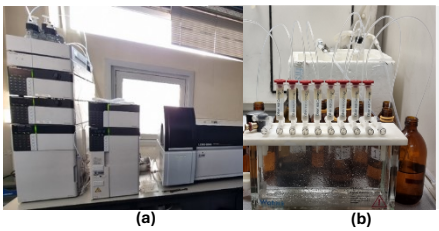
KEYWORDS: Liquid Chromatography-Tandem Mass Spectrometry / Solid Phase Extraction / Micropollutants / Environmental Monitoring

More than 50 organic micropollutants (OMPs) were monitored in surface and wastewater matrices by solid-phase extraction and liquid chromatography-tandem mass spectrometry (SPE-LC-MS/MS). Monitoring campaigns included seven Portuguese rivers and the entire Portuguese Coast. Moreover, water samples from aquaculture, drinking, and wastewater treatment plants were analysed. Many OMPs belonging to different classes, such as pharmaceuticals, pesticides, industrial compounds, and UV filters, were detected, ranging from a few to thousands ng L^{-1}. Whenever relevant, other physicochemical parameters were evaluated and risk assessments were performed.

Introduction

A significant hurdle in effective water resource management is the presence of organic micropollutants (OMPs) in aquatic systems (< mg L^{-1}). OMPs encompass many classes of compounds, such as pharmaceuticals, personal care products, industrial chemicals, pesticides, and other substances that, in general, are not efficiently removed by conventional water/wastewater treatment systems. Consequently, OMPs may enter receiving water bodies, spreading through different environmental compartments and accumulating in living organisms. Although there are no legal discharge limits for OMPs, regulations addressing this concern have been introduced. Specifically, Directive 2013/39/EU establishes Environmental Quality Standards (EQS) for a list of 45 priority substances (PSs) and emphasizes the need for monitoring these and other potentially harmful OMPs still under investigation, such as the contaminants of emerging concern (CECs) included in the Watch Lists for Union-Wide Monitoring.

The identification and quantification of PSs and CECs in aquatic environments, along with understanding their degradation and potential risks, highly depend on fast, sensitive, and reliable analytical methods capable of identifying and quantifying a broad spectrum of OMPs. For most OMPs, solid-phase extraction and liquid chromatography-tandem mass spectrometry (SPE-LC-MS/MS; Fig 1) stand out as the recommended analytical methodology. Nonetheless, SPE-LC-MS/MS analyses require the development of robust analytical methods that ideally cover a wide range of OMPs, consider the specific matrix under study, and incorporate internal standard calibration. Consequently, sample preparation techniques such as SPE must be meticulously studied/optimized to ensure the efficient extraction and concentration of OMPs. This involves minimizing interferences from respective matrices, embracing the principles of green analytical chemistry, and avoiding additional sources of environmental contamination.



(a) (b)

Fig. 1. (a) Ultra-High Performance Liquid Chromatography coupled to tandem Mass Spectrometry (UHPLC-MS/MS) apparatus;

Given the increasing concern about the occurrence of OMPs, the focus of this research topic is to contribute to gaining relevant data in this domain through monitoring PSs and CECs in distinct water matrices. By doing this, we can support regulatory agencies in making informed decisions. Moreover, the information on the occurrence and distribution of OMPs provides comprehensive insights that can help to develop mitigation and remediation strategies seeking water quality and ensuring the long-term safety of aquatic ecosystems and human health. Beyond monitoring of OMPs and risk assessment, other parameters have been evaluated to complement water analysis.

Current Development

SPE-LC-MS/MS methods were developed and optimized for the determination of OMPs in surface and wastewater matrices. Regarding surface water, CECs from the Watch List launched in 2015 were monitored in the Ave and Sousa rivers [1], while those from the Watch List of 2022 were recently monitored in the Douro River. From 17 CECs, 8 were detected in the Ave river (diclofenac, erythromycin, clarithromycin, azithromycin, imidacloprid, thiamethoxam, clothianidin and 2-ethylhexyl-4-methoxycinnamate - EHMC) and 13 were identified in the Sousa river (E1, diclofenac, 2,6-ditert-butyl-4-methylphenol - BHT, EHMC, erythromycin, clarithromycin, azithromycin, imidacloprid, thiacloprid, thiamethoxam, methiocarb, oxadiazon, and triallate). The most frequently found CECs were diclofenac (33-67%), azithromycin (27-73%), EHMC (13-67%) and imidacloprid (7-60%) in the Ave River, and diclofenac (53-80%), azithromycin (33-67%), clarithromycin (40-93%), and EHMC (67-93%) in the Sousa River [1]. The highest concentrations were registered for imidacloprid (~ 500 ng L^{-1}), diclofenac (~ 400 ng L^{-1}), and EHMC (~ 8000 ng L^{-1}) in the Ave River; and diclofenac (~ 3200 ng L^{-1}) and EHMC (40000 ng L^{-1}) in the Sousa River, with seasonal fluctuations. EHMC was identified as the only OMP demonstrating the highest tendency to pose a risk [1]. In another recent work (*manuscript in preparation*) monitoring 32 OMPs in the Douro River, the most frequently detected compounds were within the UV filters class. The 3 benzotriazole UV filters (< 191 ng L^{-1}) and avobenzone (< 235 ng L^{-1}) were determined in all sampling points and at the highest concentrations. The most frequently determined pharmaceuticals were: the antibiotics clarithromycin and clindamycin, which were always quantified at relatively constant levels along the river (~ 9 ng L^{-1} and 30 ng L^{-1}, respectively); carbamazepine and fluconazole, which were also quantified in all sampling locations with slight variations along the river (< 28.3 ng L^{-1}); and irbesartan and climbazole, which were detected in most sampling points (< 14.3 ng L^{-1}). Azoxystrobin was the pesticide quantified in all sampling points (< 38.7 ng L^{-1}), whereas tebuconazole was detected frequently but at lower concentrations than azoxystrobin (up to 3.9 ng L^{-1}) [1]. Both studies provide the first monitoring results of CECs listed in EU Watch Lists for Portuguese rivers. The occurrence of a multi-class of PSs and CECs was also evaluated in 4 stressed rivers in Portugal (Ave, Leça, Antuã, and Cértima) [2]. Isoproturon (< 92 ng L^{-1}), 11 pharmaceuticals (< 396 ng L^{-1}), and the UV-filter EHMC (< 562 ng L^{-1}) were detected in all rivers. Moreover, Leça River was

selected as a waterbody case study for the assessment of fluorescence excitation-emission matrices (EEMs) in collaboration with Professor Lee Blaney from the University of Maryland Baltimore County (USA). These results matched the spatial distribution trend of OMPs along the river, with stronger fluorescence response and higher concentrations being found downstream of industrial areas and urban wastewater treatment plants (Fig 2a) [1]. Furthermore, the presence of 18 per-and polyfluoroalkyl substances (PFASs) and respective potential risk were evaluated in the same 4 rivers [3]. PFAS contamination was confirmed in all studied sites, with perfluoro-octane sulfonate (PFOS) and perfluorooctanoate acid (PFOA) being the most frequently detected compounds. Most of the detected PFAS showed low risk to organisms at different trophic levels, except perfluoro-tetradecanoic acid (PFTeA), for which a high risk for fish and daphnids was estimated, as well as a medium risk for green algae (acute exposure) (Fig 2b) [1].

