Additionally, several carbohydrates, terpenes and fatty acids as well as the class of pyrrolidizine alkaloids are also being described for the first time in *Calendula* genus. Despite the similarity in the main components a differentiation among the *taxa* can be made which was verified through PCA analysis.

In conclusion, the compounds detected for the first time as well as the first description of the lipophilic composition of *C. suffruticosa* subspecies *lusitanica* and *algarbiensis* provides in-depth information about the chemical composition and variation of *Calendula* genus. Through the accomplished findings, including a PCA, a taxonomic differentiation among the *taxa* is suggested, although this requires the analysis of further samples. Additionally, some of the compounds found in significant quantities are known for their medicinal and nutritional properties which could prove the medicinal and nutritional applications of *C. officinalis* and *C. arvensis* and highlight the potential of the other species in this area.

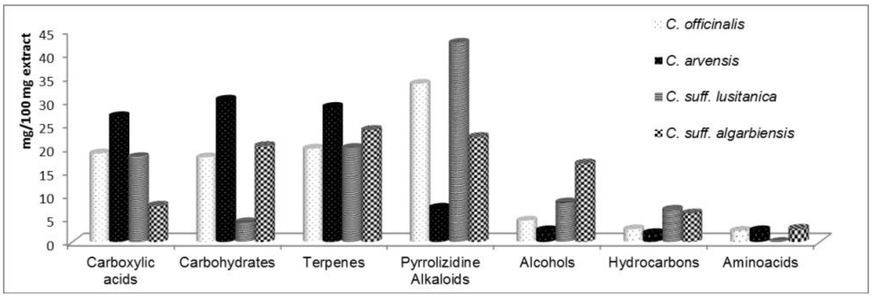

Fig. 3. Variation of the chemical composition among the four studied taxa

Acknowledgements
We thank the Instituto da Conservação da Natureza e das Florestas for allowing the collection of the samples of *C. suffruticosa* subsp. *lusitanica*. We would like to thank University of Aveiro and FCT/MEC for the financial support to the QOPNA Research Unit (FCT UID/QUI/00062/2013), to the CESAM RU (UID/AMB/50017) and to the cE3c centre (project UID/BIA/00329/2013), through national founds and where applicable co-financed by the FEDER, within the PT2020 Partnership Agreement.

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Chromone derivatives as novel dienes in Diels–Alder reactions

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Chromones are a group of heterocyclic compounds widespread in Nature and an interesting scaffold because they have been involved in a range of chemical transformations [1]. Following our previous studies on Diels–Alder (DA) reactions of chromone derivatives [2], novel 2-[(1*E*,3*E*)-4-arylbuta-1,3-dien-1-yl]-4*H*-chromen-4-ones **1** were synthesized to further study the reactivity of their two diene systems (α,β:γ,δ versus 2,3:α,β) in DA reactions (Fig.1).

A series of dienophiles were reacted with chromones **1** under microwave-assisted conditions. The best yields of adducts **2** were achieved using *N*-methylmaleimide as dienophile and $Sc(OTf)_3$ as Lewis acid in solvent-free conditions. The crucial role of $Sc(OTf)_3$ relies on the chelation with carbonyl group of adducts **2** avoiding both the occurrence of a second DA reaction and the formation of bisadducts **6**. The α,β:γ,δ-diunsaturated system of chromones **1** showed to be the most reactive diene for maleimides, dicarboxylates and azo-dicarboxylates, affording adducts **2**, **4** and **5**, respectively. Adducts **2** were dehydrogenated to the corresponding flavone derivatives **3** using DDQ as oxidizing agent (Fig.1).

Computational calculations confirmed the experimental findings on DA reactions and helped to explain the unexpected lack of reactivity of some dienophiles.

All the experimental procedures and extensive 1D and 2D NMR characterization of the final adducts and intermediates will be presented and discussed.

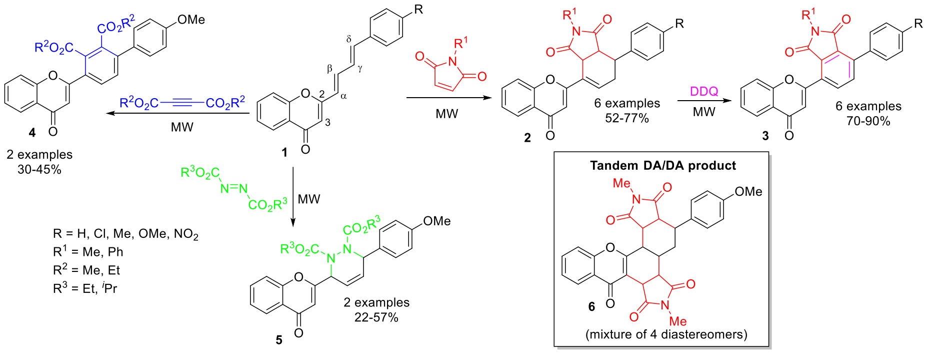

Fig.1. Microwave-assisted Diels–Alder reactions on chromones derivatives **1**

Acknowledgments
Thanks are due to University of Aveiro and FCT/MEC for the financial support of the QOPNA research unit (FCT UID/QUI/00062/2013) and CIQ-UP (Pest-C/QUI/UI0081/2013) through national founds and, where applicable, co-financed by the FEDER, within the PT2020 Partnership Agreement, and to the Portuguese NMR Network, as well as to the Instituto Politécnico de Bragança. H.M.T.A. and C.F.R.A.C.L. are grateful to FCT for their PhD (SFRH/BD/86277/2012) and Post-doc (SFRH/BPD/77972/2011) grants, respectively.

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Influence of structural features of amino-based pyranoanthocyanins on their acid-base equilibria in aqueous solution

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The equilibrium forms of three different families of dimethylamino-based pyranoanthocyanins (pyranomalvidin-3-glucoside-4-(dimethylamino)-cinnamyl (A) [1], vinylpyranomalvidin-3-glucoside-4-(dimethylamino)-cinnamyl (B) [2] and pyranomalvidin-3-glucoside-butadienylidene-4-(dimethylamino)-cinnamyl (C) [3] were studied in aqueous solutions at different pH values from 1 to 10 using UV-Visible spectroscopy. The forms present in those conditions are strongly correlated to the pyranoanthocyanin structural features. The increase of the electronic delocalization helps the protonation at the amino group. At very acidic pH condition (pH<0) the protonation at the amino group for the three pigments occurs, but under less acid conditions (pH~1) it was only observed for pigment C and in a lower extent for pigment B. At higher pH values the deprotonation at 7-OH occurs for the three pigments being more favoured for pigment C. The second deprotonation at 4′-OH was only observed for pigment C in the pH conditions studied (pH 1–10).

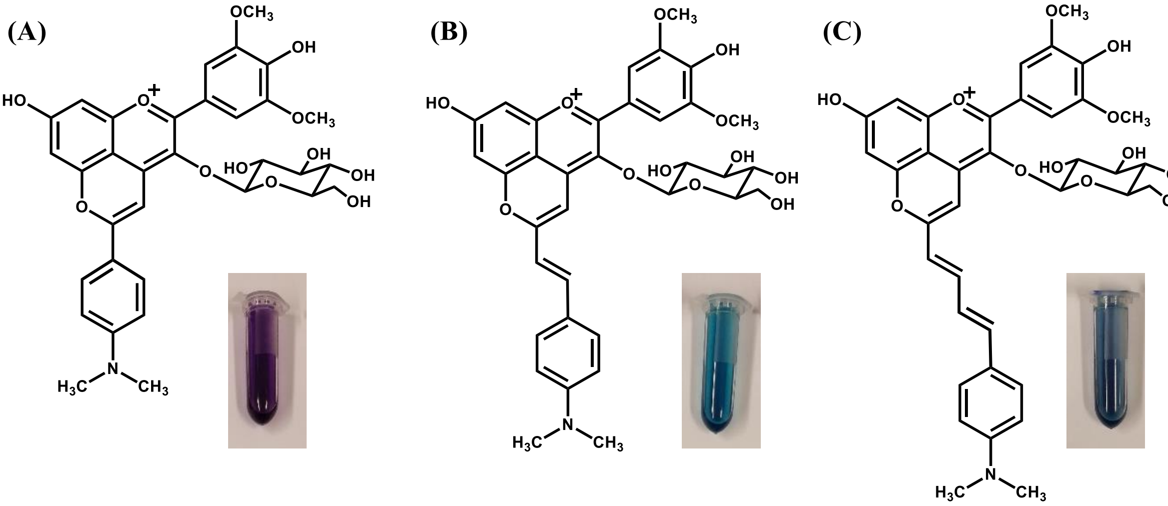

Fig.1. Structure of the amino-derived pyranoanthocyanin pigments studied (1, 2 and 3)

Acknowledgements
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Total facial discrimination of 1,3-dipolar cycloadditions in a *D*-erythrose 1,3-dioxane template. Computational studies of mechanisms

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A new D-erythrose 1,3-dioxane derivative was synthetized from D-glucose[1] and found to be a highly *stereo*-selective template as dipolarophile in 1,3-dipolar cycloadditions. Different *regio*-selectivities were obtained depending on the 1,3-dipole nature: it is complete with alkyl azides and diazomethylbenzene, but is inexistent with nitrile oxides. Computational studies were performed to understand the mechanisms of cycloadditions with the three types of 1,3-dipoles. The theoretical study gave full agreement with the experimental results. The *stereo*-selectivity was shown to be due to the steric effect of the hydrogen atom at C-8a; the *regio*-selectivity is dependent on the charge density of the reactive nucleous within the 1,3-dipole, but the nature of substituents do not display a important impact. In the diazo compound case the possibility of hydrogen bonding formation directs the *regio*-selectivity of the reaction. Cycloadditions of alkyl azides *vs* diazomethylbenzene provides an interesting example where an apparent similar chemistry was found to proceed *via* different mechanisms.

