DCE 19 3rd DOCTORAL CONGRESS IN ENGINEERING

DOCTORAL CONGRESS IN ENGINEERING

Book of Abstracts

Symposium on Environmental Engineering

U.PORTO
FEUP FACULDADE DE ENGENHARIA
UNIVERSIDADE DO PORTO

DCE 19 3rd DOCTORAL CONGRESS IN ENGINEERING

Book of Abstracts

of the

Symposium on Environmental Engineering

Editors:

Fernando Veloso Gomes

António Fiúza

Cidália Botelho

Luís Filipe Malheiros

Maria Cristina Vila

Vanessa Ramos

Porto

June 2019

This volume contains the abstracts presented at the Symposium on Environmental Engineering, within the 3rd Doctoral Congress in Engineering - DCE19, held in Porto, between June 27th and 28th, 2019.

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WELCOME

We would like to warmly welcome all participants in the Symposium on Environmental Engineering, held in the scope of the 3rd Doctoral Congress (DCE19), which is hosted at FEUP, Porto, Portugal, on the 27th and 28th of June 2019. We also like to acknowledge members of the Scientific and Organization Committees of this Symposium and DCE19.

The impressive quality of oral and poster presentations covers a wide range of extremely important subjects for Environmental Engineering: i) water and coastal resources management, ii) water quality and water treatment, iii) ecosystems and environmental processes, iv) waste management, v) renewable energy, vi) air quality.

With pleasure we welcome keynote speakers which provide a remarkable participation in this Symposium, highlighting the role and importance of a PhD in Environmental Engineering, namely, to answer Sustainable Development and Circular Economy Challenges.

Thank you all!

Porto, June 2019

Symposium Organizing Committee

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COMMITTEES

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The idea of this session was, on one hand, to provide PhD students and professionals in Environmental Engineering with the opportunity to understand the challenges of researchers and companies in topics such as the Sustainable Development and Circular Economy, and, on the other

hand, to promote the discussion about the role of PhD students and professionals and how they can collaborate to help to answer these challenges.

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- Joana Maia Dias **(*FEUP*)**
- Castorina Vieira **(*FEUP*)**
- Manuel São Simão **(*Ernesto São Simão, Lda.*)**

KEYNOTE SPEAKERS and SESSION MODERATORS

Session Moderator - Carlos Afonso Teixeira

Assistant Professor

UTAD

Environmental Engineer, Director of the Department of Biology and Environment at University of Trás-os-Montes and Alto Douro.

Scientific Researcher at CITAB – Centre for the Research and Technology of Agro-Environmental and Biological Sciences.

Member of the Working Group for the Review of the Portuguese Strategic and Sectorial Plan for Urban Waste (PERSU2020 +).

Treasurer of the Order of Engineers of Portugal.

Main sills & activities related on Waste Treatment, Environmental Risk Assessment, Solid Waste Management, Life-Cycle Assessment and Environmental Impact Risk Assessment.

Keynote Speaker - Castorina Vieira

Assistant Professor

FEUP

Castorina Silva Vieira is Assistant Professor at the Civil Engineering Department of the Faculty of Engineering of the University of Porto (FEUP), Portugal. She is Integrated Member of the research unit CONSTRUCT - Institute of R&D in Structures and Construction. She received her Ph.D degree in civil engineering from the University of Porto, Portugal, in 2008. Currently her major research interests are Sustainable Geotechnics; Management of Construction and Demolition Waste; Construction and Demolition recycled materials; Geosynthetic Reinforced Soil Structures; Soil-Geosynthetic Interaction; Seismic Behaviour of Geosynthetic Reinforced Systems.

She is member of Technical Committees of the International Geosynthetic Society and of the International Society for Soil Mechanics and Geotechnical Engineering. She is the coordinator of the Work Group on "Regulation on waste, recycled and artificial aggregates in Geotechnics" promoted by the Portuguese Geotechnical Society and member of the Portuguese Waste Technical Commission.

She is author/co-author of several scientific papers published in International Journals and Conference Proceedings - http://orcid.org/0000-0001-6328-4504

Keynote Speaker - Diana Nicolau

Environmental education technician

LIPOR – Intermunicipal Waste Management of Greater Porto

Since 2004, Diana Nicolau, is environmental education technician in the Department of Education, Communication and Marketing of LIPOR – Intermunicipal Waste Management of Greater Porto.

She has a degree in Biology and Geology by the University of Aveiro.

Throughout her career, she has been keynote speaker in several sessions in the area of Sustainability and Circular Economy.

Keynote Speaker/Session Moderator - Fernando Veloso Gomes

Full Professor

FEUP

Veloso Gomes was born in Viana do Castelo, having a degree, PhD and aggregation in Civil Engineering (Hydraulics) by FEUP, being also the holder of a Master in Ocean Engineering and Naval Architecture by University College London (1974).

Since 1997 he has been a Full Professor at FEUP, teaching subjects in the areas of Hydraulics, Water Resources and Environment. In this institution he also has several functions, namely the role of Director of the Doctoral Program in Environmental Engineering, coordinator of protocols between FEUP and Agência Portuguesa do Ambiente on Coastal Zones (1993-2013) and Director of the Instituto de Hidráulica e Recursos Hídricos (up to December 2017).

He is also a member of the CIIMAR Research Centre and is responsible for a research group.

Main scientific area of research: Coastal Engineering and Coastal Management (Coastal and Maritime Studies, Coastal Hydrodynamics and Morphodynamics, Coastal and Maritime Management, Coastal Protection and Beach Nourishment, Coastal Physical Modeling, Hydraulics).

Throughout his career, he has supervised more than 60 Master's Dissertations, 19 PhD Theses, and 6 Post-Doctoral students, having more than 369 scientific publications. He has oriented and participated in more than 100 research projects and consulting studies.

Keynote Speaker - Inês dos Santos Costa

Secretary of State for the Environment

Ministry of the Environment and Climate Action

Inês dos Santos Costa was born in Lisbon in 1979.

She graduated in Environmental Engineering from Instituto Superior Técnico in 2002, completed his Master of Engineering Policy and Technology Management and Doctorate in Environmental Engineering, both at Instituto Superior Técnico, in 2005 and 2011 respectively.

Between 2002 and 2010, she developed research work at IN + Centre for Studies in Innovation, Technology and Development Policies, especially in the areas of corporate sustainability and industrial ecology. Within these areas, she has worked on environmental policies, waste management, eco parks and industrial symbiosis. She is the author and co-author of scientific articles, books and technical documents in the field of industrial ecology. In 2006, she was a guest researcher at the Center for Industrial Ecology at Yale University in the United States.

She also worked as a senior consultant at 3Drivers - Engenharia, Inovação e Ambiente, Lda., where she developed sustainable resource management projects in various sectors, namely with managing entities of specific waste streams, energy sector, municipal councils, among others. In 2016 she was invited to work as an aid for the area of circular economy, assisting the Minister of the Environment and the Minister of Environment and Energy Transition, since 2016 and 2018, respectively, at the 21st Constitutional Government.

Keynote Speaker/Session Moderator - Joana Maia Dias

Assistant Professor

FEUP

Joana Maia Moreira Dias has a degree and a PhD in Environmental Engineering (since 2010). She is an Assistant Professor at the Department of Metallurgical and Materials Engineering at FEUP and a Senior Researcher at the Laboratory for Process Engineering, Environment, Biotechnology and Energy under the topic Environmental Sciences and Technologies. She is currently the Director of the Integrated Master in Environmental Engineering and chairman of both the Scientific Committee and the Course's Monitoring Committee. She is also a member of the FEUP Commission for Sustainability.

Her pedagogical activities are mainly dedicated to MIEA, being responsible of course units on the topic of Solid Waste Treatment Technologies and Systems. She is also currently responsible for a continuous education course in Circular Economy, taught at FEUP in partnership with FEP. In her career as a teacher she was distinguished by FEUP with two pedagogic incentive awards.

Her research activities focus on waste management and treatment and biofuels production. She has an H-index of 13 and features over 70 publications, including book chapters, articles in international journals and in conference proceedings, having supervised dozens of MSc theses and being also supervisor of PhD thesis in the areas of waste and by-product management and biofuels production, in direct collaboration with several companies.

She was a member of the scientific committee and organizer of several national and international conferences in the area of waste management, environment and sustainability. She is also a representative appointed by FEUP in various working groups in national institutions on topics related to her scientific and pedagogical activities.

She has participated in several research projects and also has an active contribution in conducting consultancy studies for national entities in the environmental and waste areas.

Keynote Speaker/Session Moderator - Joaquim Poças Martins

Associate Professor

FEUP

Born in Vila Nova de Gaia in 1953, Joaquim Poças Martins holds a degree and a PhD in Civil Engineering from the University of Porto, a Master of Science and a PhD from the University of Newcastle upon Tyne, England and a degree in Business Management, from IESE.

He is an Associate Professor with Aggregation of Civil Engineering and Environmental Engineering at the Faculty of Engineering of the University of Porto, where he continues his academic career since 1974.

He is President of the Ordem dos Engenheiros of North Region of Portugal.

He was the President of the setting-up committee of Águas do Douro e Paiva and Águas do Cávado and Director of the Project of Integrated Management of Northern Water Resources (1989-93).

He was the Chairman of the Board of AdP - Águas de Portugal and EPAL (2004-2005), Águas do Douro e Paiva (2004-2006) and Águas de Gaia (1997-2004) and led the technical restructuring process of the company Águas do Porto (2007-2013).

He is the author of two books and one hundred scientific, technical, pedagogical and business publications.

In September 2014, he published the book Management of Change in Water Companies: in Search of Sustainability and Excellence.

He has worked as an international consultant for the World Bank, European Commission and NATO in South America, Middle East, Eastern Europe and Africa.

Keynote Speaker - Manuel São Simão

CEO

Ernesto São Simão, Lda.~

Manuel São Simão holds a degree in Mechanical Engineering from the Faculty of Engineering of the University of Porto, since 1978. Since then, he fulfilled his wish to continue with the family business, being, today, the CEO of the company Ernesto São Simão.

Keynote Speaker - Márcia Pereira

Startup Founder

UPTEC

Mom of two little girls, energy saver addict and renewables enthusiast, CEO and Co-Founder of Bandora, PhD candidate from MIT Portugal in Sustainable Energy Systems from FEUP and e-learner of Data Science Program from Harvard.

Marcia has a degree in Mechanical Engineer, Applied Thermodynamics branch, from University of Lisbon. She started to work in several sectors of the market, public and private, small and big corporations, with special emphasis of ADENE – National Energy Agency and GLINTT, where she performed energy efficiency projects in commercial, residential and industrial buildings. She performed as well renewable projects like a Concentrated Photovoltaic project, implemented in Évora with 1MW of peak power; the development of a micro hydropower systems, with 4kW of peak power, connected to the grid in Leiria and a 40kW Photovoltaic stand-alone project implemented in Mozambique, in order to supply energy to a Maternity and local Portuguese speaking radio.