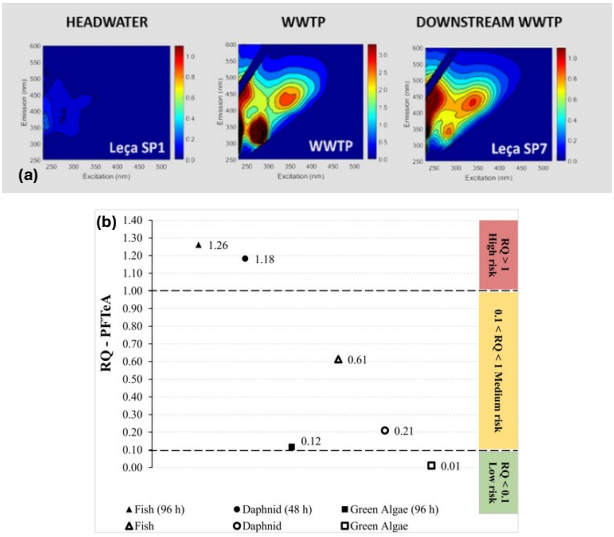


Fig. 2. (a) Fluorescence EEMs for two Leça river samples (SP1 - headwater and SP7 - downstream WWTP) and one WWTP sample; (b) Risk assessment of the higher detected PFTeA concentration (acute toxicity - bold symbols and chronic toxicity - open symbol).

Another study conducted under this topic provides the first spatial distribution of 37 OMPs in the entire Portuguese coast [4]. High concentrations of diclofenac, tramadol, and carbamazepine were determined. Regarding detection frequencies, atrazine and alachlor were found in most of the samples. The risk was assessed, and carbamazepine, atrazine, and alachlor showed medium to high risk for algae [4]. Other studies of the team focused on the removal of OMPs also reported the determination of these compounds by SPE-LCM/MS, namely in aquaculture effluents [5] and a river supplying a Portuguese drinking water treatment plant [5]. In both cases, several target OMPs were detected in the collected samples, highlighting the concern about the possible effects of these substances in the aquatic environment [5,6].

An SPE-LC-MS/MS protocol to analyse illicit drugs and pharmaceuticals, mainly used to treat COVID-19, was also developed for the identification and quantification of these OMPs in wastewater influents provided by a Portuguese urban wastewater treatment plant facility (*manuscript in preparation*). This study aimed to establish occurrence patterns through 3 phases of the pandemic, including the first wave (18th March - 1st July), the reopening phase (1st July-14th October), and the second wave (14th October – 31st December). It was found that the frequencies of detection of fluoxetine and remdesivir decreased from the first wave to the reopening phase. Additionally, the measured concentrations of atenolol and tramadol increased significantly between the first wave and the reopening phase, while the frequencies of detection of cocaine and metoprolol slowly increased over time. These tendencies could be related to the modified lifestyle imposed by the COVID-19 pandemic and the restrictions implemented by the Portuguese government (*manuscript in preparation*).

Recently, the acquisition of a gas chromatography-tandem mass spectrometry (GC-MS/MS) apparatus has expanded our analytical capabilities, enabling the future analysis of less polar OMPs that were previously not feasible to be analysed using LC-MS/MS.

Future Work

The European guidelines concerning OMPs are constantly being updated and thus, in order to accompany these changes, we aim to continue being at the forefront of analytical chemistry/ environmental monitoring. Therefore, analytical methods will be developed and applied to different aqueous matrices for: (i) monitoring azole compounds listed in the latest Watch List, with respective risk assessment (work to be developed under an individual call to scientific employment stimulus recently attributed by FCT to a junior researcher on our team); (ii) monitoring OMPs from the current proposal for a new EU Urban Wastewater Treatment Directive (UWWTD) and CECs from the current Watch List in wastewater and surface waters (work to be performed under the framework of STAR FCT project); and (iii) monitoring OMPs from the Watch List of substances and CECs included in the new Directive 2020/2184/EU for water intended for human consumption (work to be performed under the framework of DRopH2O FCT project). With the acquisition of the GC-MS/MS, we will expand our analysis window to encompass a large number of OMPs.

Related Sustainable Development Goals

Outputs

PhD Theses

Marta Oliveira Barbosa, Multi-layer carbon cartridges for determination of EU multi-class organic micropollutants, PDEQB, FEUP, 2021

Ana Margarida Gorito Gonçalves, Micropollutants in aquaculture: constructed wetlands and advanced oxidation technologies as prospective treatments, PDEA, FEUP, 2023

Master Dissertations

João Bernardo Nunes Simão, Pandemic impact on the consumption patterns of pharmaceuticals and other emerging contaminants, MIB, FEUP, 2022

Beatriz Rocha da Mota, Monitoring of micropollutants in Douro River, MIEA, FEUP, 2023

Selected Publications

[1] J.C.G.Sousa et al., Sci. Total Environ. 649, 1083 (2019)
[2] Marta O. Barbosa et al., Sci. Total Environ. 644, 1128 (2018)
[3] Marta O. Barbosa et al., Molecules 28, 1209 (2022)
[4] J.C.G.Sousa et al., Mar. Pollut. Bull. 154, 111120 (2020)
[5] A.M.Gorito et al., Sci. Total Environ. 644, 1171 (2018)
[6] A.M.Gorito et al., J. Environ. Chem. Eng. 9, 105315 (2021)

Team

Adrián M.T. Silva. Associate Professor; **M. Fernando R. Pereira.** Full Professor; Ana R. L. Ribeiro. Principal Researcher/Group Leader; Ana M. Gorito. Researcher (Doctorate Initial level); Marta O. Barbosa. Researcher (Doctorate Initial level); Joaquín A. Marrero. PhD Student/Project Research; **Beatriz Mota**. Project Research; **Leonor Barroca**. Project Research.

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LA LSRE-LCM Funding, UID/EQU/50020/2019, 2019
LA LSRE-LCM Funding, POCI-01-0145-FEDER-006984,2013-2018
InSpeCt, NORTE-01-0145-FEDER-031049, 2018-2022
Healthy Waters, NORTE-01-0145-FEDER-000069, 2021-2023
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Enantioselective Analytical Tools

KEYWORDS: Liquid Chromatography-Tandem Mass Spectrometry / Solid Phase Extraction / Micropollutants / Environmental Monitoring

Considering that enantiomers may behave differently in biological systems, enantioselectivity should be considered for an accurate risk assessment of chiral drugs in the environment. Enantioselective methods based on liquid or gas chromatography coupled to mass spectrometry after sample preconcentration were developed for 28 chiral drugs. Enantioselective studies were developed to monitor 23 chiral drugs in the Douro River estuary, to monitor 7 drugs of abuse in both the liquid phase and the suspended particulate matter of wastewater influents, and to evaluate the ecotoxicity of the racemate or the isolated (*R*)- and (*S*)- enantiomers of a synthetic cathinone. These studies have demonstrated that the environmental occurrence, distribution, and ecotoxicity towards non-target organisms may be enantioselective.