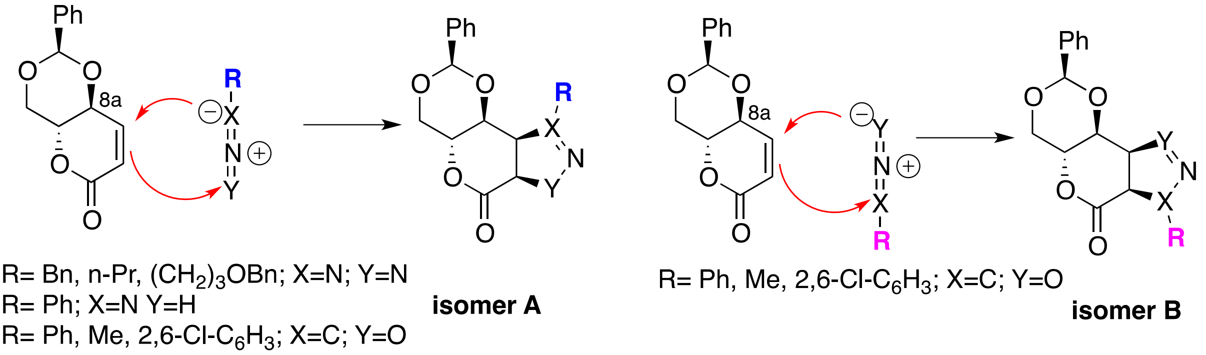

Fig.1. 1,3-Dipolar cycloaddition mechanisms of D-erythrose 1,3-dioxane **1** with alkyl azides (isomer A formed), diazomethylbenzene (isomer A formed) and nitrile oxides (A and B isomers; 1:1 ratio)

Acknowledgements
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Porphyrin derivatives and mRNA alternative splicing induced by photodynamic therapy

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Nowadays, chemotherapy using platinum-based compounds is world-wide used to treat several tumours including breast cancer resistant to first line therapy, ovarian, and colorectal cancers. However, there are several cancer cells which are gaining resistance to these type of therapy [1,2].

Photodynamic therapy (PDT) is a clinically already approved treatment for cutaneous lesions and some oncologic diseases (head and neck, brain, lungs, pancreas and skin cancers). PDT relies on a photosensitiser (PS) that accumulates in tumour cells and when activated by visible light leads to an oxidative stress causing cell death by apoptosis or necrosis [3]. Taking advantage of PS fluorescence, this approach can also be used to determine with precision the localization of a tumour allowing its fluorescence guided resection [3].

Mostly, ninety-five percent of the pre-mRNA undergoes alternative splicing (AS). This process contributes largely to the diversity and the flexibility of the proteome when compared to the genome. The isoforms generated from a single pre-mRNA often have modified functions and in some instance opposite functions. For example, the shift from Bcl-xL to Bcl-xS favour apoptosis [4]. This type of aberrant isoforms is mainly present in cancer cells and can influence the resistance to anti-cancer drugs depending on which isoform is transcribed [5].

It is known that porphyrins derivatives are used as PS in PDT with success [6]. So it becomes interesting to see if photodynamic therapy of tumours using porphyrins can interfere with AS.

In this communication, we will discuss the synthesis and photophysical characterization of "regular" and *N*-confused porphyrin derivatives (Fig 1) and the biological assessment results on MCF-7 cells (breast cancer cells).

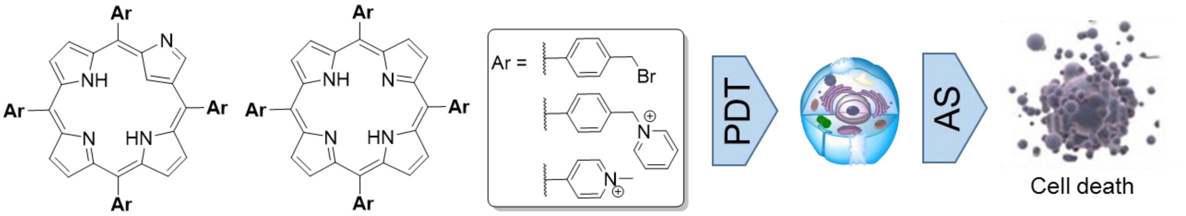

Fig.1. Porphyrins derivatives prepared in this work

Acknowledgements
Thanks are due to the University of Aveiro (Aveiro, Portugal), FCT (Portugal), the European Union, QREN, COMPETE for funding the Research Unit QOPNA (project Pest-C/QUI/UI0062/2013; FCOMP-34701-0124-FEDER-037296). N. M. M. Moura thanks FCT for the PhD grant SFRH/BD/84216/2012 and to the Belgian FNRS, and ARC.

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Camps quinolone synthesis and Hammett σ constants

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The aim of this work was to explore the usefulness of 2-arylquinolin-4(1H)-ones (and their N-methylderivatives) as probes for Hammett σ constants through their several 1H and 13C NMR shifts and shed some light on their substituent's effects.

Linear Gibbs Energy relationships (LGER), such as the Hammett equation, are very useful tools when rationalizing many of the observed trends in the reactivity of a family of compounds. Hammett's model relates the equilibrium or rate constants of two reactions, one being the standard, through a substituent specific constant (σ) and a reaction sensitivity constant (ρ). These constants find great use in mechanism elucidation and as parameters in QSAR studies [1,2].

The quinoline-4(1H)-one moiety is renowned for its ubiquity in Medicinal Chemistry, particularly in the field of antibiotics.[3] It is therefore worth understanding the effects of its substituents at a deeper level. Furthermore, they can be easily synthesized through the cyclization of amides (Camps synthesis – Figure 1) [4].

In this work a small set of quinolones was synthesized in good yields and their N-methyl analogues were obtained in significantly poorer yields. The precursor amides were obtained in very good yields. All products were characterized by NMR. Some interesting substituent effects were observed with promising correlations to Hammett σ constants.

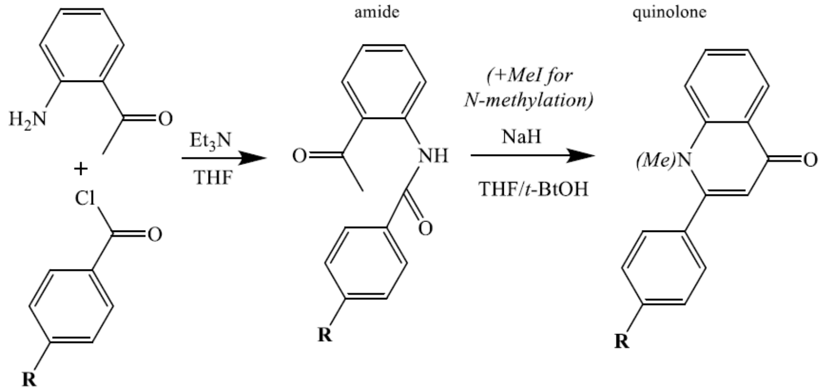

Fig.1. Scheme of the synthetic route used to obtain the various quinolin-4(1*H*)-ones

Acknowledgements
Thanks are due to the University of Aveiro and Fundação para a Ciê ncia e a Tecnologia (FCT) FCT/MEC for the financial support of the QOPNA research Unit (FCT UID/QUI/ 00062/2013) through national funds and, where applicable, cofinanced by the FEDER, within the PT2020 Partnership Agreement.

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Síntese e avaliação *in vitro* de corantes esquarílicos para terapia fotodinâmica do cancro

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O cancro é uma das principais causas de mortalidade, apesar das inúmeras campanhas de prevenção e deteção precoce. A descoberta da sua cura ou de terapêuticas mais eficazes é um alvo de investigação constante.

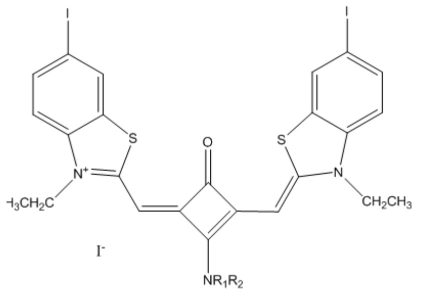
De entre as diversas terapias utilizadas para o combate do cancro, a Terapia Fotodinâmica (PDT) tem suscitado muito interesse, devido ao seu elevado potencial e ao baixo risco para as células não cancerígenas [1].

A PDT é uma terapia não evasiva, consistindo na administração, sistémica, local ou tópica, de substâncias fotossensíveis que se acumulam preferencialmente no local onde se reúnem as células cancerígenas [1]. Estas substâncias, quando irradiadas, com luz de comprimento de onda adequado, desencadeiam um conjunto de eventos que provocam a morte das células tumorais sem causar danos significativos nas células não malignas [2].

Este trabalho teve como objetivo a síntese de diferentes corantes esquarílicos para utilização como potenciais fotossensibilizadores na Terapia Fotodinâmica contra o cancro.

Foram sintetizados cinco novos corantes aminoesquarílicos iodados derivados do benzotiazole e substituídos no anel central com diferentes grupos aminas (Figura 1), apresentando absorção dentro da denominada “janela fototerapêutica” (650-800 nm). A sua citotoxidade foi testada em quatro tipos diferentes de linhas celulares tumorais humanas (HeLa, MCF-7, HepG-2 e NCI-H460) e numa cultura primária de células de fígado de porco (PLP2), não tumorais.

Os compostos sintetizados (1a-e) apresentaram diferentes atividades consoante o tipo de linha celular e, para cada linha, quando irradiados e quando mantidos no escuro. Embora apresentem citotoxicidade na linha celular não tumoral, a diferença de IC50 quando comparada com as linhas tumorais é significativa.



1a. $R_1 = R_2 = H$

1b. $R_1 = H$, $R_2 = CH_3$

1c. $R_1 = R_2 = CH_2CH_2OH$

1d. $R_1 = H$, $R_2 = CH_2CH_2OH$

1e. $R_1 = CH_3$, $R_2 = CH_2CH_2OH$

Fig.1. Estrutura química dos corantes sintetizados

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Synthesis of biocompatible compounds for potential application in medical imaging

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Macrocycle tetrapyrrolic, namely porphyrins, chlorins and bacteriochlorins, have been extensively studied for application in diverse areas, for example, catalysts, optoelectronic and medicine [1,2]. The medical application implies that macrocycles are biocompatible [3] and in this sense several studies have been developed, namely, the incorporation of polar groups in their structure [4]. In the past years, there has been an intense research in this area, once the development of compounds with ideal characteristics for application, for example, as contrast agents, to improve medical diagnosis [5].

In this work, we will present the synthesis of new pegylated porphyrins as well as their structural characterization by nuclear magnetic resonance spectroscopy and mass spectrometry in order to evaluate their potentiality for NMR fluorine contrast agents.