With the pretension of starting her own business, she founded Bandora, a startup that empowers autonomous buildings with Artificial Intelligence, recently with presence in USA.

At the same time, eleven years before attending the first edition of the MIT Portugal Program, Marcia felt the need to conclude what was left in the past, but now in University of Porto.

Session Moderator - Maria Cristina Vila

Assistant Professor

FEUP

Assistant Professor at the Mining Engineering Department of the Faculty of Engineering of University of Porto (FEUP). Director of the MSc Program in Mining and Geo-environmental Engineering. Assistant Director of the MSc Program in Environmental Engineering. Member of the Scientific Committee of the PhD Program in Environmental Engineering.

Long experience in engineering education, with emphasis on “Aquifer and Soils Rehabilitation” and “Quantitative Environmental Risk Analysis”. Research activities mostly oriented to remediation of contaminated soils (assessment and applicability of technologies, mathematical modeling of chemical, physical and biological processes); mining environmental impacts (storage, disposal and management of mine wastes and waters) and biologic processes applied to soils remediation and to metal recovery from mineral raw materials (bioleaching).

ORAL PRESENTATIONS

Sewage sludge-based fertilizers applied to soils, a new path to contamination?

Sara Ramos[1], Vera Homem[1], Lúcia Santos[1]

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Abstract

The application of a sewage sludge-based fertilizer in an agricultural soil proved that there is a considerable accumulation of synthetic musk compounds (SMCs) and ultraviolet filters (UVFs), both classes of emerging contaminants, in the soil.

The analysis of soil samples was possible due to the optimization of a Quick, Easy, Cheap, Effective, Rugged and Safe (QuEChERS) methodology followed by gas chromatography – triple quadrupole mass spectrometry (GC-MS/MS). This methodology was successfully validated for the analysis of 13 SMCs and 6 UVFs.

The analysed natural soils show low levels of the target compounds (usually below 100 ng g-1 dw), whereas both amended-soil and sewage sludge-based fertilizer have concentrations between 1 and 17 µg g-1 dw, respectively, posing a major threat to agricultural fields.

Keywords: Sewage sludge-based fertilizers, soils contamination, waste management, emerging contaminants.

1. Introduction

Last year, in the first semester, the production of sewage sludge in Portugal was estimated to be around 261,965 ton as a result of water treatment in wastewater treatment plants (WWTPs). Out of this amount, 1,193 tons were incinerated, 1,047 incorporated in landfills, 128,088 tons transformed into treated compost and applied in in agricultural fields as fertilizers and 131,231 tons had no destination clearly identified (1). Personal care products (PCPs) are considered emerging pollutants due to their massive utilization, continuous input and persistence in the environment. So far, conventional WWTPs are not completely efficient in their removal. Therefore, parent compounds and degradation products are discharged through effluents into surface waters (mostly hydrophilic compounds) or sorb into sludge (lipophilic ones) (2,3). Within PCPs, synthetic musks compounds (SMCs) (fragrance fixatives) and UV-filters (UVFs) (sunscreen active agents) are examples of compounds commonly used in cosmetics and toiletries (4). They have already been detected in wastewater effluents and sewage sludge and their transfer to soils has also been described (5).

So, the main objectives of this work were to validate a fast, easy, rugged and green analytical methodology to analyze 6 UVFs and 13 SMCs from soils and study the presence of those contaminants in soils with different origins, including amended-soils with sewage sludge-based fertilizers. Most of these compounds were never studied before and they may pose a threat due to their potential persistence in the environment, ability to bioaccumulate and biomagnify in biota trophic networks and due to their estrogenic potential.

2. Materials and Methods

Soil samples were collected near a beach, on agricultural land, in a garden and in an industrial area (Matosinhos), a school yard (Porto) and an agricultural soil near a construction site (Vila Real). Samples were sieved through a 2 mm sieve opening (mesh n. º 10), thoroughly mixed and kept frozen (-20 °C) in glass containers until analysis. The fertilizer used in this study was bought in a local agricultural cooperative. The organic carbon (OC) was determined in a PrimacsSNC Carbon-Nitrogen/Protein Analyzer from Skalar (Breda, The Netherlands) and the particle size distributions for determination of the clay content were measured with the COULTER LS 230 laser diffraction analyzer from Beckman (West Hialeah, USA). Extraction was performed by a Quick, Easy, Cheap,

Effective, Rugged and Safe (QuEChERS) methodology assisted by ultrasounds, using a mixture of acetone/hexane (1:1, v/v) as extraction solvent, MgSO4 and NaCl in the partitioning step and C18 in the dispersive solid-phase extraction step. The instrumental analysis was performed with a GC–MS/MS system from Bruker (Massachusetts, EUA).

3. Discussion

This methodology was successfully validated for the analysis of 13 SMCs and 6 UVFs. Recoveries of the target compounds ranged from 81% (traseolide) to 122% (musk moskene), with good precision, with relative standard deviation less than 10%. Quantification limits ranged between 0.03 and 46 ng g-1 dw.

School yard soil presented the higher number of compounds (8 out of 19), with a total concentration of 196 ng g-1 dw of UVFs and SMCs (benzophenone was the predominant compound). The quantity of the target compounds increased a lot in the amended-soil for all compounds, especially for galaxolide (341 ng g-1 dw), drometrizole (56 ng g-1 dw) and even 4-methylbenzylidene camphor (14 ng g-1 dw).

4. Conclusions

A QuEChERS methodology was successfully adapted and validated for the extraction of 13 SMCs and 6 UVFs from soils. The analysis of real samples showed that soils from different areas, present different levels of UVFs and SMCs. Benzophenone was the compound detected at higher concentrations (2.8-158 ng g-1 dw). Regarding the studies with the amended-soil, UVFs and SMCs were found in concentrations ranging from 1.04 and 341 ng g-1 dw. The analysis to the amended-soil showed that there is an accumulation potential.

Acknowledgments

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Mechanical damage induced by incinerator bottom ash on geosynthetics: a comparison with other aggregates

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Abstract
The adoption of more sustainable solutions in the different industrial activities cannot be postponed. Aiming the preservation of the resources of planet Earth, actions including reuse, reduce and recycling of waste should be a priority. Nevertheless, finding solutions to manage the waste that is generated in considerable amounts, such as incinerator bottom ash, is not a simple task. Over the recent years, it has been studied the possibility of using incinerator bottom ash in engineering applications, such as road construction, in which this residue can be in contact with geosynthetics. This work aimed to analyse the mechanical damage caused by incinerator bottom ash on geosynthetics, in comparison with other aggregates. The attained results allow considering the hypothesis of using this residue as filling material, in replacement of conventional aggregates.

Keywords: Incinerator bottom ash, waste valorisation, geosynthetics, mechanical damage.

1. Introduction

The sustainability of planet Earth depends strongly on the effectiveness of the strategies that are being implemented in terms of waste management. Regarding municipal waste, the goals are clearly defined in the Directive 2008/98/EC: efforts should be carried out in order to boost the reuse and recycling of this residue to a minimum of 55% by weight up to 2025. To achieve this target, solutions involving the valorisation of municipal solid waste must be developed.

Incineration is a procedure used to treat municipal solid waste. This procedure leads to the production of significant amounts of a residue known as incinerator bottom ash (IBA), which has been subject of several studies over the last years. In engineering domain, IBA showed potential to be used as raw material for developing alternative cementitious materials and as recycled aggregate in road construction and for manufacturing concrete (Xuan, Tang, and Poon 2018). If IBA is employed as filling material, it may be in contact with geosynthetics.

Geosynthetics are construction materials used in a wide range of engineering applications in which they can perform different functions such as protection, separation, filtration, drainage, reinforcement or fluid barrier. These are interesting materials by virtue of their high efficiency, ease of application and no need for skilled labour force. However, in geotechnical applications, the placement and compaction of filling materials can induce mechanical damage on the geosynthetics, which may lead to unwanted changes on their original properties. Therefore, when exploring the possibility of using IBA as filling material, it is essential to investigate if this recycled aggregate does not cause a higher level of mechanical damage on geosynthetics, in comparison with the natural aggregates commonly used.

2. Materials and methods

Mechanical damage under repeated loading tests (hereinafter MD tests) according to EN ISO 10722:2007 were performed with different geosynthetics (materials with different structures and/or masses per unit area). These tests consisted of placing the geosynthetics between two layers of an aggregate and submitting them to a cyclic loading between 5 and 500 kPa at a frequency of 1 Hz for 200 cycles. The aggregates used in the MD tests included IBA and, for comparison purposes,

different natural aggregates (sand 0/4, gravel 4/8 and tout-venant) and corundum (standard synthetic aggregate). The damage suffered by the geosynthetics (in the MD tests) was evaluated by monitoring changes on their short-term tensile and puncture behaviours.

3. Results and discussion

The MD tests with IBA did not provoke very pronounced changes in the tensile and puncture properties of the geosynthetics. Compared to the different natural aggregates and corundum, IBA tended to induce less damage (lower degradation of tensile and puncture properties) to the geosynthetics. In terms of mechanical damage induced to geosynthetics, this opens good perspectives for the use of IBA in geotechnical works as a viable alternative to filling materials obtained from natural sources. However, before such use, it is also important to evaluate the effect of IBA on the long-term behaviour of the geosynthetics. In addition, the environmental impacts of IBA must be also addressed. The outcomes of these investigations will be a key step to assess the feasibility of using IBA in engineering applications, promoting its valorisation.

4. Conclusions

The effect of IBA on the short-term mechanical behaviour of the geosynthetics tended to be lower than the effects of the natural and standard aggregates. This way, IBA showed potential to be used as filling material (by replacing natural aggregates) in contact with geosynthetics in civil engineering applications, thereby contributing to the adoption of more environmentally friendly solutions in construction.

Acknowledgments

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Physicochemical characterization of dried vs. freeze-dried Marine Macroalgae Waste aiming further recovery

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Abstract

Marine macroalgae waste biomass was collected in a beach at Northern Portugal and further characterized concerning the main physicochemical properties (moisture, ash, nitrogen, proteins, lipids and total carbohydrates), using two different initial biomass conditions: dried (MMW1) and freeze-dried (MMW2). *Saccorhiza polyschides* (brown algae) was the most represented species in the collected biomass. MMW1 had a residual moisture of 1.34 wt.% and MMW2 of 8.2 wt.%. The biomass presented low lipid content (0.13 wt.% for MMW1 and 0.40 wt.% for MMW2), high carbohydrate (MMW1: 39.3wt.%; MMW2: 41.1 wt.%) and protein content (MMW1: 9.6 wt.%; MMW2: 9.8 wt.%) and a very high ash content (50.8 wt.% for MMW1 and 48.7 wt.% for MMW2) in agreement with reported values in the literature. Taking into account the differences found between both products, lyophilization is not justified aiming its further recovery.

