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SMART METAL-FREE MATERIALS FOR PERSULFATE ACTIVATION AND DEGRADATION OF WATER ORGANIC MICROPOLLUTANTS

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Abstract

Conventional urban wastewater treatment plants (WWTPs) are not designed to eliminate water organic micropollutants (MPs). As consequence, the presence of these contaminants in surface water and drinking water is a concern that can lead to adverse effects on the environment and human health. Thus, it is essential to found suitable treatment technologies, such as those based on advanced oxidation and technologies (AOTs), which can mitigate this problem. In this domain, AOTs based on sulfate radicals ($SO_4^{\bullet-}$) have recently become a focus of attention for the scientific community.

This study aims to explore the potential of the smart design of metal-free carbon materials for the activated persulfate oxidation and degradation of three organic fluoroquinolone antibiotics (ofloxacin, ciprofloxacin and enrofloxacin). To achieve this goal, N-doped reduced graphene oxide (rGO-M) was prepared from graphite, using melamine as nitrogen source. This material was then used to manufacture two different types of carbon-based catalytic membranes (supported and polymeric membranes). The performance of the catalytic membranes for the removal of MPs by activated persulfate oxidation was investigated, as well as the impact of employing river water as matrix instead of laboratory-grade (UP) water.

Activated persulfate oxidation experiments performed in continuous mode of operation with both membranes demonstrated the effectiveness of these materials for the degradation of MPs in UP water (conversions of 83 - 90% after 24 h of operation). The efficiency of the treatment processes decreased considerably when surface water (SW) was employed instead of UP water. Two reaction by-products were observed in the experiments performed with both membranes. Lastly, the catalytic stability of the metal-free carbon supported membrane was evaluated in UP water. Although partial deactivation occurred, this membrane still maintains a considerable catalytic activity for degradation of the target MPs even after 90 h of operation in continuous mode.

Keywords:

Contaminants of emerging concern (CECs)

Metal-free catalytic membranes

N-doped reduced graphene oxide

Activated persulfate oxidation

Water matrix effect

Resumo

As estações de tratamento de águas residuais urbanas convencionais, não são desenhadas para eliminar os micropoluentes orgânicos das águas. Consequentemente, a presença desses contaminantes na água superficial e na água potável podem causar efeitos adversos no ambiente e na saúde pública. Por isso, é essencial encontrar tecnologias adequadas de tratamento, tais como aquelas baseadas em tecnologias avançadas de oxidação, que podem mitigar esse problema. Neste domínio, as tecnologias avançadas de oxidação baseadas em radicais de sulfato ($SO_4^{\bullet-}$) têm sido, recentemente, alvo de atenção por parte da comunidade científica.

Este estudo visa explorar o potencial do desenho inteligente de materiais de carbono, livres de metais, para a ativação do persulfato e a degradação de três antibióticos orgânicos da classe química das fluoroquinolonas (a saber, a ofloxacina, a ciprofloxacina e a enrofloxacina). De modo a alcançar este objetivo, foi preparado um material de óxido de grafeno reduzido e funcionalizado com azoto a partir de grafite, usando a melamina como precursor. Este material foi utilizado para fabricar dois tipos diferentes de membranas catalíticas à base de carbono (designadas de suportadas e poliméricas). Em seguida, foi avaliado o desempenho das membranas catalíticas para a remoção dos micropoluentes por oxidação com ativação de persulfato, bem como o impacto de utilizar água do rio como matriz em vez de água ultrapura.

Os testes de oxidação com ativação do persulfato, realizados em modo contínuo com ambas as membranas, demonstraram a efetividade desses materiais na degradação de micropoluentes na água ultrapura, correspondendo a conversões na gama dos 83-90% após 24 h de operação. A eficiência do processo de tratamento diminuiu consideravelmente quando água do rio foi utilizada em vez de água ultrapura. Dois subprodutos de reação foram observados nos ensaios realizados com os dois tipos de membranas. Por fim, a estabilidade catalítica das membranas suportadas à base de materiais de carbono, livres de metais, foi avaliada em água ultrapura. Apesar de ocorrer desativação parcial, esta membrana ainda manteve uma atividade catalítica considerável para a degradação dos micropoluentes alvo, mesmo após 90 h de operação em modo contínuo.

Palavras-Chave: Contaminantes de preocupação emergente

Membranas catalíticas livres de metais

Óxido de grafeno reduzido e funcionalizado com azoto

Oxidação com ativação do persulfato

Efeito da matriz aquosa

Declaration

I hereby declare, on my word of honor, that this work is original and that all non-original contributions were properly referenced with source identification.