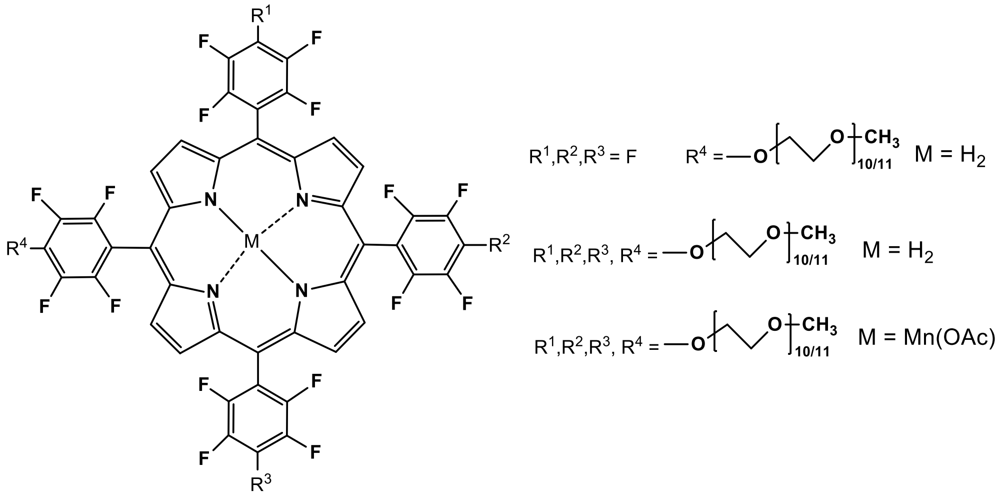

Fig.1. Chemical structure of biocompatible pegylated porphyrins

Aknowledgments
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Novas cianinas tioesquarílicas: síntese, caracterização espectroscópica e determinação do rendimento quântico de oxigénio singuleto

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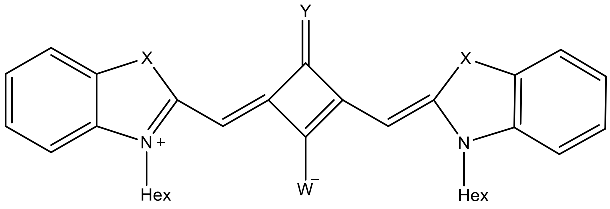
As cianinas tioesquarílicas (CTE), apresentam estruturas polimetínicas 1,3-zwiteriónicas, com um anel central de quatro membros, o qual possui um ou dois átomos de S e, anéis heteroaromáticos laterais. Um grupo de CTE apresentou um desvio batocrómico de cerca de 25 nm relativamente às análogas cianinas esquarílicas (CE) [1], tendo-se ainda constatado que um composto ditioesquarílico tinha um aumento no rendimento quântico de oxigénio singuleto (Φ_Δ) de cerca de 90% relativamente ao análogo esquarílico [2]. Estas características fazem com que as CTE sejam boas candidatas a serem utilizadas como potenciais fotossensibilizadores para Terapia Fotodinâmica do Cancro (PDT).

O presente trabalho teve como objetivo sintetizar novas CTE com anéis heteroaromáticos laterais de benzotiazole e de benzoselenazole (Fig. 1: **3**-**6**) e, estudar a influência da presença de átomos de S no anel central nos valores de Φ_Δ. Neste sentido, foram sintetizadas as CE **1** e **2** e, a partir destas, as correspondentes monotioesquarílicas **3** e **5** e, as ditioesquarílicas **4** e **6**, de acordo com métodos adaptados da literatura [1]. As cianinas sintetizadas foram caracterizadas pelas técnicas de EMAR-ESI-TOF, RMN de ^{1}H e de ^{13}C, IV, UV/Vis e p.f. e, posteriormente determinado o seu Φ_Δ.

Os resultados obtidos permitem concluir que a presença de átomos de S no anel central de quatro membros nos derivados do benzoselenazole **5** e **6** não afeta o valor de Φ_Δ relativamente ao seu análogo **2**. Pelo contrário, nos derivados do benzotiazole **3** e **4**, a presença de átomos de S duplica o valor de Φ_Δ relativamente ao seu análogo **1**, sendo, no entanto, o valor obtido igual para as cianinas **3** e **4**, isto é, para este caso verifica-se que o número de átomos de S não afeta o valor de Φ_Δ, contrariamente ao referido na literatura [2].



1: X= S, Y=O, W=O; **2**: X= Se, Y=O, W=O
3: X= S, Y=S, W=O; **4**: X= S, Y=S, W=S
5: X= Se, Y=S, W=O; **6**: X= Se, Y=S, W=S

Fig.1. Cianinas tioesquarílicas sintetizadas **3**-**6**

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Synthesis and structural characterization of novel pyrano-deoxyanthocyanin dyes

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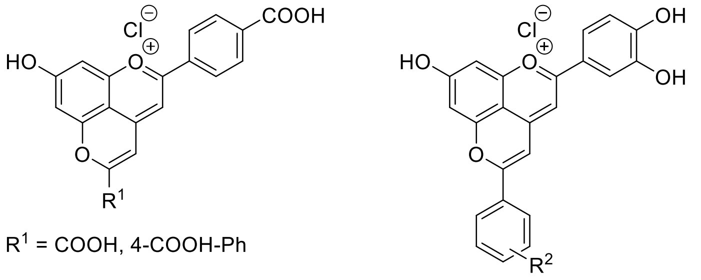
Pyranoanthocyanins are anthocyanin-derived pigments characterized by the presence of an additional D ring in their skeleton, which can be found in fruit beverages, such as red wine. This new class of compounds includes portisins (blue pigments found in aged Port wines) [1], pyranoanthocyanin dimers [2] and pyrano-3-deoxyanthocyanins [3], and has been the subject of several studies in order to understand their formation mechanism and explore their physical-chemical and antioxidant properties. In particular, pyrano-3-deoxyanthocyanins have attracted much attention due to their promising applications, since their 3-deoxyanthocyanins precursors have been used as food colorants, hair dyes, and photosensitizers for medical (*e.g.*, photodynamic therapy, PDT) and energy applications (*e.g.*, dye-sensitized solar cells, DSSCs) [4].

In this work, new pyrano-deoxyanthocyanins (Fig.1) were synthesized through cycloaddition reactions of deoxyanthocyanins, previously prepared, with the appropriate cinnamic acid derivatives. The structures of all new compounds were established by LC-MS and 1D and 2D NMR studies. The experimental details and obtained results will be presented and discussed in this communication.



R^1 = COOH, 4-COOH-Ph

R^2 = 4-N(Me)$_2$, 3,4-OH

Fig.1. Structures of the synthesized pyrano-deoxyanthocyanins

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Synthesis and characterization of long alkyl chains BODIPYs as new donor materials for organic photovoltaic cells

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Derivatives of boron-dipyrromethene (BODIPY) constitute an important class of visible light absorbing dyes, with a wide variety of applications from cellular imaging, photodynamic therapy or drug-delivery to organic photovoltaics [1-3].

Due to their properties, such as photochemical and chemical stability, high molar absorption coefficients, excitation/emission wavelengths in the visible spectral region, good solubility and adequate HOMO-LUMO energy orbitals levels, BODIPYs are excellent donor materials for photovoltaic cells [2]. Since it is known [4] that the presence of hydrophobic alkyl chains can reduce the aggregation, improving the injection of electrons and decreasing the recombination, we planned and synthesized a new series of BODIPY molecules (Fig.1, structures 2a and 2b) with double long hydrophobic aliphatic groups. Also, in order to enhance the physical interaction of the BODIPYs with polar substrates (both organic or inorganic) that are used in photovoltaic cell fabrication, we also planned and synthesized a cationic BODIPY bearing a quaternary ammonium group at the end of one of those hydrophobic alkyl chains (Fig.1, structure 3).

In fact, in the present work, we describe the synthesis of the precursor’s aldehydes and then the synthesis of the planned BODIPYs, via a one flask – three step synthesis. The final compounds (2a, 2b and 3) were fully characterized by absorption and emission spectroscopy and cyclic voltammetry in order to study their properties as donor materials in photovoltaic cells. All the synthetized cationic BODIPY were obtained with a reasonable yield (39 % to 64 %) and show good solubility in organic solvents and good chemical and photochemical stability. All the BODIPYs have photophysical and electrochemical characteristics adequate to be donor materials in organic photovoltaic cells.

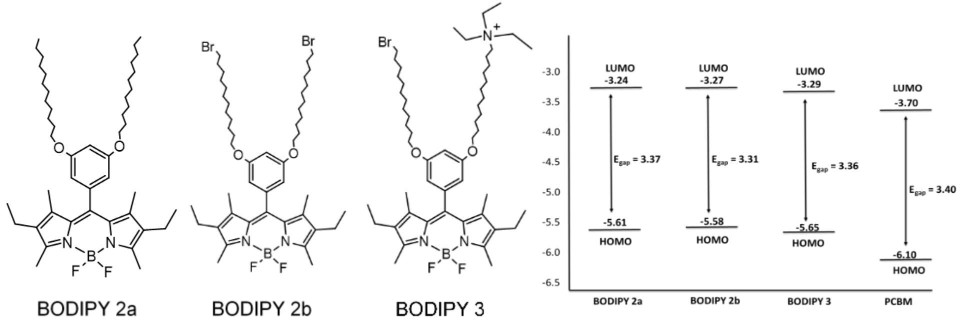

Fig.1. Structure of BODIPY 2a, 2b and 3 (left) and comparison of frontier orbitals energy of all three synthetized BODIPY and PCBM ([6,6]-phenyl-C61-butyric acid methyl ester), an acceptor standard material in organic photovoltaic cells (right) [5]

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Mesoporous organosilica hybrids functionalized with carbohydrates

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With the increasing progress in the area of medicinal chemistry, we read headlines almost every day about potential new promising drugs on the horizon for diseases like cancer. However, they are usually limited by poor stability, high toxicity, small half-lives, aggregation tendency and the transport is hindered by biobarriers such as the blood brain barrier or cell membranes. To solve these problems, researchers from different areas, such as biology, materials science, pharmacy medicinal chemistry and chemistry, have oriented their work namely with the aim to develop more efficient drug delivery systems [1]. In the past decades the advances of nanotechnology have facilitated the development of several nanovehicles as drug delivery systems, as an advantage in the field of Medicinal Chemistry [2]. Among the nanomaterials proposed, hybrid mesoporous organosilicas have aroused significant interest as candidates for nanomedical applications. These materials are defined by IUPAC as materials with pore sizes between 2 and 50 nm [3]. The studies involving mesoporous materials have attracted much attention because of their unique properties, dense and uniform distribution of organic groups covalently embedded within the silica framework walls, high specific surface area, large pore volume, and a wide range of pore compositions allowing the tuning of the interactions of the host structure with guest molecules, low toxicity, poor reactivity with chelating groups presents on the system, chemical stability and the possibility of surface modification [4]. Many studies have been done to functionalize these systems with polymers derived from inorganic components [3] to increase its applicability, mechanical properties, barriers and permeation. Carbohydrates are currently considered the most versatile functionally natural products and can be processed into products with great importance in many areas, particularly in the pharmaceutical industry [5]. The importance of carbohydrates and their conjugates have been recognized in many biological processes, and consequently the medicinal chemistry of carbohydrates has been developing over the years [6]. The use of carbohydrates in the formation of monosilylated precursors is an innovative work. Many properties of these compounds like their biodegradability, great solubility, the possibility to forming conjugates with a large number of compounds, enable carbohydrates the possibility of their use in biomedicine.