Introduction

Wastewater treatment plants (WWTPs) are the major source of excreted licit and illicit drugs and their metabolites, and unused/expired medicines/drugs wrongly discharged into sewage networks [1]. Their removal is often incomplete at WWTPs since these are not designed to completely eliminate residual organic contaminants of emerging concern (CECs). Moreover, their partial degradation may originate other metabolites and/or transformation products (TPs), respectively by biological and abiotic processes. All these pseudo-persistent CECs are often detected in WWTP effluents, surface water, groundwater, marine waters, and even in drinking water. The long-term exposure to mixtures of these substances (pharmaceuticals, their metabolites and TPs) at residual concentrations has been targeted as a great concern due to the possible adverse effects on ecosystems and human health, namely endocrine disruption, development toxicity, and antimicrobial resistance (AMR). However, the scientific approaches used so far have been focusing on the effects triggered by single or few compounds at concentrations that are not environmentally relevant, thus ignoring the real impact of this environmental problem. While most environmental studies on drugs rely on their occurrence and hazardous effects, the ecological concerns about the aquatic contamination go far beyond and include crucial aspects completed ignored to date by environmental risk assessment. Moreover, the metabolites and TPs produced in the environment, the additive or synergistic effects of their mixtures at trace levels, and the role of stereochemistry are completely disregarded. In fact, many pharmaceuticals and illicit drugs are chiral and administrated as pure enantiomers or as mixtures. Enantiomers can display different behaviour in chiral medium (Fig. 1) and thus, biological activities, including toxicity, are enantioselective [2].

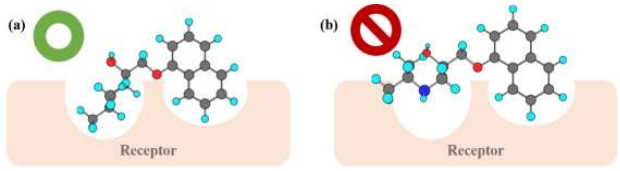

Fig 1. Interactions of the enantiomers of the chiral pharmaceutical propranolol with its target receptor representing: (a) the interaction with the more potent enantiomer (S)-(-)-propranolol; and (b) the interaction with the

Although chirality is rarely considered in environmental studies, the control of stereoselectivity in the environmental fate, distribution, (bio) transformation/degradation, adsorption, ecotoxicity, (and AMR), and bioaccumulation of chiral drugs is crucial to get a realistic environmental risk assessment of this type of substances [3].

Current Development

An enantioselective method was developed and validated to quantify chiral drugs (CDs) in surface water, being applied to the monitoring of Douro River. Many classes of CDs were targeted, including beta-blockers, antidepressants, one beta 2-adrenergic agonist, non-steroidal anti-inflammatory drugs, stimulants, and some illicit drugs. Amphetamines, cocaine and its metabolites were included, totalizing 23 compounds. The analytical method was based on a pioneering approach of solid phase extraction (SPE) that allows the simultaneous extraction of acidic/basic/neutral analytes, followed by analysis by liquid chromatography-tandem mass spectrometry (LC–MS/MS). Two chiral columns were used for enantiomeric separation in reverse elution mode, a Chirobiotic™V and a Pirkle type Whelk-O® 1, for basic and acidic compounds, respectively. The validated method was successfully applied to monitor daily variations along one week in Douro surface waters. The metabolite *N*-desmethyl-tramadol was quantified at higher concentrations than tramadol and both presented high concentrations near the affluent of a tributary river, while the second eluted enantiomer of *O*-desmethyl-tramadol was found at high concentrations at the mouth of the Douro River. The Watch List compound venlafaxine was determined at high concentrations near the affluent of the same tributary river, but its metabolite *O*-desmethyl-venlafaxine was found at concentrations 3 times higher. Cocaine was found every day at all sampling points along the estuary, with slight variations.

Enantiomeric profiling can provide useful insights on chiral drug misuse patterns, to discern between prescribed and illegal drug use, as well as to indicate the actual consumption of drugs or the direct disposal, since drug synthesis is linked to various chiral signatures and enantioselective metabolism may occur before excretion, also altering the enantiomeric profiling. Therefore, wastewater based epidemiology (WBE) is an interesting tool to routinely estimate drug consumption using both non-enantioselective or enantioselective methods. A recent study (*manuscript under preparation*) was conducted under a collaboration with Professor Cláudia Ribeiro (PI of project ENANTIOTOX) to estimate the consumption of some conventional drugs of abuse: amphetamine-like and synthetic cathinones. In this work, the enantiomeric profiling of the samples was studied, exploring for the first time the possible enantioselective sorption of these drugs onto suspended particulate matter, using 24-h composite raw wastewaters collected from a conventional WWTP located in the north of Portugal. The results showed a low and non-enantioselective adsorption to suspended particulate matter at environmental relevant levels. Amphetamine was the most frequently found drug, predominantly enriched or exclusively determined as (*S*)-form. Nevertheless, (*R*)-amphetamine was also detected, suggesting illicit consumption of this drug. Further, the enantiomeric profiling suggested the abuse of

methamphetamine, 3,4-methylenedioxymethamphetamine and the synthetic cathinones buphedrone and 3,4-dimethylmethcathinone. The findings of this first WBE campaign of drugs of abuse in Portugal may be useful to enforce preventive measures.

The ecotoxicity of the racemate or the isolated (*R*)- and (*S*)-enantiomers of butylone was evaluated using *Daphnia magna*, as well as the efficiency of advanced oxidation technologies (AOTs) for its removal and reduction of toxicity in wastewaters (*manuscript under preparation*), under a collaboration with CESPU, FFUP, UTAD, and UM (project ENANTIOTOX). The pure enantiomers obtained by chiral semi-preparative liquid chromatography were tested against the racemate in a 9-day sub-chronic assay, with the racemate spiked at 0.10, 1.0 or 10 μg L^{-1}, whereas each enantiomer was spiked at 0.10 or 1.0 μg L^{-1}. Changes in morphophysiological, behavioural, biochemical and reproductive endpoints were observed, which depended on the form of the substance and the life stage of the organism (juvenile or adult). The removal rates of butilone in spiked wastewater (10 μg L^{-1}) treated with different AOTs (ultraviolet, UV; ozonation, O_3; and UV/O_3) were similar and lower than 29 %. The 48-h *D. magna* acute toxicity assays demonstrated a reduction in the toxicity of the treated spiked effluents, but no differences were found among AOT treatments performed. These results warn for the contamination and negative impact of butylone on ecosystems and highlight the need of efficient removal processes.

Recently, the acquisition of an automatic SPE apparatus and a Circular Dichroism Spectrophotometer apparatus has expanded our analytical capabilities, enabling the high throughput analysis of environmental matrices and the assignment of absolute configuration of enantiomers, respectively.