Keywords: Waste, Marine Macroalgae, Saccorhiza polyschides.

1. Introduction

The increase of Marine Macroalgae Waste (MMW) at coastal regions, like Portugal, is a reality, being associated with tide events and natural biomass accumulation (Lemesle et al. 2015). The lack of appropriate management of MMW, which are mostly left unmanaged or sent to landfills, leads to environmental impacts, health problems, coastal degradation and loss of renewable resources (Barbot et al. 2016). Marine Macroalgae (MM), classified into three main groups (brown, green, red), include in their physicochemical composition polysaccharides (4 - 76 %), proteins (5 - 30 %), minerals/ash (7 - 38 %), lipids (1 - 5%) and a high amount of water (80 - 90 %) (Rodrigues et al. 2015, Sudhakar et al. 2018). The preferential applications of MM (human food, cosmetics and pharmaceutical areas) are considered incompatible with the use of waste biomass, for safety reasons (Rodrigues et al. 2015). In agreement, the aim of the present study was to perform a physicochemical characterization of MMW collected at Northern Portugal, under different biomass initial conditions (dried and freeze-dried), in order to evaluate the influence on the composition of MMW and further recovery of this resource.

2. Materials and Methods

MMW was collected from Marbelo beach (Vila Nova de Gaia municipality) in july 2018 and directly stored in the freezer (-20 °C) till use. Before analysis, MMW1 was oven dried at 105 ± 2 °C during 24 h, and MMW2 was freeze-dried (Labconco freezone 2.5 plus). Both MMW were ground to < 1 mm in a laboratory mill (Retsch GM200) before characterization.

The following physicochemical parameters were determined: residual moisture, ash, nitrogen, proteins, total lipids and carbohydrates. The ash content was determined according to AOAC (2012) in a furnace by sample calcination at 500 °C up to constant weight. The nitrogen content was obtained using the Kjeldahl method (AOAC, 2012). The protein content was obtained following Angell et al. (2016), using a nitrogen-to-protein conversion factor of 5, instead of the usual 6.25. The total lipids were determined by the Soxhlet method and the total carbohydrates calculated by difference considering the results obtained for lipids, ash and protein. All determinations were

performed at least in triplicate and the results were expressed in dry weight and corrected for residual moisture (measured in an infrared balance, Kern DBS).

3. Results and Discussion

The collected MMW was mainly composed by Saccorhiza polyschides (brown seaweed). Table 1 shows the results of the oven dried (MMW1) as well as the freeze-dried (MMW2) biomass.

Table 1: Characterization of Marine Macroalgae Waste (oven dried and freeze-dried, < 1mm)

Parameter	MMW1 ($\bar{x}$ ± s)	MMW2 ($\bar{x}$ ± s)
Moisture (wt.%)	1.34 ± 0.04	8.20 ± 0.5
Ash (wt.%)	50.8 ± 0.7	48.7 ± 0.1
Lipids (wt.%)	0.13 ± 0.02	0.40 ± 0.02
Nitrogen (wt.%)	1.9 ± 0.1	1.96 ± 0.04
Protein (wt.%)	9.6 ± 0.7	9.8 ± 0.2
Carbohydrates (wt.%)	39.3 ± 0.9	41.1 ± 0.2

Results are expressed on dry basis and correspond to the sample mean value ± standard deviation.

The samples ash content, in both cases, is similar to the reported values in the literature, which are in the range of 27 to 50 wt.% for Saccorhiza polyschides (Jensen et al. 1985, Rodrigues et al. 2015, Rupérez 2002, Sánchez-Machado et al. 2004).

The nitrogen content obtained in the present study is also in agreement with those reported by Michalak et al. (2017), for Baltic seaweeds (around 1.9 wt.%). The protein contents are also in the range of the values reported in the literature by Sánchez-Machado et al. (2004) for seaweeds of the Northwest Iberian Coast (around 13 wt.%) and Rodrigues et al. (2015) for macroalgae from Buarcos Bay (around 14 wt.%). Garcia et al. (2016) evaluated Saccorhiza polyschides samples collected in the Barbate Estuary (Spain) which presented a protein value close to 7 wt.%. Vieira et al. (2018) also studied samples from North-Central coast of Portugal and obtained a protein value of 12.4 wt.%. The differences between the values obtained and those in the literature should relate with the use of different nitrogen-to-protein conversion factors.

The samples have low lipid contents (less than 1 wt.%), as expected. Maceiras et al. (2016) showed a lipid content of 0.4 wt.% in Saccorhiza polyschides from Galician beaches. Also, Sánchez-Machado et al. (2004) and Rodrigues et al. (2015) obtained low lipid contents in their studies, namely 0.7 wt.% and 1.1 wt.%.

The values for total carbohydrates are in the ranges reported by Rodrigues et al. (2015), being around 46 wt.%, and Sudhakar et al. (2018) which reported values between 30 and 50 wt.% for brown seaweeds.

The presented results concerning to MMW1 and MMW2 are in the range of the reported values for such biomass, as stated. Variations between the results of both materials are in general less than 5 %, except for the lipids content, where the difference is more expressive due to the low content of this component. Taking into account the heterogeneous nature of these materials, such differences are not considered relevant, since results still fall in the expected range. Accordingly, lyophilisation as a sample preparation treatment does not seem to be justifiable aiming further recovery.

4. Conclusion

The physicochemical characteristics of the MMW analysed in the present study are in agreement with the values reported in the literature for Saccorhiza polyschides, the predominant seaweed in the analysed biomass.

No relevant differences were found when comparing the biomass initially dried or freeze-dried taking into account the heterogeneous nature of such type of material. In agreement, considering the main parameters evaluated, samples lyophilisation is not justified for further recovery of this material.

Acknowledgments

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Presence of metals in crumb rubber used in synthetic turf fields

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Abstract

Different digestion conditions have been tested to allow the identification and quantification of metals in crumb rubber obtained by a mechanical recycling process of tires (Zanetti et al. 2015; Menichini et al. 2011). In this work, crumb rubber samples were subjected to a digestion process (with four different solvents) assisted by a microwave unit before metal quantification in an inductively coupled plasma equipment with an optical emission spectrometer (ICP-OES). A total of 31 elements (heavy metals and macro-elements) were targeted. The first digestion was done with a mixture of perchloric and nitric acid; the second with hydrogen peroxide and nitric acid; the third with pure nitric acid and the fourth with *aqua regia*. The main goal of this study is to understand which digestion process is more efficient (complete sample digestion, more elements identified, etc.) and to evaluate the overall concentration of metals.

1. Introduction

End-of-life tires (ELTs) can be recycled and reduced to granules of different sizes ("crumb rubber") (Zanetti et al. 2015). This material can be used in a number of applications, including as infill material in turfs of synthetic football fields (Watterson 2017). It is known that tires have commonly in their composition natural or synthetic rubber that include polycyclic aromatic hydrocarbons, volatile organic chemicals, nitrosamines, benzothiazoles, latex and heavy metals (Bocca et al. 2009). Because of their high degree of toxicity, zinc, lead and cadmium rank among the priority metals that are of public health importance. These metals, and others found in tires with high concentrations such as barium and iron, for example, are also present in crumb rubber. For this reason, it is necessary to perform an environmental risk assessment to evaluate its levels and its toxicity degree, firstly in granulates and in the future in leachate and air (Marsili et al. 2014). In the studies regarding crumb rubber, zinc levels were the highest (Marsili et al. 2014), which is expected since zinc oxide is used as an activator in the rubber vulcanization process (Bocca et al. 2009). Different mixtures of acids were used in sample digestion in order to identify and quantify metals in crumb rubber. Preliminary studies performed in this work demonstrated that the combination between perchloric and nitric acid seems to provide the best digestion results, with clear solutions. This mixture of acids was reported by Zanetti et al. (2015) in crumb rubber digestion used in paving applications.

2. Materials and Methods

A microwave-assisted acid digestion was done in order to have a total sample (crumb rubber) decomposition. All chemicals were of analytical grade. Four reagent combinations were done to reach the highest recoveries for the target elements. A representative sample of 0.1 g was digested in: a) 9 mL concentrated nitric acid and 3 mL perchloric acid; b) 2 mL of hydrogen peroxide and 3 mL of nitric acid; c) 9 mL of hydrochloric acid and 3 mL of nitric acid; d) 10 mL of nitric acid based on Zanetti et al. (2015), Marsili et al. (2014), Zhang et al. (2008) and Application Note HPR-PL-14 - Rubber (2019), respectively. The sample and acids were placed in the same inert polymeric microwave vessels and those were sealed and heated in the microwave system (MA079 StartD from Milestone, Sorisole, Italy). A digestion is required to allow specific reactions and in this case the process reached 200 ± 5 ºC in 15 minutes and remained at 200 ± 5 ºC for other 15 minutes for the completion of specific reactions. The highest pressure involved during the reaction was 45 bar.

However, the equipment adjusts the pressure development during the acid digestion as a result of the temperature employed and the possible formation of gaseous substances.
After cooling down at room temperature (during at least 1 hour), the vessel contents were filtered with 0.20 µm celulose GD/X syringe filters from Whatman (Pittsburgh, PA, USA) and diluted with ultrapure water to a final volume of 100 mL. Finally, all samples were analyzed by ICP with an optical emission spectrometer (ICP–OES) (ICAP 7400 from ThermoScientific, Waltham, MA, USA). All solutions and stock were prepared immediately before being used. Ultrapure water obtained from a Millipore water purification system (18 MΩ, Milli-Q, Millipore, Molsheim, France) was used in all assays.

3. Results and Discussion

Regarding the performance of the microwave-assisted digestion, Table 1 shows the final aspect of the different acid digestions mentioned above. The goal of every digestion process is the complete decomposition of the matrix and consequent dissolution of the analytes. Under this assumption, the acids used in the 4th process were unable to digest the sample because the particles aggregated. It is possible to observe that the clearest solution in the 1st process being the most completed digestion. Although the 2nd and the 3rd process have small particles inside, they were considered to metal quantification by ICP-OES, as well as the first process.
Samples from the 1st, 2nd and 3rd digestion processes were analyzed for a total of 31 elements. Some of them have been emphasized concerning their higher presence in crumb rubber and, by decreasing order of concentration, for the first process was revealed that Zn>Fe>K>Al>Mg>Co. In the second, concentrations were Zn>Al>Fe>K>Mg>Co,very similar to the third one (Zn>Al>Fe>K>Mg>Co). Hence the six more predominant elements remained the same in all processes, with Zn as the prevailing element, in line with literature (Marsili et al. 2014). Some studies revealed that after Zn, Ba and Fe are the most frequent elements presented (Menichini et al. 2011). However, in the current study Al, K, Mg and Co showed higher amounts comparing with Ba. Other elements such lead and cadmium, for example, are more dangerous for public health but there is no legislation in Europe that specifically applies to rubber granulate.