The aim of this work is to synthesize monosilylated precursors with a carbohydrate derivative covalently bonded to the inorganic support. These precursors were herein used to prepare mesoporous organosilica hybrid envisioning their future potential use as an anti-tumoral drug delivery platform. The first part of the present work was the synthesis of the organic components. Some carbohydrate derivatives were synthesized from D-glucose, D-ribose, D-xylose and methyl-α-D-glucopyranoside. In the second part of the work was prepared the mono-silylated precursor involving a cross-link between the carbohydrate derivatives and ICPTES 3-(triethoxysilyl)propyl isocyanate. Actually, these hybrid precursors are being used to prepare functionalized mesoporous organosilica hybrids with the aim of achieve new materials for biomedical applications, opening the opportunity to link it with potential new drugs or others already in the market, in particularly to have a controlled release of them, giving new and better ways to hit the disease target.

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Hidrodimerización de flavonoides promovida por SmI_2: síntesis de 2,2'-biflavonoides

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Los biflavonoides son pequeñas moléculas de naturaleza polifenólica que están constituidas por dos subunidades flavonoide y que se encuentran ampliamente en el reino vegetal [1].

En los últimos años, los biflavonoides han ganado mucho terreno como moléculas moduladoras de respuestas fisiológicas y patológicas. Existen diversas publicaciones en las que se reconocen los compuestos derivados de la dimerización de flavonoides como moléculas que poseen una elevada bioactividad [2].

Teniendo en cuenta la potencial actividad biológica de los biflavonoides, así como su potencial uso como agentes farmacológicos, en nuestro grupo de investigación nos fijamos como objetivo la preparación de 2,2'-biflavonoides. En este sentido, y relacionándolo directamente con nuestros últimos resultados en la síntesis y evaluación biológica de compuestos fenólicos, nos interesamos en la preparación de estos compuestos orgánicos empleando, para ello, metodologías sintéticas desarrolladas en nuestro grupo de investigación. Así, en esta comunicación presentamos nuestros primeros resultados concernientes al desarrollo de una metodología sintética, que permite el acoplamiento reductivo de 4-oxo-4*H*-1-benzopiranos, a través de sus posiciones 2, empleando para ello diyoduro de samario (SmI_2) [3] en presencia de un medio prótico [4]. El procedimiento resultó ser suave, sencillo, simple y general para las flavonas y isoflavonas que se han estudiado. En la Figura 1 se muestra un resumen de los resultados obtenidos.

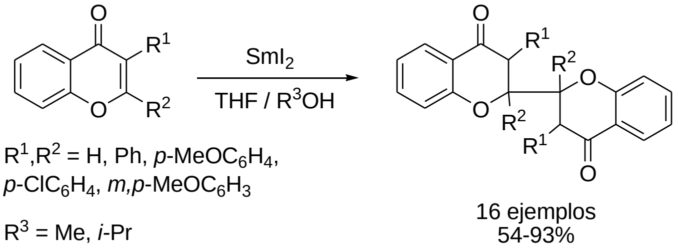

Fig.1. Síntesis de 2,2'-biflavonoides promovida por SmI_2

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Los autores agradecen el Ministerio de Economía y Competitividad (España) por la financiación concedida a través del Proyecto CTQ2014-55015-P y también a la Universidad de Aveiro, FCT / MEC para el apoyo financiero a la Unidad de Investigación QOPNA (FCT UID / QUI / 00062/2013), a través de fondos nacionales y, cuando proceda, cofinanciado por el FEDER, dentro del Acuerdo de Asociación PT2020, y también a la Red portuguesa de RMN.

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Design of ethoxylated serine-based surfactants and study of the aggregation properties

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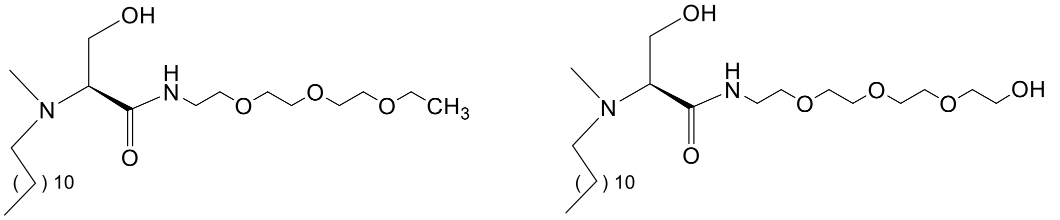
Ethoxylated surfactants have been widely used in various applications as nonionic surfactants, due to their higher water solubility conferred by their polar ethoxylated groups that are strongly solvated in aqueous media. These surfactants have also an enormous versatility due to the possible optimization of the hydrophilic-lipophilic balance resulting from their molecular structure.[1] Furthermore, surfactants derived from amino acids have been widely studied because of their biocompatibility, biodegradability and low cytotoxicity.[2] However, the development of ethoxylated surfactants derived from amino acids has been little explored. Therefore, the aim of this work consists in the synthesis of new ethoxylated surfactants derived from serine and the study of their aggregation properties.

The synthesis of new serine-based ethoxylated surfactants was divided into two parts. Initially, different ethoxylated amines were synthesized by the functionalization of two different oligoethylene glycols tri(ethylene glycol)monoethyl ether and tetraethylene glycol. Then, these amines were condensed with a previously synthesized lipophilic serine derivative, yielding ethoxylated surfactant precursors with an amide bond. From these precursors, two new ethoxylated serine-based nonionic surfactants were successfully obtained (C12SerE3Et and C12SerE4). The surfactants were structurally characterized by nuclear magnetic resonance 1H and 13C spectroscopy and by high resolution mass spectrometry.

The interfacial properties and aggregation behavior of the newly synthetized surfactants were then studied by a tensiometry technique (through the Wilhelmy plate method). The temperature-dependence of this surfactants was also determined by the cloud point, which is characteristic of this type of ethoxylated surfactants.



$C_{12}SerE_3Et$ **$C_{12}SerE_4$**

Fig.1. Ethoxylated serine-based surfactants synthetized

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Catalytic reduction of α,β,γ,δ-unsaturated esters to synthesize stereoselectively tetrasubstituted olefins

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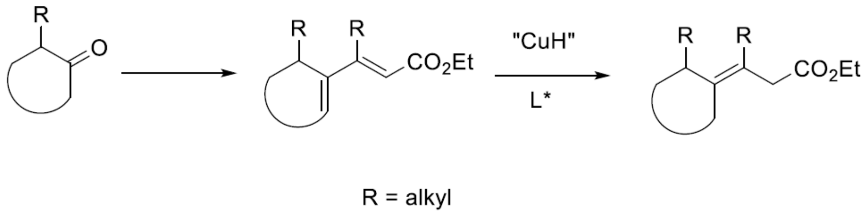
The tetrasubstituted olefin moieties can be found in a plethora of biologically active natural products and pharmaceutical drugs and have also been used as building block precursors of other functionalities. Interestingly, the congested nature of the double bond has made the synthesis of tetrasubstituted olefins, a formidable challenge over the last decades. While the classical Wittig reaction and variants have found important applications in the stereoselective formation of mono- and disubstituted alkenes from aldehydes, these reactions offer poor stereoselectivity or low reactivity when applied to the synthesis of tetrasubstituted alkenes from ketones. Despite the recent developments of promising synthetic strategies to tetrasubstituted olefins such as carbometallation of alkynes and palladium-catalyzed cross coupling processes, new stereoselective and efficient strategies are still needed [1].

We describe here our initial results on the development of stereoselective synthetic strategies to (Z)-tetrasubstituted functionalized olefins from ketones, using a catalytic reduction of an α,β,γ,δ-unsaturated ester.



Aknowlegements
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XXII Encontro Luso-Galego
Química

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Química Verde

Ohmic heating in organic synthesis: state-of-the-art and examples of its use in the synthesis of nitrogen heterocycles

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Ohmic heating (ΩH) is a novel highly energy-efficient heating process in which an AC electrical current of tunable high frequency crosses the conductive reaction medium (which behaves as an *in situ* electrical ohmic heater). ΩH allows a fast, volumetric and uniform *in situ* heating and drives an increase of reaction fluid and charged species dynamics which leads, in many cases, to an increase of the overall reaction kinetics, selectivity and yields [1–5].

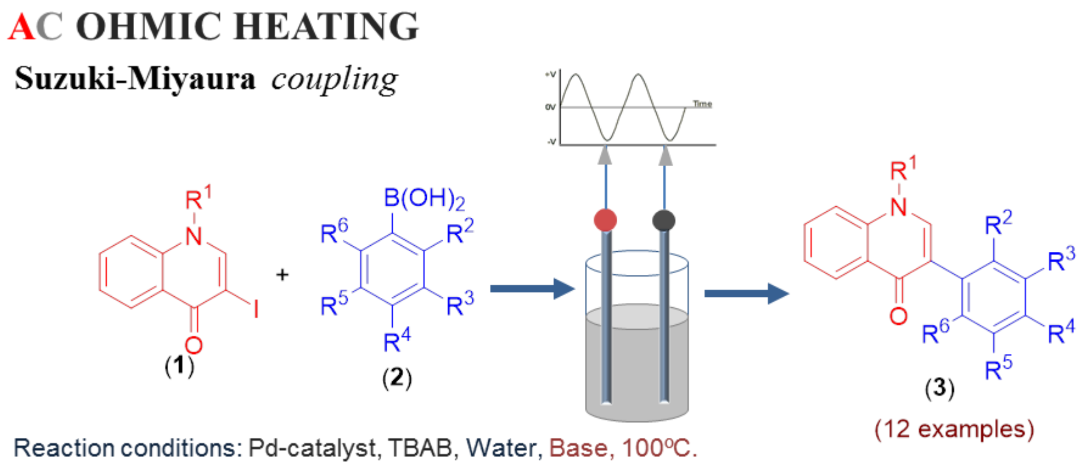

Fig.1. Ohmic heating-assisted synthesis of 3-arylquinolin-4(1*H*)-ones (**3**)

The combination of ΩH with water as solvent offers great opportunities for sustainable chemistry. In our group, ΩH has been used to heat reaction mixtures, chiefly aqueous ones, being a competitive alternative to microwave irradiation method [1,3-5]. To date, several different types of organic reactions were performed using an home-made ΩH reactor prototype [1-5].