Future Work

Presently, it is urgent to develop a disruptive strategy to tackle pharmaceuticals and illicit drugs (or any other group of CECs), based on a holistic approach that involves monitoring, risk assessment, evaluation of ecotoxicity and bioaccumulation, and removal by biodegradation and advanced treatments. Monitoring chiral substances, namely antibiotics and psychoactive substances, while assessing their enantiomeric fractions will be crucial to: (i) understand the relationship between the molecular structure and (bio) degradability of chiral drugs (work related to an ERC grant and STAR FCT project); (ii) evaluate the respective ecotoxicity and bioaccumulation of chiral drugs (work related to an ERC grant and the ENANTIOTOX FCT project). Furthermore, knowing that the environmental CECs occur as a mixture (cocktail effect), the potential negative impacts on aquatic organisms of such combinations need particular attention.

Related Sustainable Development Goals

Outputs

Master Dissertations

Ana Rita Teixeira Carvalho, Toxicity of butylone and its enantiomers to Daphnia magna and its degradation by advanced oxidation technologies, MACSP, ESS-IPP, 2023

Selected Publications

[1] J.C.G.Sousa et al., J. Hazard. Mater. 344, 146 (2018)
[2] A.R.L. Ribeiro, et al., TrAC – Trends Anal. Chem. 124, 115783 (2020)
[3] A.R.L. Ribeiro, et al., Handb. Environ. Chem. 19, 249 (2023)

Team

Adrián M.T. Silva. Associate Professor; **M. Fernando R. Pereira.** Full Professor; Ana R. L. Ribeiro. Principal Researcher/Group Leader; Ana M. Gorito Researcher (Doctorate Initial level); Joaquín A. Marrero. PhD Student/Project Research; **Beatriz Mota**. Project Research

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LA LSRE-LCM Funding, UID/EQU/50020/2019, 2019
LA LSRE-LCM Funding, POCI-01-0145-FEDER-006984,2013-2018
ENANTIOTOX, PTDC/CTA-AMB/6686/2020, 2021-2024
STAR, 2022.02842.PTDC, 2023-2026
FCT Grants: 2022.00184.CEECIND

KEYWORDS: Adsorption / Solid-phase extraction / Stir-bar sorptive extraction / Micropollutants / Water monitoring and treatment

Carbon-based materials were investigated as adsorbents in two distinct applications: (i) the extraction and preconcentration of trace contaminants from environmentally relevant water matrices, for further monitoring of these compartments; and (ii) the removal of different pollutants from water samples, aiming the detoxification. The results obtained indicate that these materials are a promising solution for water monitoring and treatment.

Introduction

Over the last few years, there has been a growing interest in understanding the fate and effects of a diverse range of organic micropollutants (OMPs) in the aquatic environment. These pollutants, found at residual concentrations (ng L^{-1} to µg L^{-1}), encompass natural and anthropogenic substances, including pesticides, industrial compounds, pharmaceuticals, steroid hormones, among others.

A notable characteristic of many of these compounds is their pseudo-persistent nature, since transformation and removal rates of these substances are surpassed by their continuous introduction into the environment. Combined with this recalcitrant character, their polarity facilitates the dispersion and interchange between aquatic compartments. Conventional urban wastewater treatment plants (UWWTPs), designed without a focus on low-concentration organic compound removal, discharge these pollutants into various water bodies, including surface water and groundwater compartments, posing significant concerns for aquatic and public health safety. In this context, robust analytical tools and simple and efficient removal processes are crucial to monitor and remove these OMPs, respectively.

Several analytical techniques have been tailored to achieve high sensitivity and reproducibility for detecting these contaminants. To address resource limitations and time constraints, novel analytical methods that enable the simultaneous determination of different chemical compounds at trace levels (*i.e.*, meeting the multi-class purpose), while streamlining the time required for sample matrix cleanup and analyte extraction (*i.e.*, the most time-consuming analytical steps), are preferred.

The choice of an appropriate sorbent in sample preparation is crucial for achieving good extraction conditions, influencing key parameters such as selectivity, affinity, and capacity. The development of novel materials as sorbents for solid-phase extraction (SPE) and stir-bar sorptive extraction (SBSE) has been extensively explored to create more selective materials with higher adsorption capacity.

On the other hand, considering the concerns about water contamination, adsorption emerges as one of the most suitable and applicable processes for pollutant removal due to its simplicity and ease of operation. In particular, carbon-based materials, with their unique properties like possible high surface area and the potential for controlled functionalization, stand out as promising materials for two complementary applications: (i) sample preparation to extract the target pollutants at trace concentrations; and (ii) adsorption process to remove these OMPs from water matrices.

Current Development

Hollow carbon spheres (CSs) have gained increased interest in adsorption applications, especially because of their potential to store substances within their inner cavities. To confirm this premise, different nanostructured CSs were synthesized and applied as adsorbents [1]. Adsorption kinetic and equilibrium studies were carried out with diclofenac and venlafaxine as model OMPs. Equilibrium studies demonstrated that CSs prepared with an ethanol/water ratio of 7 (CS_7) (Fig. 1) was the best-performing material when considering both OMPs. The synthesized material was promising for the removal of diclofenac and venlafaxine from water, and the removal efficiencies with CS_7 were between 71% and 100% when considering 24 target OMPs in secondary urban wastewater. Thus, they are an interesting option for water or wastewater treatment.

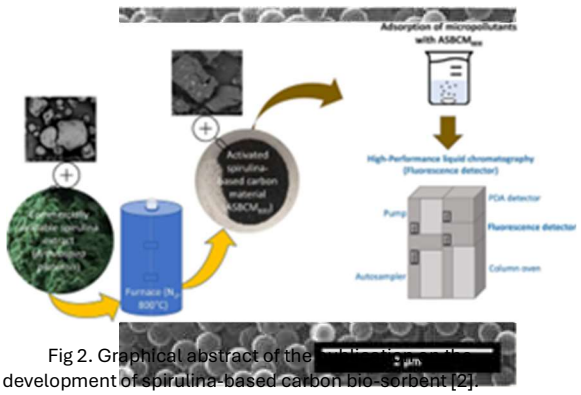

Fig 1. Scanning electron microscopy micrographs of CS7

Moreover, activated spirulina-based carbon material ($ASBCM_{800}$) with a high specific surface area was developed to eliminate a wide range of micropollutants (MPs) frequently detected in wastewater (Fig. 2). The high efficiency of this bio-sorbent for removing most of the 20 target OMPs (14 pharmaceuticals and 6 pesticides) from effluents of UWWTPs demonstrated that this is a good strategy to eliminate trace OMPs from complex water matrices while contributing to control spirulina algal blooms. This work was performed in collaboration with two research groups from *Universidad Politécnica de Madrid* and the University of Belgrade [2]. Given its excellent performance, $ASBCM_{800}$ was tested in a miniaturized extraction method based on SBSE for sample preparation of various water matrices and preconcentration of OMPs. Carbon materials, namely activated carbon and multiwalled carbon nanotubes (MWCNTs), were tested as a sorbent coating on the magnetic stirrer and compared to activated spirulina. The produced coated magnets were tested for adsorption-desorption of 4 model pharmaceuticals, under various pH of sample and elution solvents. Spirulina-based SBSE performed better than all the other coated magnets and even better than the commercial-based SBSE (*manuscript in preparation*). More than 89% adsorption was observed for 4 pharmaceutical compounds, whereas desorption recoveries were reproducible and between 51 and 63%. A proof-of-concept of the SBSE for adsorption-desorption cycles was

Fig 2. Graphical abstract of the development of spirulina-based carbon bio-sorbent [2].

demonstrated to analyse wastewater matrices by ultra-high performance liquid chromatography coupled to tandem mass spectrometry (UHPLC-MS/MS).