Table 2. Illustration of digestion processes tested in crumb rubber samples.

1st process	2nd process	3rd process	4th process
3 mL $HClO_4$ and 9 mL HNO_3	2 mL H_2O_2 and 8 mL HNO_3	10 mL HNO_3	9 mL HCl and 3 mL HNO_3
			

4. Conclusions

The presence of metals in crumb rubber used as infill in synthetic turf of sports facilities can be a problem due to the transfer into the environment and organisms. Concerning this complex matrix, it can be noticed that the most present metals are the heavy ones, in particular zinc. Other heavy metals (namely lead and cadmium) appear in lower levels but could also be very dangerous. With this work it was possible to make a complete screening of metals in crumb rubber and further studies intend to make the risk assessment to understand the effect of these metals on the environment and the users of the targeted facilities.

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Low-cost portable sensors for air quality monitoring

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Abstract

Air pollution is one of the major health concerns globally and low-cost sensors provide a unique solution to monitor it. This work aimed to perform a SWOT analysis to observe the pros and cons of using low-cost sensors for air quality monitoring. The pros include their low-cost, low maintenance requirement, flexibility, and ease of usage, however they can have weak reliability and reproducibility, cross-sensitivity and calibration issues. Data accuracy due to improper characterization (grey literature), and data violation can be major threats associated with this technology. But these threats are greatly offset as they provide diverse application opportunities by enabling community driven science, personal exposure monitoring and scalability of pollutant detection.

Keywords: low-cost sensors, air quality monitoring, metal oxide semiconductor, electrochemical sensor, PM

1. Introduction

Exposure to polluted indoor and outdoor air causes around 7 million premature deaths every year (WHO, 2019). Traditional approach of air pollution monitoring uses high cost, complex, stationary devices which puts a limit on the data access, application flexibility and overall budget and low-cost portable sensors give the opportunity of changing this status quo (Snyder et al. 2013). However, existing scientific information published regarding the usage of low-cost sensors for air quality monitoring, i.e., both gaseous pollutants and particulate matter (PM), is sparse. The main objective of this work was to perform a SWOT analysis on the practical usage of low-cost sensors for air quality monitoring, both indoors and outdoors.

2. Materials and Methods

An up-to-date analysis (from 2010) was performed reviewing the most suitable publications by searching in ScienceDirect and MDPI databases. The following exclusion criteria were applied: i) research papers consisting of only temperature and humidity measurements were excluded; and ii) commercially available devices with no scientific proceedings were excluded.

3. Results and Discussion

Low-cost air quality sensors can be used to economically analyse air quality in near real time. Some strengths are the user-friendly interface and the low maintenance requirement making them an easy-to-use and convenient device (Castell et al. 2013). Scalability of pollutant detection is also an advantage by complementing the already existing fixed sensor networks. However, low-cost sensors have associated weaknesses. Cheap devices can be accompanied by design compromises making their readings less trustworthy and data less reliable. Low-cost gas sensors usually suffer from high cross-sensitivity and interference from other pollutants. They were also found to be sensitive to changes in ambient conditions and suffer from a drift in calibration over a period of time (Peterson et al. 2017).. The challenge associated with light scattering PM sensors is their limit of detection (LOD) of approximately 0.3 µm below which particles do not scatter enough light (Koehler and Peters 2015).

There is room for a plethora of development opportunities associated with these sensors. Improvement of calibration curves with regression modelling techniques or artificial neural networks is a very attractive option. This can address the issue of both the meteorological impact and cross-sensitivity. Although creating controlled conditions for calibration can help in most calibrations, with low-cost sensors that has been showed to be worthless, because in the field they

show different behaviours. Cross-sensitivity can be compensated by using a sensor array having multiple gas-sensing technologies, thus, accounting for any cross-interference of the gases by communication between the sensors. This would need to be accompanied with regular recalibration in case of any baseline drift over the deployment period due to a non-target gas being deposited on the sensing layer. Due to their portability, it could also be possible to conduct personal pollutant monitoring. Post-monitoring, one can choose less polluted routes while commuting. The use of these low-cost sensors make room for community-driven science, i.e., people can contribute by collecting air quality data.

With increased communication of data from community spaces and homes, the **threat** of data violation arises. Further, partial or false information provided by vendors regarding the modules including calibration drift, signal to noise ratio, or the stability for either MOS or EC sensors can hamper the practical usage of such sensors. This improper characterization and the use of grey literature for calibrating these devices can also be a major issue with increase of use of these devices. Preparing performance guidelines by developing standardized assessment tests can be a potential solution to the challenge of low data accuracy and the partial/false information by the vendors.

4. Conclusions

If there is a regulation in place for selling these sensors only after standardized assessments, it would greatly increase the reliability of using these sensors. The onus of carrying out these development opportunities should be on the manufacturer and peer reviewed literature to scientifically test and validate the practical real world usage of low-cost sensors for air quality monitoring. Hence, further research in this area is crucial.

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Biomass gasification: predicting syngas uses according to quality index

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Abstract

Biomass is considered a carbon-neutral feedstock, so it may constitute an option to fossil fuels in several sectors (Chen, Lin et al. 2015, Hosseini, Wahid et al. 2015). Thermochemical methods decompose carbonaceous materials, converting the initial feedstock into energy simultaneously reducing or eliminating the disposal of these materials (Balat 2008). Gasification is one of the most widely used thermochemical methods as it is clean and shows high efficiency, producing a commercial gas (syngas) composed of CO, CO2, H2 and light hydrocarbons (Siedlecki and de Jong 2011). Syngas may be further utilized in the electricity, transports and chemical sector (Couto, Silva et al. 2015). Therefore, optimizing gasification operational conditions allows to fine-tune the composition of the produced syngas, ultimately enabling the recommendation of its subsequent uses.

To the best of the authors' knowledge, there are scarce reports directly relating syngas properties with its future applications. In the present work, a parametric study of the gasification of different biomass streams was performed and syngas quality indicators were calculated. Subsequently, the potential uses of the syngas produced were suggested. The gasification of miscanthus (M), peach stone (PS) and a blend of polyethylene and vine pruning (PET-VP) was modelled. Temperature (T), equivalence ratio (ER) and steam to biomass ratio (SBR) were varied, while syngas lower heating value (LHV) and cold gas efficiency (CGE) were assessed. Figure 1 (a-c) depicts the results for the parametric study.

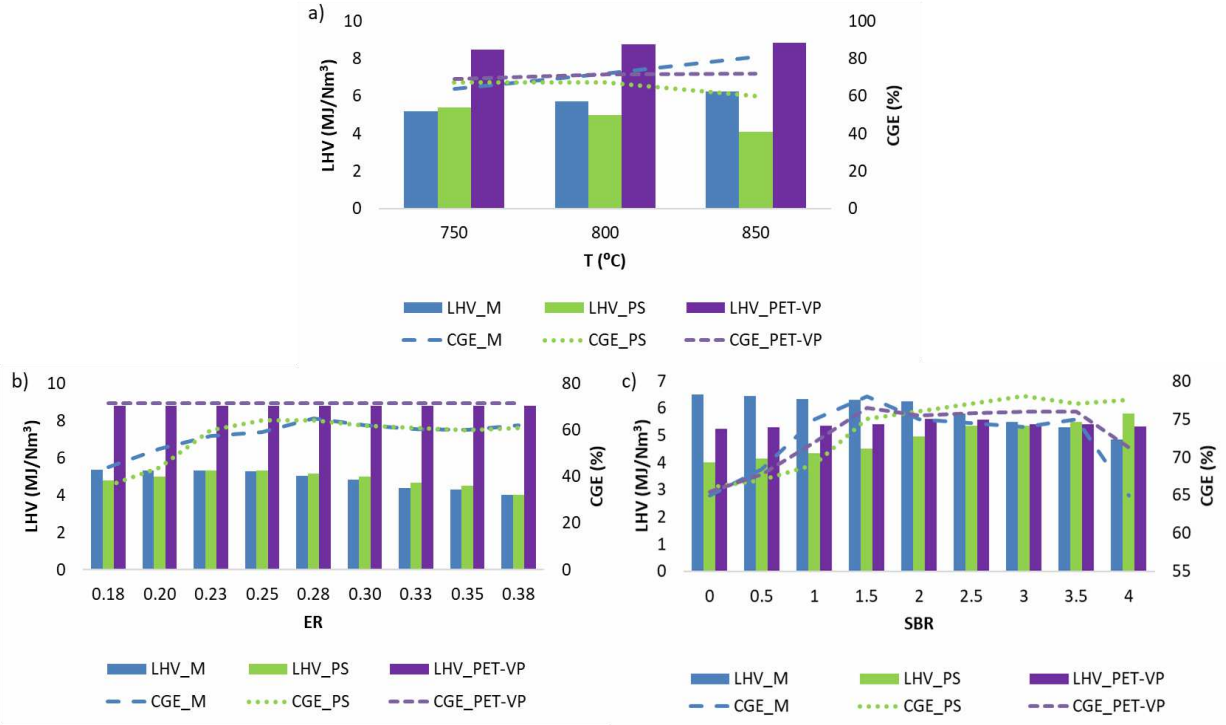

Figure 1: Parametric study for syngas LHV and CGE when varying T (a), ER (b) and SBR (c) respectively.

Improved calorific contents were seen for higher temperatures, lower ER and moderate SBR values. Therefore, using the optimized conditions for each feedstock, it was possible to achieve high-quality

syngas and calculate the quality indicators, presented in Table 1.

Table 1: Syngas quality indicators achieved under optimized experimental conditions.

Quality Indicators	**H_2/CO**	**H_2+CO (%)**	**LHV (MJ/Nm^3)**
Miscanthus	1.00	34.0	6.45
Peach stone	0.77	31.0	5.80
PET-vine pruning	0.86	79.7	10.9

The values attained enabled syngas potential applications to be inferred. Hence, PET-vine pruning blend depicted the highest LHV and H2+CO > 80%, enabling the production of fuel gas or chemicals, respectively (De Filippis, Borgianni et al. 2004, Couto, Silva et al. 2015). Miscanthus and peach stone afforded adequate syngas for the production of synthetic fuels, due to suitable H2/CO ratios (De Filippis, Borgianni et al. 2004). This work suggests that biomass and its mixtures with synthetic wastes may be utilized to replace fossil fuels in some applications, supporting the growing market of renewable energy, ultimately contributing to
achieve the goals professed by circular economy.