In this communication we will present our ΩH reactor prototype and some examples regarding its use in organic synthesis, especially in the synthesis of 3-arylquinolin-4(1*H*)-ones (**3**) [3].

Acknowledgments

Thanks are due to the University of Aveiro, and the FCT/Ministério da Educação e Ciência (MEC) for financial support to the QOPNA research project (FCT UID/QUI/00062/2013) and CIQUP (Project: PEst-C/QUI/UI0081/2011) through national funds and as applicable co-financed by the FEDER within the PT2020 Partnership Agreement. V.L.M.S. thanks FCT for her post-doctoral grant (SFRH/BPD/108807/2015).

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Tunable hydrophobic deep eutectic solvents based on terpenes

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Nowadays the modern chemistry is usually linked to the green concept, demanding for new eco-friendly solvents able to dissolve a large spectrum of solutes. The actual foci are supercritical fluids, ionic liquids (ILs) and eutectic solvents, particularly the deep eutectic solvents (DES). Due to their similar physicochemical properties, DES have been proposed as ILs substituents, due to their cheap, quick and easy way of preparation.

DES have been mostly prepared through the combination of a salt, or an ionic liquid, with nontoxic and biodegradable compounds such as carboxylic acids, polyols, and sugars; being the majority hydrophilic. To the best of our knowledge, only a few works reported hydrophobic eutectic mixtures and, among them, the absence of phase diagrams is common, despite their importance to give the composition and temperature range for operating these systems. Moreover, a thermodynamic evaluation of the physical properties of these systems is rarely presented.

Due to their very low solubility in water, terpenes arise as candidates to prepare sustainable and cheap hydrophobic solvents. This vast class of natural organic compounds is constituent of essential oils and produced in large-scale for application in the chemical, pharmaceutical, cosmetics or food industries.

The main goal of this work is to prepare eutectic solvents and DES composed by terpenes and monocarboxylic acids, and mixtures of terpenes. Phase diagrams of these mixture were characterized and analyzed in the whole composition range, through differential scanning calorimetry (DSC). Moreover, some physico-chemical properties such as density, viscosity and water solubilities were measured in order to understand their impact in these systems. Finally NRTL and UNIFAC were used to model solid-liquid equilibrium, and the eutectic composition solvent evaluated for possible biomolecule extractions.

Results show that mixtures between thymol or menthol and caprylic acid, capric acid, lauric acid or myristic acid form normal eutectic solvents. The eutectic temperature of these mixtures increase with the increase on number of carbons in the monocarboxylic acid. Moreover, the eutectic composition also varies depending on the monocarboxylic acid used. On the other hand, mixtures of terpenes L(–)-menthol, thymol, (R)-(+)-camphor and (–)-borneol form DES. Mixtures of terpenes containing thymol were found to be low transition temperature mixtures.

Acknowledgements
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Comparison of bioethanol production strategies

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The increasing in CO_2 emissions and the demand for energy has led to raise the interest in alternative, renewable substitutes for fuel-derived sources of energy. One interesting feedstocks is lignocellulosic material, which can provide transportation fuels, like bioethanol, in the short-term [1 - 3].

Paulownia tomentosa is a fast growing lignocellulosic material [4] useful for second generation bioethanol production, using an efficient and environmentally friendly treatment like autohydrolysis [5]. With this treatment, cellulose is more susceptible to enzyme hydrolysis, leading to glucose rich solutions that can be convert into ethanol by microorganisms. These two steps, enzymatic hydrolysis and biological conversion can be carried out jointly (called SSF, Simultaneous Saccharification and Fermentation) or consecutively (called SHF, Separated Hydrolysis and Fermentation) [6].

In this work, non-isothermal autohydrolysis was used to improve the enzymatic susceptibility of Paulownia for 2nd bioethanol production, to compare ethanol production through the two different strategies (SSF and SHF). The results show that SSF rises higher concentrations of ethanol (up to 36.90 g ethanol/ L and 98.90% of conversion in optimal conditions, see figure 1) than SHF (up to 28.36 g ethanol/L and 76.04% of conversion).

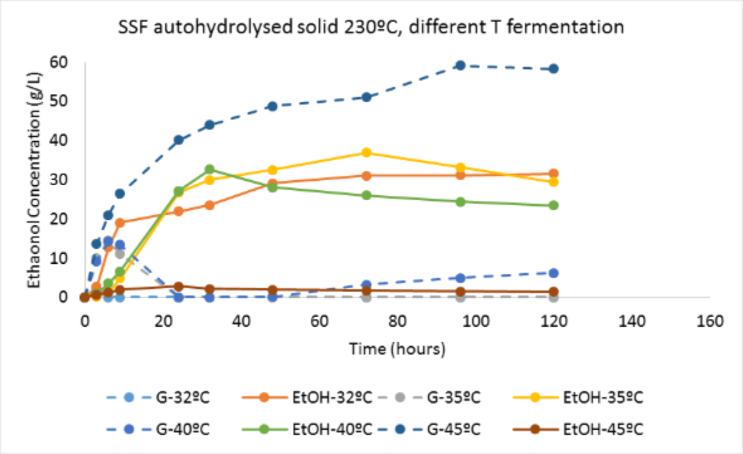

Fig.1. Comparison of temperature effect in SSF (*Paulownia* autohydrolyzed at 230ºC)

Acknowledgments
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Synthesis and oxidation studies of naphthalene chalcone derivatives under biomimetic conditions

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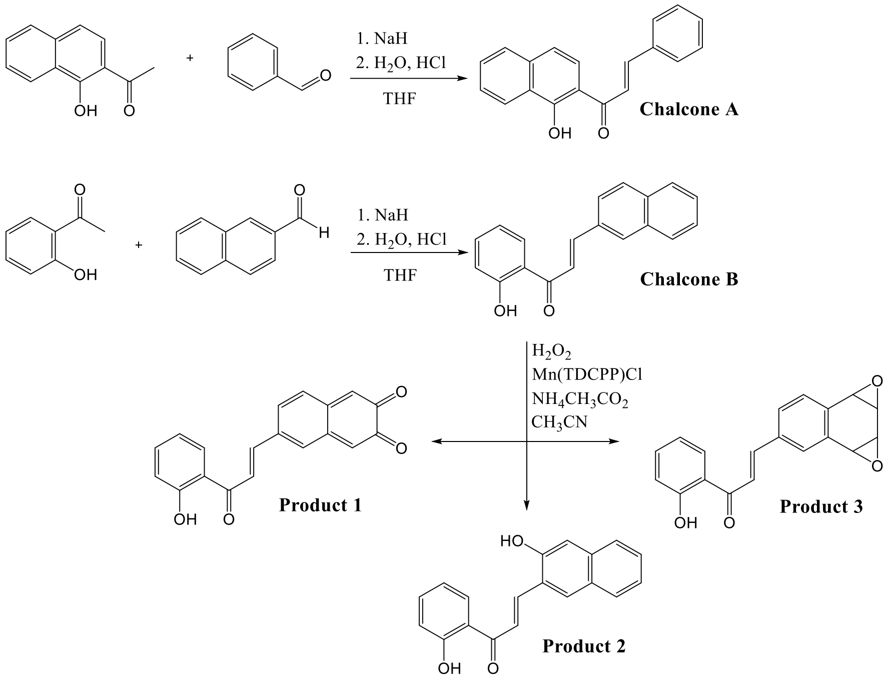
Chalcone derivatives are ubiquitous natural compounds that can be found in superior plants, fruits, and vegetables. Chalcones are the precursors of several other flavonoids and consequently their abundance is limited [1]. Nevertheless, they participate in diverse physiological activities such as colouring and immunity. However, it's their great pharmacological potential, namely as antiviral, antioxidant, anticancer, and anti-inflammatory agents, that is responsible for the great attention from the scientific community. In particular, hydroxylated chalcones merit a special interest due to their anticancer and anti-inflammatory properties [2].

In this communication the access to chalcones A and B using the conventional Claisen-Schmidt condensation [3], and the products obtained from chalcone B oxidation under biomimetic conditions using a metalloporphyrin as catalyst, will be reported. All the experimental details, namely the structural characterization of the obtained diepoxide, quinone, and hydroxyl derivatives will also be discussed.



Scheme 1. Synthesis of the naphthalene chalcone derivatives and the products obtained under oxidative biomimetic conditions

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Searching for eco-friendly biosynthesis of gold and silver nanoparticles: the case of the brown seaweed *Saccorhiza polyschides*

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Seaweeds are a great source of bioactive compounds with a wide variety of applications [1]. Recently they have been named as "bionanofactories" due to their ability for the synthesis of metal nanoparticles [2]. Nowadays, the development of green synthesis methods is in potential growth because they present significative benefits over the classical chemical and physical methods. Among other advantages they reduce the use of toxic and expensive reagents, thus being eco-friendly and cost-effective.