Another technology for adsorption-desorption of OMPs was developed. Pristine and functionalized MWCNTs were investigated as adsorbent materials packed in SPE cartridges for extraction and preconcentration of 8 EU-relevant organic micropollutants (with different p*K*a and polarity) before UHPLC-MS/MS analysis of surface water [3]. The recoveries obtained were higher than 60% for 5/8 target pollutants. The optimized SPE procedure with pristine MWCNTs has the great advantage of using an eco-friendly solvent (ethanol) for both conditioning and elution steps. Additional advantages of this carbon-based cartridge are the small amount of adsorbent that is needed (50 mg), representing a ~75% cost reduction in comparison with the commercial cartridge (while obtaining similar recoveries), and the ability to be reused at least three times without substantial impact on the retention capacity of the adsorbent.

Multi-layer carbon cartridges with MWCNTs and carbon xerogels (CXs) were tested as a proof of concept [4]. The optimized cartridge configuration was able to extract the 8 target OMPs (with different p*K*a and polarity ranges) at once, using an eco-friendly solvent and a low load of sorbents. Furthermore, this cartridge can be reused at least three times without affecting the extraction efficiency. Therefore, an analytical methodology based on SPE-UHPLC–MS/MS was then validated using the innovative multi-layer carbon-based cartridge. The potential of this method for monitoring EU-relevant OMPs was demonstrated through a monitoring campaign focusing on surface water upstream and downstream, a drinking water treatment plant and also water samples collected from the tap, which confirmed the occurrence of a wide range of OMPs (at ng L^{-1} levels).

All synthesized carbon materials used in these studies were characterized by several techniques, such as thermogravimetric analysis, N_2 adsorption-desorption isotherms, temperature-programmed desorption (Fig. 3), attenuated total reflection Fourier transformed infrared spectroscopy, scanning and transmission electron microscopies, among others.

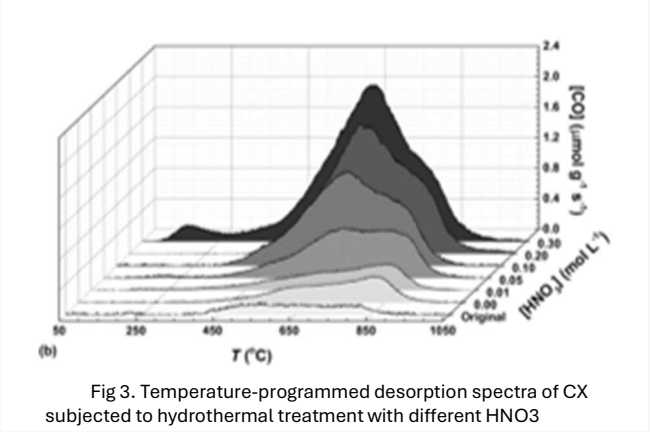

Fig 3. Temperature-programmed desorption spectra of CX subjected to hydrothermal treatment with different HNO3

Moreover, we have submitted a request for patenting packing material for SPE and preconcentration of coronavirus proteins and OMPs [P1], but the full application did not proceed further since the coronavirus issue was no longer timely.

Future Work

Further work comprises the study (*i.e.*, production, functionalization, and characterization) of other carbon materials, such as carbon fibers, graphene, graphene oxide, and also bio-based carbon materials, in line with the principle of circular economy, as adsorbents for both the extraction and removal of different OMPs from environmental relevant water matrices.

The knowledge derived from these research studies has groundbreaking and innovative implications in two crucial areas: water monitoring and treatment.

Related Sustainable Development Goals

Outputs

PhD Theses

Marta Sofia Oliveira Barbosa, Multi-layer carbon cartridges for determination of EU multi-class organic micropollutants, PDEQB, FEUP, 2021

Master Dissertations

Ana Luísa Santos Vieira, Development of nanostructured carbon spheres for environmental applications, MIEQ, FEUP, 2021

Patents

A.M.T. Silva, R.S. Ribeiro, A.R.L. Ribeiro, M.F.R. Pereira, M.O. Barbosa, Packing material for solid-phase extraction and preconcentration of coronavirus proteins and organic compounds (Ref. PAT386), Provisional Patent Application, submitted to INPI - National Institute of Industrial Property (Portugal), 2021

Selected Publications

[1] A.L.S Vieira et al., J. Environ. Chem. Eng., 10, 107348, (2022)
[2] M. Pedrosa et al., Environ..l Nanotechnol. Monit. Manag., 18, 100720 (2022)
[3] M.O. Barbosa et al., Sci. Rep., 11, 13817 (2021)
[4] M.O. Barbosa et al., Sci. Rep., 10, 22304 (2020)

Team

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Funding

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LA LSRE-LCM Funding, UID/EQU/50020/2019, 2019
LA LSRE-LCM Funding, POCI-01-0145-FEDER-006984,2013-2018
InSpeCt, NORTE-01-0145-FEDER-031049, 2018-2022
DRopH2O, 2022.08738.PTDC, 2023-2026
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KEYWORDS: Membranes/ Catalysts/ Carbon materials/ Integrated processes/ Organic contaminants

Water remediation can benefit from a combination of technologies, with membranes playing a significant role in ensuring the removal of contaminants to obtain safe drinkable water or proper wastewater for reuse, and also for desalination purposes. An alternative approach that has been investigated to enhance the efficiency of treatment processes relies on the combination of advanced oxidation processes (AOPs) with membrane technologies. Thus, advances in membrane development and integrated processes can contribute significantly to improve water purification.

Introduction

The growing severity of water scarcity emphasises the urgency of finding viable and efficient solutions for water and wastewater treatment. Achieving and maintaining high-quality water production is essential to ensure its suitability for consumption and reuse in other activities, such as irrigation. Membranes play a pivotal role in different water remediation strategies, separating contaminants and/or contributing as catalytic membranes in degradation reactions. Alternative approaches have been investigated to enhance the efficiency of water treatment by combining AOPs with membrane separation technologies.

Current Development

Various carbon materials have been developed as catalysts and incorporated as active phases during the fabrication of membranes for water treatment, thus promoting reusability and eliminating the need for powdered catalysts separation from the reaction media at the end of the treatment process. Given the promising catalytic activity of graphene derivatives for several reactions, their immobilization can be an effective water treatment option, with most studies reporting their use in photocatalysis, PS/PMS activation and electrocatalysis [4].