Keywords: biomass, gasification, syngas, quality index

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Exposure to air pollution while exercising: case study of Oporto city

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Abstract
Physical exercise improves the health of the individuals. In cities, it is common to exercise outdoors as it is the most accessible form of physical activity. As exercising in polluted areas can diminish or even outweigh the benefits of physical activity, this work aims to identify the relevant pollutants that individuals are subjected to while exercising and to assess the respective exposure. The study was conducted for Oporto city. The data treatment of the available information on pollution levels showed that traffic related pollutants, namely NO_2, $PM_{2.5}$ and PM_{10} were the most relevant ones. The data treatment evidenced that the frequency of the available data on pollution levels decreased between years 2015 to 2017, for some of the pollutants for more than 80%.

Keywords: physical exercise, air pollution, exposure

1. Introduction

Various national and international organizations recommend conducting aerobic activities, such as exercising on regular basis since it improves the overall health and well-being of the individuals. The benefits that can be obtained from physical activities may vary on environmental factors and on the place where exercise is carried out. In cities, it is widely common for inhabitants to exercise outdoors as it is one of the most accessible forms of physical activities. However, in urban areas with ambient air pollution, outdoor exercising may lead to individuals' increased exposure (on short-term) to high levels of air pollutants (Pasqua, 2018). Subjects exercising in polluted areas are then at a higher risk of adverse health outcomes due to an exercise-induced amplification in respiratory uptake, lung deposition and toxicity of inhaled pollutants (Sharman, 2004). This work aimed to estimate exposure to air pollution while exercising with a specific objective to evaluate the available data.

2. Materials and Methods

QualAr (online database of the Portuguese Environment Agency) was used to identify the available data for the exposure assessment (Qualar, 2019). Data treatment consisted of identification of the possible places, pollutants, and analysis of the data (in terms of availability) and then calculation of the average concentrations of the pollutants.

3. Discussion

The identification of the pollutants that are relevant to this work was based on the characteristics of air pollution in Oporto, relevant emissions sources and the respective health effects. In Oporto, traffic emissions are among the major sources (Slezakova et al., 2011), hence $PM_{2.5}$, PM_{10} and NO_2 were identified as the pollutants for this study.

Two monitoring stations in Oporto were identified with two different types of influences: background and traffic. Analysis of the available data showed that different pollutants were monitored at these stations but those common at both of them were NO, NO_2, NO_x and PM_{10}; CO, $PM_{2.5}$ and O_3 were measured at one of the stations. The values are summarized (Table 3) for background monitoring station (BMS) and for traffic one (TMS).

Table 3: Data frequency (F) and annual average concentration (C) of the pollutants (μg/m^3) at two monitoring sites TMS and BMS

Year			NO	NO_2	NO_x	$PM_{2.5}$	PM_{10}	O_3	CO
2015	BMS	F (%)	85	85	85	77	69	83	-
		C (μg/m^3)	5.32	25.32	33.49	5	18	40	-
	TMS	F (%)	93	93	93	-	68	-	88
		C (μg/m^3)	62.28	64.55	159.08	-	19	-	389
2016	BMS	F (%)	27	27	27	57	-	76	-
		C (μg/m^3)	5.08	16.13	23.91	3	-	46	-
	TMS	F (%)	68	68	68	-	40	-	79
		C (μg/m^3)	54.88	74.82	158.18	-	16	-	415
2017	BMS	F (%)	5	5	5	25	-	92	-
		C (μg/m^3)	3.45	17.93	23.22	3	-	40	-
	TMS	F (%)	43	43	43	-	36	-	43
		C (μg/m^3)	55.41	54.03	136.60	-	19	-	409

As shown, the frequency of the data decreased from 2015 to 2017 for all pollutants with exception to O_3 (2016 to 2017). Furthermore, for PM_{10} at TMS, data is only available for 2015 no information exists for the consecutive years. The annual concentration limit for NO_2 (40 μg/m^3) was consistently exceeded at TMS during all years. Finally, based on the analysis of the daily and monthly averages, specific summer and winter periods were determined for the exposure and risk assessment.

4. Conclusions

The identified pollutants to which individuals are susceptible to when practising physical exercise were NO_2, $PM_{2.5}$, and PM_{10}. Year of 2015 was selected as the one with the highest frequency of data, and thus as the most suitable for the calculations of the risk assessment.

Acknowledgments

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Cynara cardunculus cultivation in Northern Portugal: Field Study

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Abstract

The accentuated growth of the world´s population arises several sustainability issues such as the high energy demand and the low representativeness of renewable resources in the energy matrix. Biofuels are presently the real renewable alternative to fossil fuels in the transport sector, although economic sustainability is not always ensured due to the feedstock price. For this reason, complementary raw- materials, less expensive and intensive, are essential to reduce economic and technical constraints associated with the process (Costa et al. 2018). The perennial culture Cynara cardunculus was cultivated as an alternative bioenergy crop. Firstly, it was sown in seedbeds and after 50 days, each plant (90 plants) was transplanted to the field at Northern Portugal (41°02'01.7"N 8°33'00.5"W). After one year, it was possible to perform the capitula harvesting of each plant and evaluate the seeds characteristics. From a cultivated area of 50 m2, after processing (grinding and sieving – 2.35 mm) 10 kg of capitula (corresponding to almost 254 capitula), it was possible to obtain almost 1 kg of seeds (200 kg.ha-1). The chemical extraction (soxhlet) of seeds oil was performed on seeds collected from 10 selected plants. It was found that the oil content among the different samples/plants varied between 17 wt.% and 30 wt.%, being in agreement with the literature (Gominho et al. 2018). A linear relationship (r2 = 0.87) between capitula´s weight and seed oil content parameters was observed in the range between 30 g and 60 g of capitula´s weight (inversely proportional). The number of capitula per plant were in average higher (12.5 capitula) than that verified in previous studies (5.3 capitula) (Gominho et al. 2011). The weight of capitula varied between 18 g and 90 g, in agreement with reported values for this crop (Gominho et al. 2009). The study showed that the characteristics of the crop and its components might have variations which enable future optimisation to follow specific valorisation routes. According to the characteristics of each plant, the selection of seeds (ecotype) should be performed taking into consideration the purpose of recovery. Due to the high oil content of the seeds, biofuels production might be explored.

Keywords: Cynara cardunculus, non-conventional oilseed crop, cultivation, biofuel.

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Cytostatics in surface waters: are aquatic organisms at risk?

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Abstract

The load of anticancer drugs into environmental waters has been increasing due to their high consumption in chemotherapy and their low degradation at wastewater treatment plants. The objective of the present work was to explore the concentrations of cytostatics in surface waters worldwide aiming at the assessment of the risk they are posing to aquatic organisms. The determination of Risk Quotients (RQs) based on measured concentrations revealed that mycophenolic acid, tamoxifen, capecitabine, bicalutamide, methotrexate, cyclophosphamide, megestrol and erlotinib may be posing aquatic organisms at risk.

Keywords: cancer, cytostatics, measured environmental concentrations, risk assessment, aquatic environment

1. Introduction

Cancer is one of the most mortal diseases and its incidence has been increasing every year, as well as the use of cytostatics for its treatment. The International Agency for Research on Cancer predicts that 26.1 million new cancer cases will be diagnosed in 2030, being expected more than 13 million deaths worldwide (WHO 2008).

After being administered, cytostatics are excreted and reach the sewage system, coming either from the hospitals, home or pharmacies (Giri and Pal 2014, Tauxe-Wuersch et al. 2006). As there are no effective treatments for these compounds in the wastewater treatment plants, they end up reaching surface waters, posing aquatic biota at risk.

The risk associated to the exposure of aquatic organisms to cytostatics may be estimated through the determination of RQs, according to the Guidelines for Environmental Risk Assessment of Pharmaceuticals (EMEA 2006). So far, most of the published studies have determined those risks based on predicted concentrations instead of measured ones because monitoring programs are very expensive, time-consuming and quite limited (Santos et al. 2017).

Therefore, the main objective of the present work was to estimate the risks to which aquatic organisms are subject to, based on reported concentrations measured in surface waters worldwide.

2. Materials and Methods

An extensive literature search was performed for all studies focused on the measurement of cytostatics in surface waters in three search engines (Pubmed, Scopus and ScienceDirect) combining the following keywords: cytostatics (along with its synonyms), measured/predicted environmental concentrations, analytical methods and risk assessment.

Toxicity data for aquatic organisms from different trophic levels were obtained from data sheets and scientific papers. RQs were calculated through Formula 1. The risk was estimated for each cytostatic by calculating the RQ for the highest concentration measured in surface waters (maximum RQ) and for a concentration equal to the lowest limit of detection reported (minimum RQ), as well as using predicted concentrations for a comparative term, with the same toxicity data. The common criterion for interpreting risk quotients was applied (EC 1996, Sánchez-Bayo et al. 2002): RQ>1 indicates high risk; 0.1<RQ<1 moderate risk and 0.01<RQ<0.1 means low risk.

$$RQ=\frac{PECs/MECs}{PNECs}$$

Formula 1: Equation for the calculation of RQ

3. Discussion

Among the monitoring studies of cytostatics in surface waters, tamoxifen, fluorouracil, methotrexate, ifosfamide and cyclophosphamide are the most studied ones possibly due to their

high consumption rates and the lack of sensitive analytical methods for other cytostatics; however, they are not the ones found at higher concentrations. Mycophenolic acid was the cytostatic found at the highest concentration in surface waters (656 ngL-1) (Franquet-Griell et al. 2017). A high concentration was also found for bicalutamide: 254 ngL-1 (Azuma et al. 2015) and tamoxifen: 212 ngL-1 (Roberts and Thomas 2006). There are many reasons for the high concentrations of these compounds in surface waters: (i) their use as a veterinary medicine and consequent excretion to the grounds (e.g. cyclophosphamide and tamoxifen) (Ferrando-Climent et al. 2014), (ii) their production by microorganisms in silage (e.g. mycophenolic acid) (Alsberg and Black 1913, Ojo 2012) and (iii) the non-effective treatments in wastewater treatment plants for these compounds.

The cytostatics that may be posing aquatic biota at high risk are mycophenolic acid and tamoxifen, with maximum RQs above 1. Capecitabine, bicalutamide and methotrexate may be inducing a moderate risk on aquatic organisms, as their maximum RQs were in the range 0.1-1. Maximum RQs lower than 0.1 and higher than 0.01 were attained for cyclophosphamide, megestrol and erlotinib, which indicate low risk. Conclusions could not be drawn for tegafur, bleomycin and chlorambucil due to the lack of toxicological data.

The analytical methods there are for some cytostatics (e.g. fluorourarcil and cisplatin) are not sensitive enough to mislead the existence of risk, since the RQs determined for the minimum possible concentrations found for these compounds (which corresponds to the lowest limit of detection reported) was above 1.