In this work we have selected the brown seaweed *Saccorhiza polyschides* (SP) for the biosynthesis of gold and silver nanoparticles. *S. polyschides* is a large, blade shape macroalgae, broadly distributed in inter and subtidal rocky shores of the NE Atlantic coast. Firstly, an aqueous extract of SP was prepared and its reducing activity and total phenolic compounds were determined. The results suggested that *S. polyschides* was a good candidate to lead the synthesis of nanoparticles by the reduction of $HAuCl_4$ and $AgNO_3$. Obtained nanoparticles were fully characterized by UV-Vis spectroscopy, Transmission Electron Microscopy (TEM), High Resolution Transmission Electron Microscopy (HRTEM) and Scanning Transmission Electron Microscopy (STEM); these technics allow us to confirm the formation of spherical nanoparticles with mean diameter of 14 ± 2 nm for Au@SP and 15 ± 3 nm in the case of Ag@SP, as can be seen in **Fig.1**. Moreover, Fourier transform infrared spectra (FTIR) of SP extract, Au@SP and Ag@SP were measured in order to identify the functional groups of biomolecules that could be involved in the formation and stabilization of the nanoparticles.

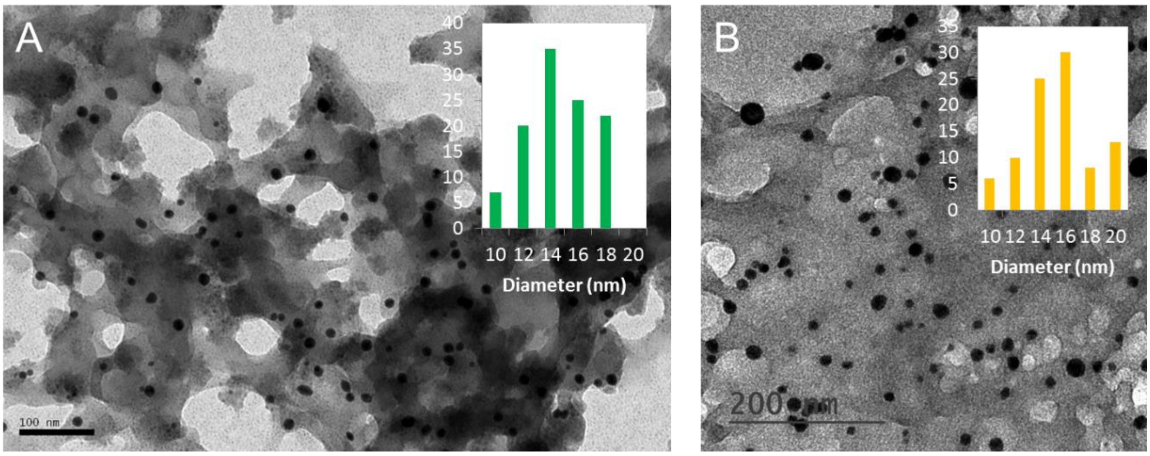

Fig.1. TEM images of (A) Au@SP and (B) Ag@SP. Inset size distribution of the nanoparticles

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Greener chiral amines with biocatalysis

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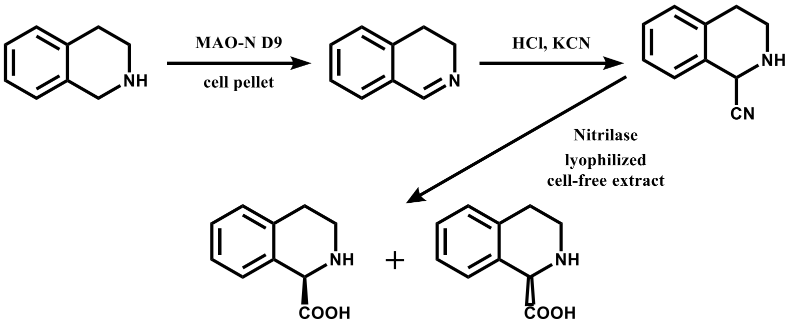
Biocatalysis represents one of the most promising routes towards a sustainable future in the industrial production of fine chemicals. Particularly, the directed evolution of enzymes and further expression in bacterium has allowed chemists to obtain complex molecules with improved stereo and regio-selectivity, at high reaction rates and with a low environmental impact [1]. Monoamine oxidase from *Aspergillus niger* (MAO-N) is a flavin and oxygen dependent oxidase that catalyses the deamination of primary amines. MAO-N has undergone successive rounds of directed evolution at the Manchester Institute of Biotechnology, and MAO-N D9 and MAO-N D11 mutants are already capable of accepting tertiary amines as substrates [2].

Enantiomerically pure chiral amines are increasingly common in the pharmaceutical industry, demanding for easy and highly selective methods for the synthesis of a broad range of compounds [3]. Tetrahydroisoquinoline (THIQ) derivatives can be included in this category, presenting antimicrobial, antibiotic, antitumor or antimuscarinic activities, among others [4].

In this work we devised a one pot three step cascade towards the synthesis of enantioenriched tetrahydroisoquinoline-1-carboxylic acids, at low temperature in water. First, MAO-N was used in the conversion of several THIQs to the corresponding 3,4-dihydroisoquinoline analogues. These were then treated with potassium cyanide in an acid environment to yield 1-cyanotetrahydroisoquinolines. The cyano compounds were selectively hydrolysed by a commercial nitrilase by Prozomix®. Finally, unsubstituted tetrahydroisoquinoline-1-carboxylic acid was obtained in 15% yield and with 88% enantiomeric excess of one enantiomer **(Scheme 1)**.



Scheme 1. Enzymatic cascade for the synthesis of tetrahydroisoquinoline-1-carboxylic acid

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FTIR technique for the determination of antioxidant properties: application in spent coffee grounds

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Coffee is one of the most consumed beverages in the world and belongs to an industry that generates a considerable amount of residues, such as spent coffee grounds (SCG) [1]. Currently, SCG have no commercial value, being considered a solid waste that is mostly burned or used as fertilizers [2]. The amount of SCG currently produced highlights the importance of recycling and recovering, once organic compounds such as caffeine, tannins and polyphenols, can be an issue for environment owing to its toxic nature [3]. Hence, SCG can have several applications due to its large variety of bioactive compounds, which could be extracted and reused. Several studies showed the presence of compounds with antioxidant properties, such as chlorogenic acid, caffeine and flavonoids in SCG, which nowadays are highly used in different industries [1]. Therefore, the valorization of SCG will promote a more sustainable way of dealing with these residues and can prove valuable for coffee industry.

There are several methods to evaluate SCG potential as a source of bioactive compounds, however they are usually expensive, time consuming and laborious. Therefore, it is extremely important to find alternative techniques that are fast, simple, reliable, with low cost and amenable to industrial application [4]. Fourier transform mid-infrared spectroscopy technique (FTIR) is an analytical tool that gathers these features and, coupled with chemometrics, enables its wide application in solving real life problems. This work intended to assess the efficiency of FTIR spectroscopy technique in the evaluation of antioxidant capacity, total phenolic and total flavonoid contents in SCG samples. To implement the FTIR technique, chemometrics was used to correlate spectra with the results of reference methods, such as reversed phase liquid chromatography.

PLS models' were used to correlate the FTIR spectra of SCG against the parameters abovementioned. Preliminary results obtained showed a good linearity (R2 close to 0.8) for the antioxidant capacity, total phenolic and total flavonoid contents. These results revealed that FTIR is an interesting approach for the evaluation of SCG antioxidant compounds once it is a low-cost, multi-parametric and reliable alternative instead of the laborious reference methods. This can help in the fastest monitoring of SCG samples in order to select the ones that are richest in antioxidant compounds, before hard steps of extraction take place.

Acknowledgements
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Fluorescent carbon nanomaterials from cork industry wastewater: towards an effective circular chemical economy

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Quercus suber L. (cork oak) contributes significantly to the Portuguese economy with exports exceeding 845 million euros in 2014 (63% of country share) [1]. After harvesting and a period of rest, the cork planks are subject to an industrial operation called cooking in which the textural and plastic properties of cork are improved. The resulting wastewater (*ca.* 400 L for each tonne of processed cork) contains large levels of water-soluble extractives. The amount of phenol- and polyphenol-based compounds in the spent cork water is usually associated to its poor biodegradability (BOD/COD = 0.16-0.21) [2]. Albeit some progress has been achieved with several treatment processes, the cork industry wastewater (CIWW) continues to represent a serious environmental issue in cork processing plants that needs further insights. Industrial valorization of such an effluent will be a must.

In this communication we report that high-valued materials can be produced directly from CIWW while parenthetically contributing to the reduction of the environmental impact of such effluents. The synthesis of luminescent carbon nanomaterials (LCNM), including carbon dots (C-dots), from the cork spent water will be described. Applications of these LCNM are envisaged for fluorescent bio-imaging and nanomedicine, sensory analysis and as photocatalysts. As a demonstration of their usefulness, the as-prepared LCNM were used in the direct detection of heme proteins (hemoglobin, myoglobin and cytochrome *c*) that have crucial roles in certain disease events of living organisms. The new LCNM are capable of efficiently detect heme proteins (limits of detection in the range 0.09-0.64 µM) at biological pH while clearly discriminating non-heme proteins (lysozyme), possibly by mixed Förster-type resonance energy transfer (FRET) and photoinduced electron transfer (PET) mechanisms.

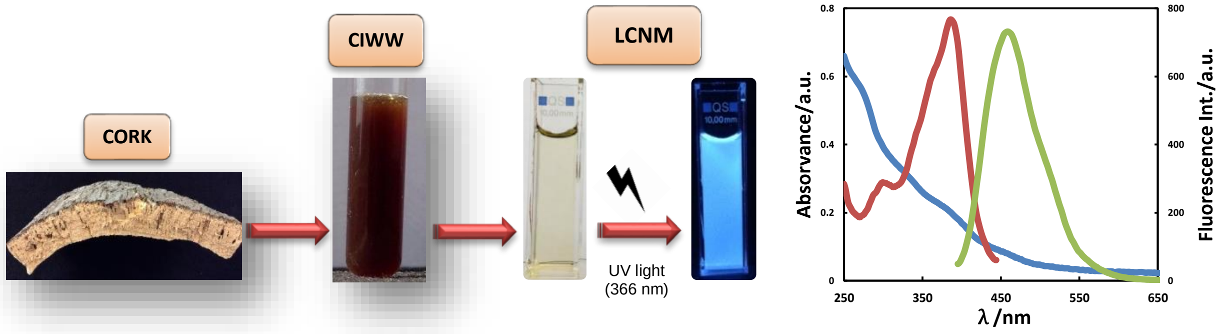

Fig. 1. Processing stages to luminescent nanomaterials and UV-Vis (blue), excitation (red, monitored at 460 nm) and fluorescence (green, λ_{exc} = 380 nm) spectra of the as-prepared LCNM in water

Acknowledgments
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Materiales de carbón eco-eficientes en la síntesis de heterociclos bioactivos. Estudio mecanístico

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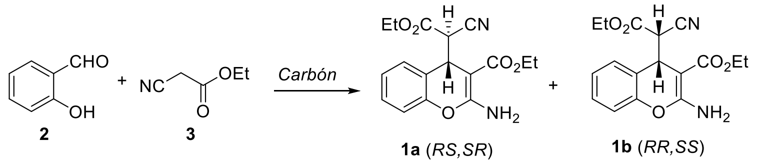
Una de las herramientas más poderosas para la síntesis de sistemas heterocíclicos, tanto desde el punto de vista académico como industrial, es el uso de reacciones multicomponente (RMC). Su utilización permite el acceso a gran diversidad de heterociclos complejos, que forman parte de la estructura de numerosos fármacos, de forma simple y selectiva.