Supported membranes were fabricated by simple vacuum filtration of nitrogen-doped reduced graphene oxide (rGO) [5] or commercial rGO [6] onto a polytetrafluoroethylene (PTFE) support and employed in persulphate (PS) activation for the degradation of phenol [5, 6], oxalic acid [5], or venlafaxine (VFX) [6] under continuous mode of operation. The presence of N- and O- functionalities appeared to promote PS dissociation into reactive oxygen species (ROS), which scavenging tests revealed the important contribution of singlet oxygen, governing the removal of water organic pollutants [5, 6]. Four water matrices (*i.e.,* distilled, bottled, surface water, and treated urban wastewater) were employed, confirming high catalytic activity obtained for operation periods of up to 2 – 3 days [6]. Another supported membrane was developed by Pd-Cu/C filtered onto polypropylene and tested in a flow-through catalytic membrane reactor (FTCMR) for the reduction of NO_3^-, NO_2^- and BrO_3^- in drinking water treatment, with promising results reducing NO_3^- in water remediation [7]. Regarding a different application, such as gas permeability and selectivity, GO membranes, prepared by vacuum filtration on cellulose, demonstrated high separation factors for small gas molecules [8]. This research study resulted from a collaboration with Dr. George Romanos from NCSR - Demokritos (Athens, Greece), where gas-phase experiments were also performed. Before water removal, all the membranes behaved as impermeable barriers but after their conditioning in high vacuum, they were transformed to effective molecular sieves, exhibiting high separation factors for small gas molecules [8].

To improve stability for long-term usage, composite membranes were prepared by incorporation of carbon nanotubes (CNTs) [9], graphitic carbon nitride (g-C_3N_4) [2, 10] and N-doped rGO [3, 11] within a polyvinylidene fluoride (PVDF) matrix. These membranes were tested for the removal of aqueous micropollutants (MPs: 3 fluoroquinolone antibiotics [11], VFX [2, 9], and a mixture of VFX, metoprolol, and diclofenac [10]) or microorganisms [3] by PS activation [3, 9, 11] or photocatalysis [2, 10]. PS activation catalysis with N-doped rGO-PVDF membranes provided 54-91% conversions of 3 fluoroquinolones, with proven resistance towards fouling [11], as well as disinfection by reducing the abundance of cultivable microorganisms (total heterotrophs, enterobacteria, enterococci) in surface water samples to values below the limit of detection (< 0.5 CFU mL^{-1}) up to 24 h operation (Fig. 1) [3]. Hence, the proposed system can be considered a promising technology for the removal of organic contaminants and harmful microbiota during drinking water production in continuous flow mode.

Moreover, plastic-derived CNTs composite PVDF membranes were active for the removal of VFX in surface water, the treated water revealing no ecotoxicity nor phytotoxicity [9]. The g-C_3N_4 has been reported as a very active visible light-driven photocatalyst and its immobilization on a PVDF network

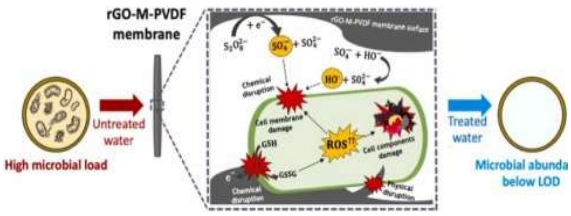

Fig 1. Schematic representation of the reaction mechanism of the catalytic N-doped rGO-PVDF membrane in PS activation for desinfection [3].

provided stable and reusable membranes for the degradation of MPs under continuous flow mode of operation with light emitting diodes (LED > 400 nm) [2, 10]. However, it was less effective when real water matrices were employed (Fig. 2) [2, 10].

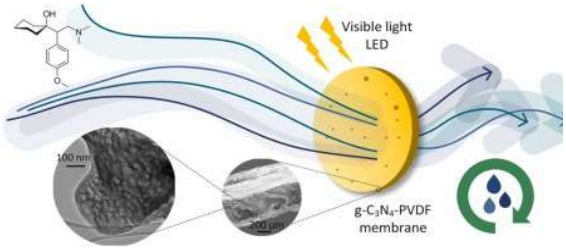

Fig 2. Schematic representation of the photocalytic g-C3N4-PVDF membrane [2].

A different microbiological study was performed to assess the performance of polycarbonate (PC), cellulose nitrate (CN), and polyethersulfone (PES) filtering membranes (0.22 μm pore

size) with very low microbial abundance natural waters [12]. Filtration time, DNA extraction yield, the abundance of selected genes, and bacterial community composition were the studied variables [12]. CN filters were cheaper, required lower filtration times and produced results that were not significantly different from PC or PES, thus being a good alternative to analyze waters with low biomass content [12].

A collaboration with the LEPABE R&D unit at FEUP, and the University of Granada, Spain, resulted in an effective alternative for treating olive mill wastewater (OMW), while simultaneously recovering water [1]. This innovative approach was introduced by integrating catalytic wet peroxide oxidation (CWPO) with direct contact membrane distillation (DCMD) (Fig. 3) [1]. OMW was initially treated by catalytic wet peroxidation [1] in a fixed–bed reactor (FBR) developed at LEPABE and working in continuous flow mode and employing a Fe–activated carbon derived–catalyst, prepared by using olive stones as precursor [1]. The resulting CWPO–treated samples of OMW were introduced in a direct contact membrane distillation (DCMD) unit at LSRE-LCM, resulting in higher fluxes than those obtained with the analogous untreated OMW samples, also showing higher rejections of organic matter from the feed solution upon DCMD, highlighting the benefits of this integrated process [1]. The produced permeate exhibited several parameters below the legislated thresholds required for direct discharge for crop irrigation (Portuguese Decree-law 119/2019) [1]. Moreover, the OMW resulting from the DCMD process (retentate), with approximately double the organic load of the initial samples, could be recirculated to the FBR, maintaining similar removal efficiencies as those previously obtained with

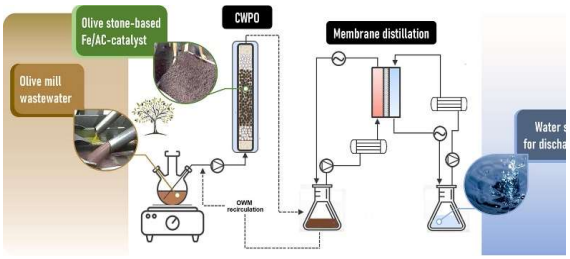

Fig 3. Schematic representation of the integrated process (CWPO and DCMD) for recovering olive mill wastewater [1]

the original OMW samples [1]. DCMD employed a commercial PTFE membrane, and it was used to separate water (vapor) on the permeate side, while particles and non-volatile undesired compounds were concentrated in the retentate side. Another DCMD configuration (with a PTFE membrane) was used to produce drinking water from seawater and it presented a high removal efficiency (≥ 99 %) of microplastics [13].