In general, RQs calculated based on measured concentrations are higher than the ones calculated through predicted concentrations (e.g. tamoxifen, bicalutamide, megestrol, erlotinib, methotrexate, cyclophosphamide, etc.), which highpoints the importance of improving the frequency and quality of monitoring plans and of determining RQs based on measured concentrations.

4. Conclusions

The impact of cytostatics in aquatic biota was estimated through the determination of RQs. It was possible to conclude that tamoxifen and mycophenolic acid may be posing aquatic biota at high risk; capecitabine, bicalutamide and methotrexate may induce moderate risk and cyclophosphamide, megestrol and erlotinib, low risk.

There is a need for improvements in the analytical methods for some compounds (such as fluorouracil and cisplatin), since RQs were higher than 1, even when calculated with the lowest concentration of detection. RQ values based on measured concentrations tend to be higher than the predicted based ones, which means that predicted concentrations are underestimating the real contamination of environmental waters by cytostatics, which highlights the need of further and complete monitoring studies.

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Wildfire management in mediterranean climates: A preliminary systematic review of the state of the art

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Abstract

Wildfires are a common feature with an ever more frequent presence in all five mediterranean climate regions. Their increasing impacts suggest the opportunity of enhancing the basis of scientific evidence on how managers and policy-makers may act effectively to address them. Systematic reviews are a useful means to gather such scientific knowledge to support policy and decision making. This study presents the preliminary results of a systematic review that aims to identify the main trends in wildfire management research in mediterranean climates. The results show that most studies are relatively recent (last ten years), from the Mediterranean Basin region, and understanding fire behavior was the most studied topic (28%). There already is a considerable amount of literature on the subject (208 studies were retrieved in the search), but so far there have been no attempts to present the available knowledge systematically, which reinforces the relevance of the present study.

Keywords: Wildfire, Fire Management, Mediterranean, Policy.

1. Introduction

Catastrophic fires have recently occurred in the Mediterranean Basin, California, South Africa, and southern Australia (Bowman, et al. 2011). Natural occurrence of wildfires is one of many similar characteristics shared by all five mediterranean climate regions, but the significant human presence in these regions is also impacting their fire regimes. Wildfires are a complex phenomenon, and their impacts are often poorly understood by policy-makers and natural- resource managers (Lindenmayer, et al. 2004). Because these regions share many features, it may be beneficial to investigate trends in wildfire management research related to any of them, as the resulting knowledge might apply to all. With this motivation, this study carries out a systematic review of scientific publications that address wildfire management experiences in mediterranean climate regions and presents its preliminary results.

2. Material and Methods

Systematic reviews are particularly useful for multi-disciplinary areas of research, such as policy and environmental sciences (Newbold and Grimshaw 2010), and one of their main uses is to summarize the best available evidence to support decision making (Collaboration for Environmental Evidence 2018). They thus present a good fit with the motivation for this study.

The scientific databases used in this study were Scopus and Web of Science. Given that the aim of this study is to understand the general trends in wildfire management research in mediterranean climates, the following broad search string was used in both bases: *fire AND ("mediterranean climate" OR "mediterranean environ*" OR "mediterranean region" OR "mediterranean eco*" OR "mediterranean forest") AND (manag* OR polic*). Once the searches were done, the following inclusion criteria were applied to select the studies to be further analyzed: Partially or totally about a region of mediterranean climate; and Addresses situations directly linked to any stage of wildfire management. The exclusion criteria were the following: Not about mediterranean climate regions; Does not focus on wildfires; Does not focus on the management of situations linked to wildfires; and Only provides information that could help in the development of management practices or public policies about wildfires.

3. Discussion

The search on both databases was performed on February 19th, 2019. A total of 1042 papers were retrieved, 613 on Scopus and 429 on Web of Science. After removing the duplicates (299), the titles and abstracts of the papers were read and by applying the inclusion and exclusion criteria, 208 papers were selected for further analysis. Most of the 535 excluded papers had a descriptive nature, comparing technologies or ecological processes, but did not address explicitly how the resulting knowledge could inform policy or management actions. The majority of the selected studies were published in the last ten years (82%) and were carried out in the Mediterranean Basin (70%). Among the research topics, four were more prominent: Fire behavior, i.e., mapping, modeling, monitoring, fire prediction and simulation (28%); Prevention and fire suppression (20%); Post-fire management (15%); and Risk management and assessment (10%). It is also worth noting that more than 25% of the selected papers were published in three journals: Forest Ecology and Management (10%); International Journal of Wildland Fire (8%); and Journal of Environmental Management (8%). Finally, no systematic reviews were found among the retrieved studies.

4. Conclusions

Although this is a preliminary assessment of the scientific publications about wildfire management in mediterranean climates, it already reveals that most studies appear to be relatively recent (last ten years), and from the Mediterranean Basin region. Understanding fire behavior seems to be the main focus of the studies (28%), followed by prevention and suppression measures (20%). No systematic review studies were retrieved, even though there is a considerable number of publications on the theme (208). This fact reinforces the relevance of this work, and may also indicate a possible lack of drive, from both practitioners and researchers, to systematically appraise the available information on wildfire management to either incorporate it into policies or identify knowledge gaps to guide further research.

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Environmental licensing as an instrument for the environmental management of Brazilian public ports

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Abstract

Appropriate environmental management initiatives have not yet been properly implemented in Brazilian public ports, and when they exist, they are still very fragmented and are not based on environmental planning, but aimed to fulfil the requirements of the environmental licensing process and mitigate the impacts generated by the implementation or port operation, when they should be made to minimize or eliminate such impacts. Environmental licensing is part of a bureaucratic process and takes years to complete, making many ports operate without the proper environmental operating license. Environmental licensing as an instrument for environmental management in ports can be considered a management tool, however, it should be replaced by planning and constant improvement of environmental compliance, both those provided for by law and in other environmental regulatory mechanisms at national and international level. It should begin with minimum compliance with existing legal requirements and be expanded voluntarily and progressively.

Keywords: environmental licensing, public ports, environmental management, environmental impact, environmental compliance

1. Introduction

Port environmental management in Brazil is mainly based on the environmental licensing processes. The constraints of these licensing processes reflect how management is not based on environmental planning, but rather on mitigating existing impacts. In addition, environmental management occurs in a fragmented and unbalanced way with port development, and national policies are needed to articulate port productive processes with environmental sustainability (Lourenço and Asmus, 2015). Environmental licensing can be considered an important management tool. The current process of environmental licensing of public ports in Brazil is still a long process and associated with a lot of unpredictability. However, as all Brazilian public ports have already been implemented, they must deal with the regularization of environmental licensing of existing activities, and usually only the Operational License.

2. Methodology

The present study presents a predominantly exploratory character. The exploratory focus is justified in this case due to the study's intention to expand the scarce Brazilian scientific knowledge base on port environmental management, and especially on the aspects of environmental licensing as a port environmental management tool and the possibility of improving public policies to the subject.

3. Results and discussion

The licensing of existing activities, which are already in operation, aims to regularize these activities, when assessing the existing environmental impacts, risks and liabilities, and plans and programs are prepared for their control, prevention, mitigation and compensation. The regularization also contemplates the evaluation of the effectiveness of the environmental management mechanisms through the continuous monitoring of environmental parameters and indicators. In the regularization of the existing activities, normally only the operation license, being dispensed the previous license and the installation license.

Environmental licensing can be considered an important management tool, but one of the greatest difficulties in the approval of this one is in compliance with the conditions that make up the

operating license, since, as a rule, they present a number of high demands, often complex, Lourenço and Asmus (2011). Therefore, the difficulty of the post-licensing phase is linked to pre-licensing issues. However, there is a lack of guidelines for environmental licensing, especially in the terms of reference and the delimitation of competencies.

Environmental licensing has become one of the country's most controversial and least understood issues. Everything is criticized in the licensing process: unwarranted delay, excessive bureaucratic demands, poorly reasoned decisions, developmental insensitivity of entrepreneurs, ideological contamination of the process. What has not yet been clearly understood, or at least not expressed accurately, is the root of the problem.

The Secretariat for Strategic Affairs of the Presidency of the Republic (SAE / PR) mentions that one of the causes of the problem is "anomie", that is, the absence of law. Environmental licensing is the realm of administrative discretion. Since the mid-1970s, the country has coexisted with scarce legislation that has long since become outdated. In the absence of clear norms that define the competencies to license, monitor and punish, as well as the stages of the licensing process, the environmental agencies act in an ungoverned way, in an environment of wide insecurity.

According to Kitzmann and Asmus (2006), the legal framework governing the port sector was built following international, federal, state and municipal laws, incorporated at various times, resulting in a "patchwork", and involves several government agencies in different areas, with conflicting views on economic issues, social and environmental development. Since then, little has changed and to aggravate the situation, the government agencies involved have a chronic shortage of skilled quantitative staff and a lack of infrastructure to meet demand. All this conspires to increase the complexity of environmental licensing.

4. Conclusions

There are many critical points throughout the licensing process, but there is still a lack of strict enforcement and punishment for those who do not comply with the law and operate in an irregular and even irresponsible manner. The current legislation requires that ports have a range of authorizations and licenses issued by different bodies and entities in the different spheres of public power. However, overlapping laws, sometimes lack of them and lack of detail on environmental licensing result in different interpretations within each licensing agent, which causes delays in the licensing process, leads to numerous legal actions and generates legal uncertainty.

Brazilian institutions need to move forward in the various aspects of port environmental licensing, in order to ensure legal certainty for the entities involved, efficiency, cutting red tape and understanding the processes, legal transparency. No less important is the need to promote the existence of a regulatory environment favourable to the entrepreneur to act responsibly, environmentally sustainable and economically competitive.

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POSTERS

Appraisal of two microbial cultures in metal bio-recovery from Panasqueira mine by-product

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Abstract

Critical Raw Materials are crucial to Europe's economy; however, there is a high-risk associated with their supply. Bioleaching is an ecological-based technique carried by iron or sulfur-oxidizing microbes, already being used to extract metals from low-grade ore deposits. In this study, the ability of two different cultures taken from Panasqueira and Neves-Corvo mine sites in Portugal were compared. Firstly, the cultures were tested for metals tolerance and adapted by three-day transference adding sodium thiosulfate as an energy source supplement. Secondly, bioleaching tests were carried in columns during established time periods, and finally, samples were taken to assess the bacterial growth, pH, ORP, sulfates concentration, and metal content in the leachate. The results indicate that the bacterial culture coming from Neves-Corvo is more efficient than Panasqueira in the bio-recovery of metals.