Los cromenos, más concretamente los 2-amino-4*H*-cromenos, son heterociclos oxigenados de gran interés industrial por sus propiedades terapéuticas. Una de las rutas sintéticas más sencillas para la obtención de cromenos se basa en la RCM entre salicilaldehído **2** y nitrilos con grupos metilenos activos **3** [1]. Sin embargo, esta RMC, a menudo, requiere el empleo de disolventes, además de tiempos de reacción prolongados y, en algunos casos, procesos de aislamiento y purificación de los productos de reacción tediosos. En este sentido, el desarrollo de nuevos catalizadores activos y selectivos en la síntesis verde de este tipo de compuestos constituye un tema de gran interés y relevancia industrial.

Es por ello que en esta comunicación se presenta el desarrollo de una nueva familia de materiales híbridos de carbón [2], preparados a partir de polímeros y de caliza y/o dolomita, de origen mineral natural. Estos materiales muestran propiedades básicas, y permiten la síntesis de 2-amino-4*H*-cromenos **1** de forma eficiente, selectiva, en ausencia de disolventes y bajo condiciones de reacción suaves, reduciendo así el impacto medioambiental (Esquema 1).

Además, se describe el mecanismo de la reacción, investigado mediante cálculos computacionales: Los estudios teóricos realizados (B3LYP/6-31G(d,p)) demuestran que la reacción tiene lugar por i) quimisorción disociativa de **3**, ii) aldolización, iii) heterociclación intramolecular asistida por trazas de H_2O, iv) deshidratación, v) adición de tipo Michael de la segunda molécula de **3**, y vi) desorción del producto.



Esquema 1. Síntesis de 2-amino-4*H*-cromenos **1** a partir de salicilaldehído **2** y cianoacetato de etilo **3**

Agradecimientos
Este trabajo se ha financiado por MICINN (referencia de proyecto CTM2014-5668-R).

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B, S and P doped g-C_3N_4 for the selective photocatalytic oxidation of benzyl alcohol to benzaldehyde

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Photocatalytic synthesis offers an alternative green route to replace environmentally hazardous processes for the manufacture of valuable compounds. Benzaldehyde (BAL) is widely used for the production of pharmaceuticals, fragrances and agriculture compounds. BAL is typically synthesized in organic solvents using metal-based catalysts, although is possible to obtain it from the selective photocatalytic oxidation of benzyl alcohol (BA).

As an analogous of graphene, carbon nitride (g-C_3N_4) has attracted much attention due to its unique chemical, optical and electronic features [1]. Due to its relatively narrow bandgap (2.7 eV), this material is a promising alternative to benchmark TiO_2 for photocatalytic applications. The main bottlenecks for the application of g-C_3N_4 in photocatalytic synthesis are the low surface area and the fast recombination of electrons and holes upon photo-excitation. Doping g-C_3N_4 with heteroatoms has been reported as an effective technique for increasing the photocatalytic performance of g-C_3N_4 [2].

In this work, g-C_3N_4 was doped with sulphur, boron and phosphorous (0.4 *wt* %) and the resulting catalysts were tested for the selective photocatalytic oxidation of BA to BAL in aqueous medium under UV (390 nm) LED irradiation. The P-doped material shows enhanced absorption in the UV-vis range and a decrease in the bandgap compared to the starting material (Fig. 1a), along with a decrease in the photoluminescence intensity (Fig. 1b). This material was the best performing catalyst, resulting in an increase of 8 and 11% of BAL yield (Y) and BA conversion (C), respectively, when compared with pristine g-C_3N_4. At the same time selectivity (S) was kept above 90% (Fig. 1c).

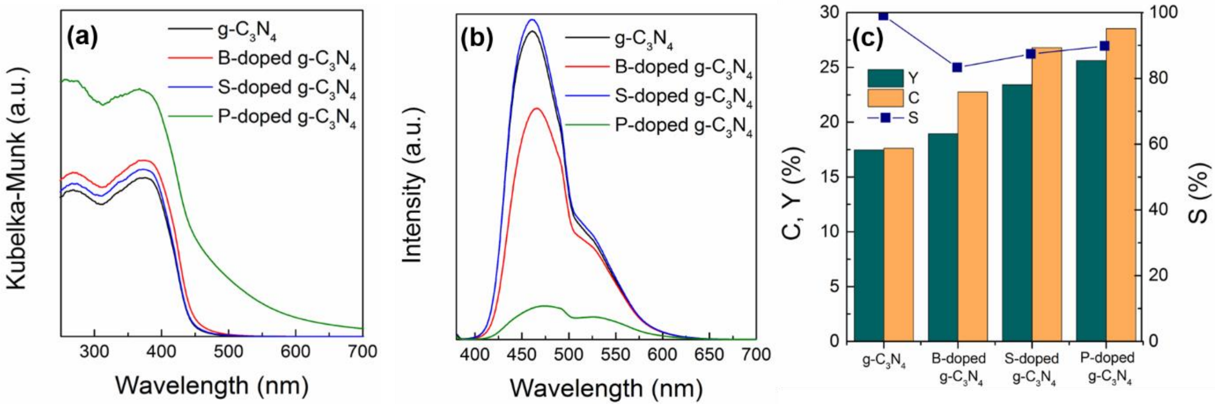

Fig.1. (a) DR UV-vis and (b) PL spectra of the g-C_3N_4 based materials. (c) BA conversion - C - and BAL yield - Y - and selectivity - S

Acknowledgments
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Greener urea-formaldehyde resins for the production of particleboards

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Urea-formaldehyde resins (UF) are the most used adhesives for the production of wood based panels [1]. Their high reactivity, good binding strength and low cost are the main reasons for their heavy use [2]. However, this type of resin presents some problems due to the emissions of formaldehyde, as it is a chemical compound classified as a human carcinogen [3] and also, because it is obtained from fossil fuels.

There are increasing concerns about the environment, and the populations health, which creates a strong demand for eco-friendly products, such as natural wood adhesives.

The goals of the research project, is to develop a greener urea-formaldehyde resin for the production of particleboards, with the incorporation of at least 30% of a natural compound. In a first approach to accomplish this goal, the incorporation of lignin in the UF resin was envisaged. Lignin is the principal byproduct of the pulp industry. In order to increase lignin reactivity, it was first hydroxymethylated. It is expected that the added reactive hydroxyl groups allow its incorporation in the urea-formaldehyde polymer.

So far, it was possible to incorporate 20% of hydroxymethylated lignin, percentage by mass, in the urea-formaldehyde adhesive.

Three-layer particleboards, 16 mm thick, were manufactured with this adhesive (amount of solid resin 6.5, in the face, and 6.1, in the core layers, based on the weight of the oven-dried particles). Boards were pressed in a laboratory hot-press controlled by computer at 190 ºC and at several pressing times, from 3 to 6 min, and then tested for several physical-mechanical properties. They presented an internal bond strength in the range of 0.44-0.50 $N.mm^{-2}$ which are above the requirements of the standard EN 312 for standard particleboards type P2 ($0.35\ N{\cdot}mm^{-2}$).

Finally, the future work will focus on a stepwise increase of the lignin content in the UF resin; optimization of the hydroxymethylation process; and reconsider lignin, on its own, as an adhesive for particleboards.

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Synthesis of the pharmaceutical precursor benzhydrol by photo-assisted processes under UV-LED irradiation

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Environmental limitations for chemical synthesis processes are driving worldwide researchers to find new facile, cost-effective and ecofriendly procedures affording high selectivity for the desired products. In this scenario new perspectives are open for the development of alternative processes for the synthesis of fine chemicals used in pharmaceutical, food and cosmetic industries [1, 2].

Benzhydrol (BH, diphenylmethanol) is an important intermediate in the pharmaceutical industry. Antihistamines, antihypertensive agents and antiallergenic agents, are the main drugs obtained from BH. Other applications are in the synthesis of agrochemicals, as a fixative in perfumery and as a terminating group in polymerizations reactions. BH is industrially produced via hydrogenation of benzophenone (BP) using sodium borohydride and metal-based catalysts. The photo-assisted production of BH from BP is an interesting alternative to the conventional production process, since it can be obtained under mild conditions of temperature and pressure and using low-cost and highly-efficient light sources for reaction activation.

In the present work, the production of BH by photochemical and photocatalytic routes has been investigated. The effect of several operation conditions such as type of solvent (Fig. 1), initial concentration of BP ($[BP]_0$), irradiance and type of catalyst has been assessed. The highest efficiency was obtained for the reaction using isopropanol as solvent and TiO_2 Evonik P25 as catalyst (86% of yield and 97% selectivity towards BH production after 60 min of UV(385nm)-LED irradiation).