Future Work

Additional investigation is still required to consolidate the development and application of catalytic and non-catalytic membranes. Eco-friendly materials and innovative membrane fabrication strategies are highly desirable, promoting selectivity and water permeability, with reduced production costs and energy requirements. For catalytic membranes, their reactivity with the generated ROS is of paramount significance, for a long-term stability and potential commerciality. Moreover, the use of environmentally relevant water matrices in research is preferable, as it resembles a more realistic scenario for the retention and/or degradation of microcontaminants and microorganisms, for the production of drinkable water or wastewater with enough quality for its reuse.

Exploring integrated approaches can be very useful in addressing a variety of contaminants, as it leverages the strengths of different treatments, overcoming their individual limitations to ensure more thorough water remediation. Additionally, life cycle assessment and cost analysis are also necessary to assess the viability of membrane processes.

Related Sustainable Development Goals

Outputs

PhD Theses

Marta Pedrosa, Graphene-based catalytic membranes for water treatment, PDEQB, FEUP, 2019

Mariana Miranda, Behavior and attenuation of microplastics in environmental compartments, PDEQB, FEUP, 2023

Master Dissertations

O. Vieira, Smart metal-free materials for persulfate activation and degradation of water organic micropollutants, Integrated Master's in Environmental Engineering, FEUP, 2019

I. Gonçalves, Persulfate activation for venlafaxine degradation in the presence of reduced graphene oxide (translated title), Integrated Master's in Chemical Engineering, FEUP, 2021

L. Azevedo, Carbon membranes for water treatment, Integrated Master's in Environmental Engineering, FEUP, 2021

J. Marrero, Catalytic membranes for water disinfection (translated title), Integrated Master's in Chemical Engineering, FEUP, 2022

Selected Publications

[1] B.M. Esteves, et al., Chem. Eng. J. 448, (2022).
[2] L. Valenzuela, et al., Catalysis Today. 418, (2023).
[3] J.A. Marrero, et al., J Environ. Chem. Eng. 11, (2023).
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[6] A. Cruz-Alcalde, et al., Chem. Eng. J. 427, (2022).
[7] A. Marí, et al., J. Environ. Chem. Eng. 11, (2023).
[8] C.P. Athanasekou, et al., Chem. Eng. J. Adv. 5, (2021).
[9] R.S. Ribeiro, et al., J. Environ. Manage. 308, (2022).
[10] J. Nieto-Sandoval, et al., J. Environ. Chem. Eng. 11, (2023).
[11] O. Vieira, et al., Chem. Eng. J. 402, (2020).
[12] J. Abreu-Silva, et al., J. Environ. Chem. Eng. 11, (2023).
[13] M.N. Miranda, et al., Desalination. 565, (2023).

Team

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Healthy Waters, NORTE-01-0145-FEDER-000069
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AIProcMat@N2020, NORTE-01-0145-FEDER-000006, 2016-2019
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Water Characterization, Desalination and Purification

Behavior and Attenuation of Microplastics in Environmental Compartments

KEYWORDS: Microplastics; Aging; Membrane Distillation; Biocatalysis; Micropollutants; Desalination; Urban Environments.

Microplastics have been classified as contaminants of emerging concern; however, several research gaps have been identified that need to be tackled to effectively fight the (micro)plastic pollution that is present in every environmental compartment (water, air, soil and sediments, and biota). Understanding the behavior of microplastics, including their aging (gradual degradation) in different environments and their interactions with co-occurring contaminants, is key to increase our fundamental knowledge on this topic and facilitate the development of solutions to prevent and remove microplastics and other micropollutants from the environment, while minimizing the impacts on biota and human health.

Introduction

The increasing abundance and dispersion of plastics in the environment and the better understanding of the resulting impacts have led to the rise of international concern among the public, policymakers, and researchers. Classifying plastics as contaminants is particularly alarming due to the constant growth of plastic production since the WWII (Fig. 1), and the consequent pressure this creates due to the use of resources and the fragmentation of plastic in the environment into smaller particles.

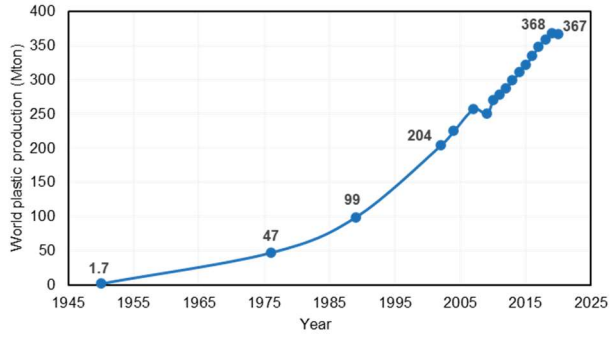

Fig 1. World plastic production from 1950 to 2020
(updated from [1] with Plastics Europe 2021 report data).

While the plastic waste polluting the environment has a variety of sizes, chemical compositions, and shapes, microplastics (longest diameter or length being less than 5 mm) are of special concern because of the current knowledge gaps with respect to the chemical and physical adverse effects on organisms, their distribution, mobility and fate in the different environmental compartments, and the necessary adequate responses to solve this environmental issue. Because of this, microplastics have been classified as one of the newest contaminants of emerging concern (CECs).

Although the risk of microplastics to human health is yet to be established, the growing amount of reports related to the detection of plastics in food, beverages, air dust and on human tissue and biological samples has been rising concern about their potential toxicological impacts to our species. In particular, the microplastics presence in drinking water is of major importance due to its universal and daily consumption.

Current Development

DPSIR stands for driving forces, pressures, states, impacts and responses, and it is the causal framework adopted by the European Environmental Agency to describe the interactions between society and the environment. This framework was applied to microplastic pollution (Fig. 2) to organize key information on this topic and define the research questions that would guide the next steps of the research group. The responses component of the DPSIR analysis was explored in more detail, providing a literature review up to the first half of 2019 on the upstream and downstream responses to the microplastic pollution:

1. Upstream: regulatory and policy instruments, environmental education, product design and biodegradable plastics, waste management, and effluent treatment;
2. Downstream: biotechnology tools, drinking water treatment plants, environmental cleanups, and other mitigation technologies and strategies for air, soil and water.

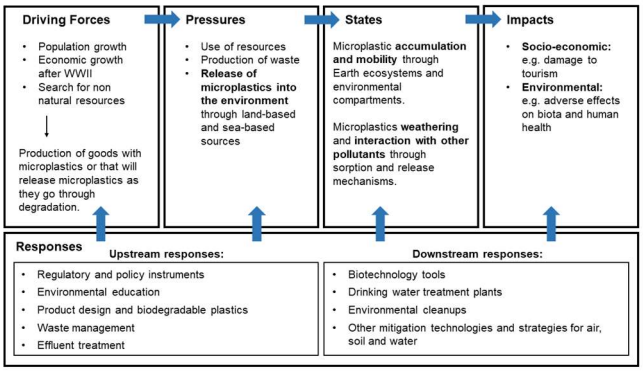

Fig 2. DPSIR analysis for microplastic pollution [1].