Keywords: Bioleaching; metals; Panasqueira mine; Neves-Corvo mine

1. Introduction

Bioleaching is a process in which microorganisms catalyze the conversion of solid metals into their water-soluble forms (Maruthi et al. 2017). This technique merges concomitantly with circular economy targets, aiming the recovery of highly demanded metal(loid)s from low-grade ores (Hannebal et al. 2015). The main advantages of using this biological-based processes are its low pollution footprint, low temperatures requirements, no chemical reagents addition, in-situ practices, and the use of autotroph microorganisms that fix CO2 (Ahmadi et al.,2015; Brierley & Brierley, 2013). Microorganisms used for these processes are acidophiles, iron or sulfur-oxidizing bacteria (chemolithoautotrophs) usually found in the Earth subsurface in the presence of metallic sulfides, which they use as electron donors. The extraction processes performed for an extended period in both study-sites (Panasqueira and Neves-Corvo mines) produced a massive volume of tailings and rock waste that cause an intense impact on the local environment. This work aims to compare two microbial cultures, one of each mine as the most capable of bioleaching metals from a by-product of Panasqueira mine.

2. Materials and Methods

Mineral sample and inoculum

The mineral sample used to test bioleaching was a by-product from Panasqueira Mine. Firstly it was milled and representatively divided, achieving a particle size distribution with a D90 of 4.75 mm. Both inocula were formed mixing the microbiological samples from the tailings of each mine with the mineral medium. In the test with tailings from Panasqueira (IP) the medium had a pH of 4.5. The test with the inoculum from Neves-Corvo (INC) the medium had a pH of 3.5. To the mother culture, three transferences were made, doubling its volume, in a three-day basis. In IP, 0.5 g of the mineral sample were added in each transference and 1 g in the case of INC experiment, in order to adapt microorganisms. Microbial cultures were incubated at 28ºC under 130 rpm in an orbital shaker.

Bioleaching tests

IP bioleaching tests were carried in two columns with a solid to liquid ratio (S:L) of 1:20 (Bio and

Abio) and one with a S:L of 1:10 (BioS) creating three continuous and closed systems. INC experiment ran in three columns with S:L of 1:10 (Bio, BioRep, and Abio). Each column was connected to a flask where the leaching solution was stored, leaving a headspace of 4.7 L of volume. The leaching solution was composed of medium and inoculum at 25% of inoculum in IP and 50% in INC [v/v]. The columns had an input tube below which took leaching liquid from the bottom of the flask at a flow of 5 mL/min, helped by a peristaltic pump, being entirely recirculated 6 times per day and an output tube which take at the same rate the leaching liquid on the top of the column by inertia of a dynamic closed system. The columns tests worked for ten days at room temperature, with the leachate storage flasks in a water bath at 28 °C under agitation during the whole experiment.

3. Results and Discussion

While IP showed a pH increase and Eh depletion, INC experiment developed a pH decrease from day four and remarkably high Redox values. The acidification of the leachate, together with the increase in the redox potential confirms the development of bioleaching reactions. The behaviour on both tests is shown in Fig.1. (a and b)

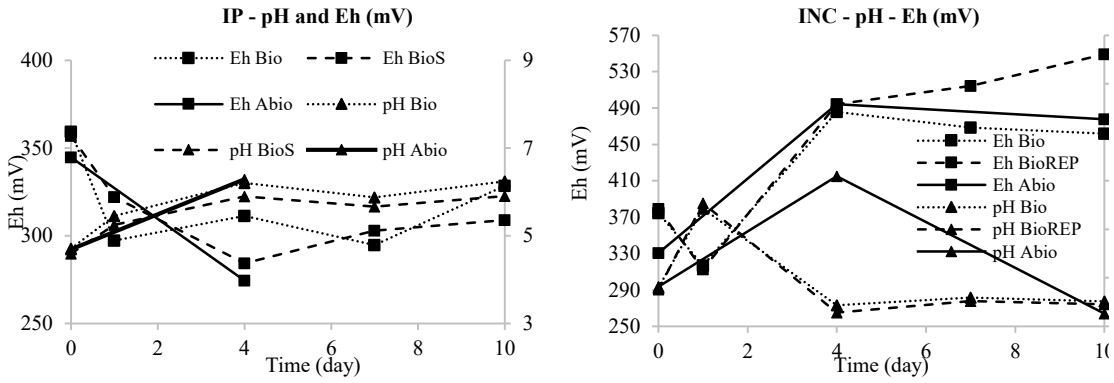

Fig.1-(a) pH and Eh variation throughout IP experiment. (b). pH and Eh variation throughout INC experiment.

The solubilized metals concentration in the leachate on the IP test is low. However, in INC, this concentration increased throughout the experiment, achieving 28 mg/L of As on day 10. The highest metal concentration was obtained with Zn, reaching 75.5 mg/L solubilized. Fig.2. a) and b) show the variation on the metal concentration of As and Zn in the leachate during the first ten days.

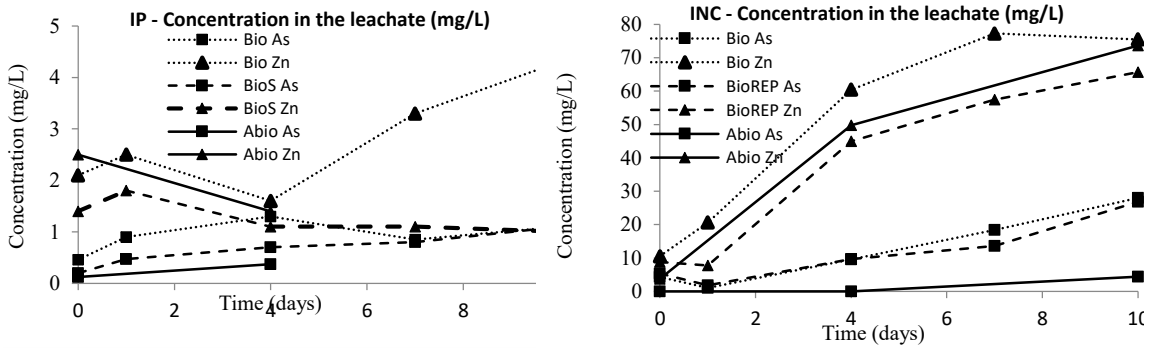

Fig.2. As and Zn concentration in the leachate in the IP (a) and INC (b) experiments.

4. Conclusions

Bioleaching is a key to remediate tailings areas getting profit from bacterial activity. This study allowed the selection of the best microbial community to remove critical metals from Panasqueira Mine. The microbial community from Neves-Corvo mine showed the best results to recover metals in comparison with the autochthonous community from Panasqueira site.

Acknowledgments

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Constructed wetlands and advanced oxidation processes to remove micropollutants from aquaculture farms

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Abstract

The occurrence of micropollutants (MPs) in aquatic systems is a worldwide issue of increasing concern due to their difficult elimination by conventional water/wastewater treatment processes. Constructed wetlands (CWs) have unique advantages as low-cost, simple operation/maintenance and eco-friendless; however, their ability to efficiently remove MPs can be affected by the refractory nature of some compounds. To overcome this shortcoming, combining advanced oxidation processes (AOPs) and CWs might be a good solution, maximizing the advantages of each process, i.e. the low-cost of CWs and the high efficiency (but high cost) of AOPs. In the present work, bench-scale experiments were performed using CWs and different AOPs (O3, UV, O3/UV and O3/H2O2) in order to assess their capacity to eliminate a set of MPs from aquaculture effluents.

Keywords: Constructed wetlands; advanced oxidation processes; micropollutants, aquaculture

1. Introduction

Recently, the presence of organic micropollutants (MPs) in aquatic environment (usually between ng L-1 and µg L-1) has received increasing attention by the scientific community. Since most of these substances are not efficiently removed by conventional water and wastewater treatment systems, they are discharged into receiving waters and scattered through environmental compartments (Barbosa et al. 2016). Although there is no regulation for MPs discharge, the European Union (EU) has demonstrated an evident concern about this problematic, listing several MPs, namely priority substances (PSs) in Directive 2013/39/EU and contaminants of emerging concern (CECs) in Decision 2018/840/EU, which should be monitored in surface water within the EU (Barbosa et al. 2016, Gorito et al. 2017).

MPs encompass several classes of substances (e.g., pharmaceuticals, steroid hormones, industrial compounds and pesticides) and for that reason they reach the environment through diverse sources, as is the case of the aquaculture farms (Barbosa et al. 2016, Gorito et al. 2017). The artificial food and medication applied in this type of food industry can originate the presence of MPs in aquaculture effluents, and moreover, the raw water used in their operation can also contain these microcontaminants. Thus, MPs can be found in both aquaculture influents and effluents and also in the resulting food products, jeopardizing the environment, aquatic organisms and human health. Nowadays, aquaculture provides near half of the fish consumed and an increase ≥ 60% is expected over the next 15 years. Therefore, cost efficient technologies are needed for the treatment of aquaculture water (Gorito et al. 2018).

Constructed wetlands (CWs) are biological systems with recognized advantages of low-cost, simple operation/maintenance and eco-friendliness. In CWs, the interaction between substrate, native microorganisms and plants, promotes the elimination of several contaminants, as is the case of organic MPs. Nonetheless, some MPs, in general those considered more recalcitrant, can be difficult to be removed by this approach (Gorito et al. 2017, Li et al. 2014). Advanced oxidation processes (AOPs) are less selective and have a high potential to destroy organic MPs, but the costs are significantly higher than those associated to CWs, and some by-products can be formed, being some of them more toxic. Combining these two processes could be an interesting alternative to maximize their individual advantages, i.e. the low cost of CWs and the high treatment efficiency of AOPs (Gorito et al. 2018, Liu et al. 2015).

Despite the general recognition of the potential of CWs to remove pollutants from contaminated water/wastewater, studies dealing with organic MPs defined in the recently launched EU legislation

are still limited to a few of these pollutants. In fact, only 20 out of a total of 41 organic PSs/classes of PSs and 8 CECs out of 17 were investigated (Gorito et al. 2017). Moreover, only two studies evaluated their removal from aquaculture effluents (Hsieh et al. 2013, Hsieh et al. 2015a, Hsieh et al. 2015b). Regarding to the combination of CWs and AOPs, studies still do not investigated substances listed in the EU Directives. Thus, for the first time, the present study intends to investigate the responsiveness of coupling these two processes to remove MPs from aquaculture effluents.

2. Materials and methods

In a first stage, bench-scale experiments were performed using planted vertical subsurface flow CWs microcosms (VSSF-CWs), assembled for evaluating the elimination of 36 organic MPs from aquaculture effluents. CWs microcosms (in triplicate) were supplemented with 2 L of aquaculture effluents spiked with 100 ng L-1 of each selected MP. The CW microcosms were operated in one-week cycle during four weeks, to assess the performance of CW systems along time. Posteriorly, bench-scale experiments in continuous mode were also performed using O3, UV, O3/UV and O3/H2O2 processes, to select the best option to eliminate the same group of MPs from surface water. Removal efficiencies were estimated by the difference of MPs concentrations at inlet and outlet of each treatment (biological or chemical), MPs concentrations being determined by liquid chromatography tandem mass spectrometry (LC-MS/MS).