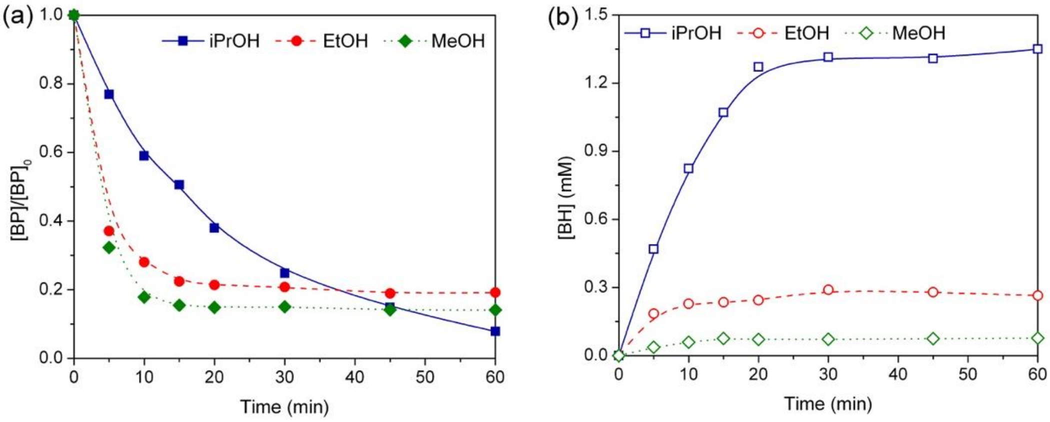

Fig.1. Effect of the type of solvent in the photochemical conversion of BP (a) into BH (b)

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Composting of phytochemical-rich plant materials: greenhouse gases emissions and evolution of total phenolic, tannins and glucosinolates compounds

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Plants produce a wide variety of secondary plant metabolites, known as phytochemicals (PCH) that are involved in the interaction of plants/pests/diseases [1]. The usage of natural substances as alternatives to synthetic chemical pesticides is appealing because they may be less persistent and have fewer non-target and toxic impacts than traditional agrochemicals [2].

Nevertheless the incorporation of fresh plants into the soil is not safe and may be toxic for crops and beneficial soil organisms. Thus, composting is considered a possible solution to reduce toxicity and simultaneously one of the most efficient processes in the improvement of soil characteristics in organic production [3]. However, the potential usage of composts as natural pesticide against plant pathogens is still poorly understood due to the lack of their phytochemical composition.

In order to assess the progress and effect of PCH-rich plant materials on composting process and at what extend this transformation process can degrade PCH, we performed a composting experiment of four agro-food wastes, namely: Broccoli, Cabbage, Chestnut and Jatropha. A windrow of 10 kg dry matter was prepared by combining each agro-food waste with wheat straw and grass to obtain an initial C/N ratio of 40. A Control treatment with straw and grass was also included. Each mixture was placed in an aerated reactor of 135 L capacity. Samples of the mixtures were collected during the course of the process and analysed to the main physicochemical properties. Total phenolic, total tannins and glucosinolates were also determined and emissions of CO_2, CH_4 and N_2O were performed in order to access the environmental impact of the process.

Results showed a significant increase on total phenolics, although with no significant differences on final composts ($p>0.05$). Relatively to total tannins, an opposite trend occurred; Chestnut presented the greater concentration in the initial mixture (7.82 ±0.98) and the lower concentration in the final compost (2.06 ±0.46). Despite of their initial content on raw materials, no glucosinolates were detected after only two days of the composting The largest emission of greenhouse gases occurred on first day. There were no significant ($p>0.05$) differences in CO_2, CH_4 and N_2O fluxes between treatments. However, relatively to cumulative emissions, Jatropha and Cabbage presented significantly higher values of CO_2 than Broccoli. No relation was observed between the phytochemical composition and the gas emissions.

In conclusion, recycling of these agro-food wastes by composting is a solution with no negative impacts on global greenhouse gas emissions. The process promoted an increase on total phenolic. On the other hand, based on the evolution of the glucosinolates content, the composts obtained are not suitable to be applied as natural pesticides, since these compounds were totally degraded during the composting process.

Agradecimentos
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Influence of deep eutectic solvent on the properties of chitosan-curcumin films

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The interest to develop biodegradable packaging materials to replace conventional petroleum-based plastics has been increasing in recent years [1]. Different types of plastics based on biopolymers (bioplastics) have been developed to replace the petroleum-derived materials. In this context, chitosan is a promising biopolymer because it is environmentally friendly and shows good film-forming properties combined with antimicrobial activity [2].

Food packaging is one of the main practical application areas of bioplastics but to make them competitive with conventional synthetic plastics, the production costs and some of their physical properties need to be improved. Regarding the use of plasticizers to improve film properties, eco-friendly deep eutectic solvents (DES), based on choline chloride have been recently used to fabricate thermo-compressed biopolymer films [3].

In this work, chitosan films with different percentages of plasticizer and dye (curcumin) were prepared and their properties were studied. The mechanical properties were studied through extension tests to evaluate the tensile strength (resistance) and elongation at break (elasticity). Sensitivity to moisture was also evaluated through water vapor permeability and water sorption isothermal measurements. SEM images were obtained in order to observe differences in the presence of plasticizer and curcumin. The results showed that increasing the DES concentration leads to an increase in the elasticity and permeability.

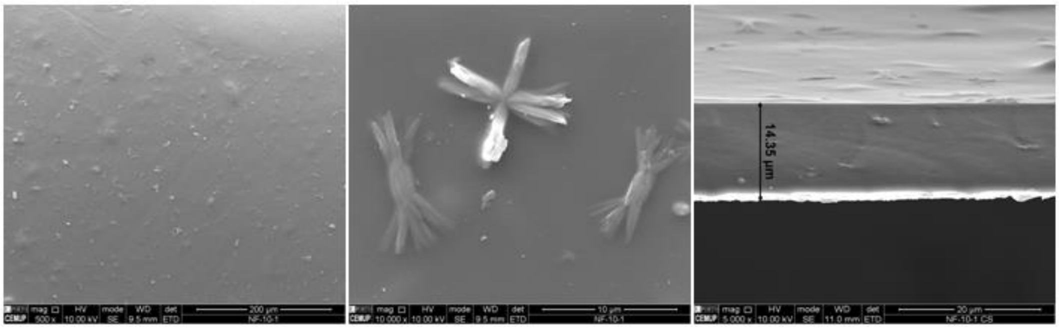

Fig.1. SEM images of chitosan-DES-Curcumin films

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Choline chloride based ionic liquid analogous as biodegradable plasticizer for chitosan biofilm production

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Despite the great advantages in using plastics on countless line productions, such as thermosealability and flexibility in thermal and mechanical properties, there are environmental, economic and political factors that progressively required the development of new biopolymer-based plastics, which can substitute, at least partially, petroleum-based plastics. One of the industrial areas with bigger interest in this replacement is food industry where the main drawback is migration of toxic elements from plastic [1]. Recently, polysaccharides derived from natural resources attracted much attention not only due to low cost but also to outstanding properties like biocompatibility, biodegradability and non-toxicity. Chitosan, obtained from deacetylation of recycled chitin of the seafood industry in coastal areas, has gained great notoriety and has been considered an active packaging material, as edible films or coatings, due to its antimicrobial activity, besides acting as a barrier against humidity, oxygen and carbon dioxide, which can be very useful in food packaging [2].

The use of plasticizers in the polymers' industry has as main objective the improvement of processability and flexibility of polymers, reducing the glass transition temperature. Plasticizers have the ability to decrease the tension of deformation, hardness, density, viscosity and electrostatic charge of a polymer, while increasing resistance to fracture and dielectric constant [3]. The compatibility between plasticizer and polymer is of major importance for effective plasticization; therefore, we previously reported a methodology based on the use of Natural Deep Eutectic Solvents (NADESs) as prospective biodegradable plasticizers [4]. These solvents fill all the principles of green chemistry, the manufacturing process is very simple, they are very versatile, cheaper and can be used for numerous applications like food industry. Herein, we describe the use of different NADESs as precursors for the production of transparent chitosan films prepared by thermocompression molding (Fig. 1). The mechanical properties, thickness, water permeability and colorimetric characteristics of the obtained biofilms were studied and discussed.

Fig.1. Chitosan film prepared by thermocompression molding using NADESs as plasticizer

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The γ-Cyclodextrin:Montelukast (1:1) adduct by co-milling and freeze-drying: a solid-state comparative study

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Inclusion compounds of cyclodextrins (CDs) are useful to alter the physico-chemical properties of pharmacologically active guests. In some cases, CDs are able to protect drugs from degradation, enhance their solubility and alter their pharmacokinetic parameters. In the present work we propose to form inclusion compounds between montelukast sodium (MLK) and γ-cyclodextrin (γ-CD), in order to improve its stability and solubility.

Inclusion compounds of MLK:γ-CD were prepared by two different procedures, lyophilization and mechanochemistry, a solvent-free method. In lyophilization a solution with an equimolar quantity of MLK and γ-CD was prepared, snap-frozen and freeze-dried, being subsequently subject to re-hydration by storage overnight in a vapor-saturated chamber. On the solvent-free method, γ-CD was subject to pre-treatment by grinding it for 60 minutes. Then, ground γ-CD was added with an equimolar quantity of MLK and this mixture was considered time zero (in minutes). The mixture was ground for 60 minutes and aliquots were collected at 5, 10, 15, 25 and 30 minutes. Samples from both procedures were analyzed by solid-state $^{13}C\{^1H\}$ CP-MAS NMR, Powder X-Ray diffraction; FT-IR spectroscopy and thermogravimetry. The powder X-ray diffractogram of the re-hydrated lyophilized adduct showed a crystalline compound with reflections different from those of MLK and γ-CD. The co-milled product revealed, using the same technique, to be an amorphous material. Moreover, the FT-IR studies of the materials obtained using both procedures showed a shift on the bands of the guest molecule. Thermogravimetry analysis revealed a modification in the degradation temperature of the inclusion compounds in relation to the physical mixture of MLK and γ-CD. Together, these results suggest that these procedures allow the formation of inclusion compounds between MLK and γ-CD.

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XXII Encontro Luso-Galego

Química

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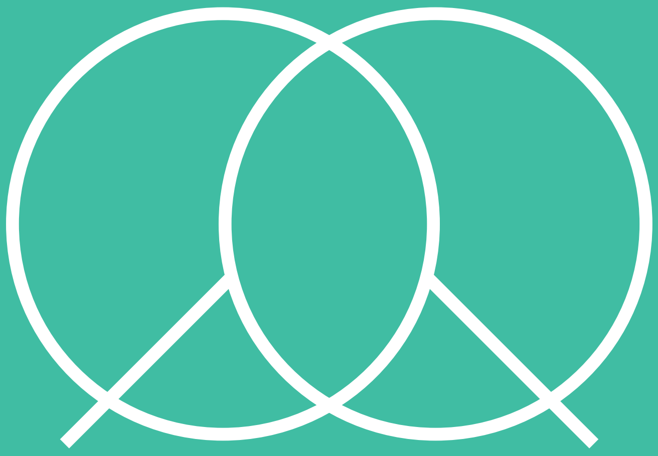

XXII Encontro Luso-Galego
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