While microplastics stand out as a threat on their own to the environment and to public health, it has been acknowledged that they can have increased adverse effects because they may act as vectors for the transport of co-occurring contaminants and microorganisms. The polymer's original characteristics influence the behavior of the microplastic particles (MPPs) in the environment. However, it is known that plastic in the environment differs from virgin plastic because: i) it undergoes aging (including weathering and consequent fragmentation), ii) additives are added during the plastic item production, iii) pollutants can be sorbed by the plastic, and iv) there is the possibility of biofilm formation on the surface of the particles.

Taking this into consideration, we started by assessing the aging of microplastics after exposing commercial virgin MPPs of LDPE – low-density polyethylene, PET – poly(ethylene terephthalate), and uPVC – unplasticized poly(vinyl chloride) to ozone, UV-C, artificial solar radiation, and real weathering conditions in a city building rooftop [2]. This allowed to investigate the aging of MPPs under urban environment stressors and identify the subsequent changes in their chemical structure (ATR-FTIR), surface morphology (SEM) and crystallinity (XRD). Additionally, the Carbonyl Index was

used as a metric of the oxidation of the MPPs, leading to the quantification of some of the changes in the chemical structure through time. This first study expanded the knowledge on the most effective aging agents for each polymer and the consequent modifications on the MPPs, while providing aged MPPs for the following experiments. The aging agents studied were demonstrated to affect the microplastics differently depending on the polymer, with LDPE being aged by all treatments (mostly by ozone and weathering), PET presumed to have been slightly aged by ozone and weathering, and uPVC aged more when exposed to the UV-C treatments and weathering.

As our next step, we focused on exploring the interaction of MPPs with co-occurring contaminants, namely with ten organic micropollutants (OMPs) that include pesticides (alachlor, clofibric acid, diuron, pentachlorophenol) and pharmaceutical substances (citalopram, diclofenac, florfenicol, tramadol, trimethoprim, and venlafaxine). Through sorption batch experiments with virgin and aged (ozone-aged or weathered) MPPs, the sorption kinetics, sorption equilibrium isotherms and the role of the MPPs aging on the sorption capacities were explored [3]. This second component of our study gave evidence of the major role that plastic aging can have in the sorption process of OMPs on MPPs (Fig. 3), while allowing to identify the affinity between the studied polymers and OMPs, and link the modifications identified for the aged MPPs to their increased sorption capacity for OMPs. Exploring the hypothesis that MPPs can act as vectors for the transport of co-occurring contaminants, phytotoxicity tests were carried out to evaluate the mobility of the OMPs sorbed on the MPPs and the potential effects on germination and early growth of the combo of MPPs and OMPs on two species of plants (*Lepidium sativum* and *Sinapis alba*). The results suggest low or no phytotoxicity effect under the conditions tested, providing insight into MPPs' potential impacts on soil-plant systems.

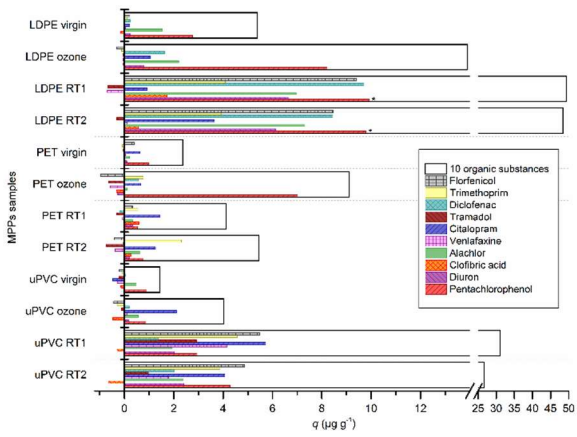

Fig 3. Sorption capacity of LDPE, PET and uPVC before and after aging by ozone gas for 1 h or weathering for 3 months in an urban rooftop (RT) during summer in Porto (RT2 includes the effect of precipitation) [4].

More recently, we explored the behavior and attenuation of MPPs during a membrane distillation treatment, at a lab-scale, namely by using the direct contact membrane distillation (DCMD) technology [5]. The main goals of this work comprised the i) assessment of MPs behavior and removal during a lab-scale treatment of seawater with DCMD, and ii) the potential impact of the presence of MPs in the DCMD process regarding the amount of water produced and its quality. For that, i) filtered seawater with known spiked amounts of MPs of unplasticized poly(vinyl chloride) (uPVC) was fed into the DCMD system, ii) the MD parameters (vapor pressure gradient, membrane permeability for water, and the interval permeate flux) were monitored during the experiments, iii) the quality of the treated water was assessed in terms of its conductivity, salinity and presence of MPs (> 1.2 µm by Raman microscopy), iv) the MPs were recovered and characterized to assess their potential aging during the treatment, v) the membrane used in each experiment was characterized. The data collected revealed that a high load of MPs (> 0.1 g L^{-1} of uPVC) can decrease the amount of treated water produced. However, under the expected loads found in the environment, the presence of MPs that are relatively resistant to temperature is expected to have minimal interference with the normal operation of a desalination unit based on DCMD. The treated water quality was good concerning conductivity (maximum 10.6 µS cm^{-1}) and salinity (0.0 ppt), with no signs of the spiked MPs being found in it. At the end of the experiments, MPs were recovered from the system, suggesting a very high removal efficiency with MD (≥ 99%). This constitutes one of the first assessments of this technology to remove MPs during desalination, with favorable results, and raises new research questions to be tackled in the future.

Future Work

Methodologies for analysing microplastics in real waters are being developed. Adsorption and biocatalysis are also under investigation as decontamination processes targeting microplastics and other water pollutants, such as polycyclic aromatic hydrocarbons (PAHs), pesticides, and pharmaceutical compounds. Bioremediation studies are being carried out with specific enzymes' biocatalytic activities. New adsorbent materials will be considered and hemeproteins less explored before are being studied, combining experimental and computational methods in collaboration with a partner at the Universidad Autónoma de Madrid, Spain. A PhD student is being supported with an FCT fellowship in the topic of Enzyme-assisted remediation processes.

Related Sustainable Development Goals

Outputs

PhD Dissertation

Mariana N. Miranda, Behavior and attenuation of microplastics in environmental compartments, PDEQB, FEUP, 2023

Master Dissertation

Iara da Mota Lameira, Metodologia de análise de microplásticos em águas: Redução das interferências causadas pela matéria particulada, MEA, FEUP, 2023

Selected Publications

[1] M. N. Miranda *et al.*, Sci. Total Environ. 718 (2020): 134968.
[2] M. N. Miranda *et al.*, Sci. Total Environ. 796 (2021): 148914.
[3] M. N. Miranda *et al.*, Sci. Total Environ. 850 (2022): 158073.
[4] M. N. Miranda *et al.*, In Proceedings of the 3rd International Conference on Microplastic Pollution in the Mediterranean Sea. ICMPMS 2022, 97-104. Springer Water (2023).
[5] M. N. Miranda *et al.*, Desalination 565 (2023): 116846.

Team

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FCT, PD/BD/137730/2018, extended by COVID/BD/152633/2022
Healthy Waters, NORTE-01-0145-FEDER-000069
DRopH2O, 2022.08738.PTDC