3. Results and discussion

The obtained results in CWs systems revealed weekly removal rates higher than 87% for all MPs, with exception of 2-ethyl-hexyl-4-trimethoxycinnamate (EHMC, 37-86%), reinforcing the potential of this unconventional technology for this type of application. Regarding to the AOPs, O3/UV and O3/H2O2 presented the highest efficiencies, but O3 alone also performed quite well. In these three processes, most of the target MPs were highly removed (>90%), acetamiprid, atrazine, chlorfenvinphos, clothianidin, EHMC and perfluorooctanesulfonic acid (PFOS) being the compounds with the lowest removals (between 5 and 80%).

4. Conclusion

Undoubtedly, CWs and AOPs are presenting encouraging results for MPs removal, however more research is needed to compare and combine these processes.

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Preparation of Ca-loaded materials for phosphate sequestration from wastewater and use as fertilizer

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Abstract

Phosphate removal from wastewater is important to avoid eutrophication of the water bodies. In the current context, the recovery of P is also increasingly imperative, as phosphate rock reserves are limited and depletable. Adsorption may contribute to phosphorus uptake and recycling. In the present work, adsorbents were developed from maritime pine bark. Tannins were extracted in aqueous solution, converted into resins and further modified with calcium. The aim is to produce adsorbents to sequester phosphate from industrial or domestic wastewater and to use them, when exhausted, as P and Ca releasers in soil. The work is still in an early stage (optimization of Ca retention in resins), but experiments already conducted indicate a feasible preparation, requiring a relatively low concentrated solution (0.2 g-Ca2+ L–1), at pH 5-6 and generating a final resin containing 32 mg-Ca per g.

Keywords: Phosphorus, tannin, biomass, calcium, biosorption.

1. Introduction

Phosphate accumulation in water bodies due to mining, industrial, agriculture and sewage discharges may have drastic ecological consequences (e.g. eutrophication). Natural reserves of phosphate are finite and will become exhausted in 1-3 centuries (Cooper et al. 2011). Thus, phosphate-rich wastewater should be considered as an alternative phosphate source, from where it can be removed and recycled through adsorption. Adsorption has the advantage of being effective with low concentrations. Here, a Ca-loaded pine bark tannin-resin was synthesised to be applied as adsorbent for removal and recovery of phosphate from water. It is expected that calcium-loading generates phosphate binding sites in the adsorbent and so that the exhausted resin could be applied directly as a fertilizer.

2. Materials and Methods

Tannins were extracted from pine bark through an alkaline extraction (90 °C, 60 min and NaOH 7.5% m/m). The freeze-dried extract was dissolved in NaOH 0.25 mol L–1 (4 mL g–1) and reacted with formaldehyde 36% (0.2 mL g–1) for 8 h at 80 °C, generating a tannin-resin (TR). Oxidized tannin-resin (TRO) was obtained by reaction with HNO3 1 mol L–1 (90 min, 50 °C). TR and TRO were subjected to calcium-loading by contacting with CaCl2 solutions (10-1500 mg-Ca L–1), at pH 6 and solid:liquid ratio 5 g L–1. The obtained materials was washed with distilled water and dried at 50 °C. Final concentrations of Ca2+ in the liquid were meausred by flame atomic absorption spectroscopy and the amount of Ca retained by each material quantified by mass balance. In addition, the loaded solid was subjected to acid digestion, Ca2+ was anlysed in the digestion liquid and the Ca-content of the resin calculated.

3. Results and Discussion

Before saturation with Ca2+ ions, Ca-content of the original TR and TRO were measured as 0.4 mg g–1 and 9.6 mg g–1, respectively. The results obtained in the preparation of Ca-modified tannin resins are present in Fig. 1. The amount of Ca retained by the solid was evaluated by two methods and different results generated. Calcium removal from the solution by TRO is highly dependent on Ca2+ concentration, reaching 89 mg-Ca g–1 (Fig. 1b). However, after separation from the liquid, the solid was washed and Ca partially leached out. Probably only the calcium ions which were stably

bound to the solid had remained. This explains the much lower Ca-contents measured in the solid, limited to ≈25 mg-Ca g–1. Regarding TR (Fig. 1a), the difference between the amount of Ca calculated by the two methods seems to be less significant. This may be an indication of the establishment of stable bonds between Ca and TR. In this case, the maximum uptake (calculated by acid digestion) was 22 mg g–1, which occurs for Ca2+ concentrations higher than 215 mg L–1. In these conditions, the proposed modification has generated an adsorbent containing 32 mg-Ca g–1 (original content plus calcium retained from the solution). Tannin-resins usually present a great chelating ability towards cationic metals, due to the abundance of adjacent phenolic hydroxyl groups. The partial oxidation has not decreased Ca uptake, but lead to the dissolution of the metal initially present in the solid which, in the end, conducted to a lower Ca content.

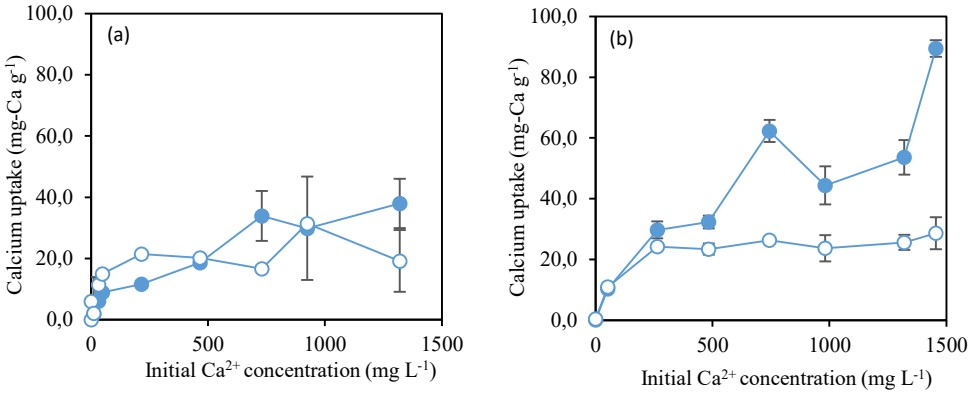

Figure 1: Influence of initial Ca^{2+} concentration on metal uptake by (a) TR and (b) TRO: results from mass balance (closed circles) and acid digestion (open circles).

4. Conclusions

Ca-loading of tannin-resins was performed in order to obtain tailored adsorbents. Maximum Ca-content (32 mg-Ca g–1) was obtained after stirring tannin-resin with 215 mg-Ca L–1 solution, at pH 6. The previous oxidation of tannin-resin has lead to lower amounts of Ca retained. Future work will include the evaluation of the produced adsorbents on phosphate uptake.

Acknowledgments

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Preparation of Ca and Mg-loaded cork for phosphate sequestration from wastewater

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Abstract

Phosphorus is an essential nutrient but its mineral reserves on earth are increasingly scarce. On the other hand, high amounts of this element are released into wastewater and solid waste, eventually contaminating the planet's water resources and causing eutrophication. The objective of this work is to use cork granulates to accumulate phosphorus from contaminated water. It is intended to use the charged solid directly as fertilizer. The work then involves the optimization of the removal process, in order to fix the maximum amount of phosphorus, creating conditions for its later release and facilitating its action as fertilizer. Cork granulates surface has been modified by Mg and Ca precipitation. The work is still in an early stage but results already obtained showed that magnesium has higher affinity for P than calcium and, at pH 7-9, modified cork with Mg is able to retain ≈ 35 mg-P per g of cork.

Keywords. Phosphorus, cork, magnesium, calcium, biosorption

1. Introduction

The increasing scarcity of P mineral reserves in the planet, together with the need to control eutrophication of water bodies, have motivated the search for economic processes, able to sequester and recover P from wastewater (Loganathan et al. 2014). For this purpose, calcium and magnesium-modified biochars have been produced from several feedstocks with good P removal efficiency (Yin et al., 2017). This impregnation/thermal treatment has not yet been tested on cork. Cork, the bark of Quercus suber L., is a natural, renewable material with great economic significance in Portugal. The byproducts of cork processing, cork granulates, are 0.5-8 mm size granules which have found wide application as biosorbents and activated carbon precursors (Pintor et al., 2012).

2. Materials and Methods

I. Modification of the cork granules with calcium for the removal of phosphate

The cork granules (20 g/L) were contacted with calcium hydroxide precipitate at pH 7, prepared from 3.3M of CaCl2. The coating was carried out in 50 ml plastic tubes, on a rotary shaker at 20 rpm and 20 °C for 2 hours. Posteriorly, it was allowed to dry in the oven at 80 °C and finally it was burned under a nitrogen atmosphere at 350 °C for 3h.

The experimental conditions of the adsorption tests were similar, using 2.5 g/L of coated cork granules and a 24h of contact time. P(V) adsorption tests were performed at pH 7 and 9 using an initial concentration of 25 mg P/L.

II. Modification of the cork granules with magnesium for the removal of phosphate

The tests performed with magnesium cork granules were subjected to the same heat treatment, however the magnesium hydroxide was prepared from 2.3M of MgCl2.

III. Washing of cork granules

In order to reduce the amount of calcium and magnesium released the cork washing was performed after thermal processing. The washing process consisted two washing cycles with distilled water in the rotary shaker at 20 rpm and 20 ºC for 20 min.

3. Discussion

In the tests carried out with the cork modified with calcium, an average adsorption of 17.2 mg P/g cork was found, releasing about 1063 mg Ca/L. When the washing process was carried out the adsorption was only 2.6 mg P/g cork, however, it was possible to reduce the amount of calcium released to 13.2 mg Ca/L.

In the case of the tests performed with cork modified with magnesium, more satisfactory results were obtained. The adsorption of P was about 34 mg P/g cork and only 316 mg Mg/L were released. When the cork was washed the amount of adsorbed P decreased to 11 mg P/g cork but the amount of magnesium released was also reduced to 36 mg Mg/L.
The results obtained in the various tests allowed to conclude that the pH variation in the neutral/alkaline range does not significantly affect the adsorption of P. However for pH 9 the release of calcium and magnesium is lower than for pH 7.

4. Conclusions

The main conclusions from this work are:
I - when the cork granules are subjected to heat treatment there is an improvement of the adsorption of phosphorus;
II - the washing of the granules after the heat treatment reduces the amount of phosphorus adsorbed, however, it also allows the reduction of the amount of calcium or magnesium released;
III - the results were more satisfactory in the case of magnesium-modified cork granules, indicating that phosphorus has a greater affinity with this element.

Acknowledgments
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