Sign and date

Index

List of figures

List of tables

Notation and Glossary

A	Effective area of membrane	m^2
[Cipro]	Concentration of Ciprofloxacin	$\mu g\ L^{-1}$
[Enro]	Concentration of Enrofloxacin	$\mu g\ L^{-1}$
[Oflo]	Concentration of Ofloxacin	$\mu g\ L^{-1}$
r^2	Coefficient of determination	*
Q	Water flow rate	$mL\ min^{-1}$
J_w	Water flux	$L\ m^{-2}\ h^{-1}$
Δt	Time between permeate collected samples	h
V	Volume of permeate collected samples	L

Indexes

i	Index referring to a specific pollutant
0	t = 0 min for the experiment

List of Acronyms

AOPs	Advanced oxidation processes
AOTs	Advanced oxidation technologies
B	Boron
Cipro	Ciprofloxacin
CECs	Contaminants of emerging concern
DPD	N,N-Dietyl-p-plenylenediamine sulfate
EC	European Commission
EU	European Union
Enro	Enrofloxacin
FD	Fluorescence Detector
ISCO	In-situ chemical oxidation
LC	Liquid chromatography
M	Melamine
MPs	Micropollutants
N	Nitrogen
NMP	1-methyl-2-pyrrolidone
Oflo	Ofloxacin
P	Phosphorus
PVDF	Poly(vinylidene fluoride)
PVP	Polyvinylpyrrolidone
PSs	Priority substances
rGO	Reduced graphene oxide
rGO-M	Nitrogen-doped reduced graphene oxide
SPS	Sodium persulfate
S	Sulfur
SW	Surface water
UHPLC	Ultra-high-performance liquid chromatography
UP	Ultrapure water
UV	Ultraviolet
WWTPs	Wastewater treatment plants

1. Introduction

1.1. Framework

Water is a vital natural resource for all living beings and ecosystems. As such, the sustainable management of water is of paramount importance. Currently, the presence of micropollutants (MPs) in water is of major concern due to the possible adverse effects on the environment and human health [1]. Recognizing the relevance of this topic, the EU has been issuing Directives (2008/105/EC and 2013/39/EU) to define priority substances (PSs) that must be monitored, as well as Decisions (2015/495/EU and 2018/840/EU) to define and update a Watch List of contaminants of emerging concern (CECs) for which additional monitoring/impact studies are required [2-5].

MPs (e.g., pesticides, synthetic and natural hormones, industrial compounds, pharmaceuticals and personal care products, among others) are typically released to the aquatic environment in trace concentrations (in the scale of ng L^{-1} to µg L^{-1}) [6]. Conventional urban wastewater treatment plants (WWTPs), implementing traditional biological treatments, are not designed to eliminate such compounds, since some of them are toxic, resistant to biodegradation and can persist in the environment for long periods [1, 7-9]. Some advanced urban wastewater treatment technologies have been studied for years, such as ozonation, adsorption on activated carbon and filtration [1]. Nevertheless, it is still essential to found more cost-effective alternatives [1]. Advanced oxidation processes (AOPs) and technologies (AOTs) have been proposed as a promising alternative [8].

AOTs based on sulfate radicals ($SO_4^{\bullet-}$) have recently gained more attention from the scientific community [8]. Peroxymonosulfate and persulfate can be both activated by different approaches for the formation of these $SO_4^{\bullet-}$ radicals (e.g., thermal, alkaline, or radiation methods, or employing metal or non-metal catalysts) [10]. $SO_4^{\bullet-}$ radicals possess high redox potential (2.5–3.1 V), thus being able to oxidize most of the organic compounds in aqueous phase [8]. The whole process is known as activated persulfate oxidation. Metal-free carbon materials, namely graphene-based materials, can act as activators/catalysts for this process [8]. Pedrosa et al. recently (2019) showed that N-doped reduced graphene oxide (rGO-M) can be shaped as a metal-free carbon-supported catalytic membrane, and then employed in activated persulfate oxidation for degradation of phenol in aqueous solution (5 mg L^{-1}) when operating in both recirculation and dead-end continuous mode [11]. This strategy avoids the constrains usually associated to the use of powder catalysts [11]. However, further studies are needed in order to increase the activity and stability of the catalytic membranes for the

removal of MPs, and to evaluate the impact of employing realistic water matrices instead of laboratory-grade water.

1.2. Objectives

The main goal of this study is to explore the potential of the smart design of metal-free carbon materials for the continuous mode activated persulfate oxidation of organic MPs that can be found in surface water and, as consequence, in drinking water. A mixture of three fluoroquinolone antibiotics (ofloxacin, ciprofloxacin and enrofloxacin) was studied, one of them recently included in the Watch List of Commission Decision 2018/840/EU. Specific objectives of this work were accordingly set as:

- Preparation of rGO-M (i.e., the N-doped reduced graphene oxide catalyst previously reported as efficient for activated persulfate oxidation);
- Preparation of a carbon-supported catalytic membrane, using rGO-M;
- Evaluation of the performance of the carbon-supported catalytic membrane in the activated persulfate oxidation of the selected MPs;
- Preparation of a nanocomposite poly(vinylidene fluoride) (PVDF) membrane, obtained by inclusion of rGO-M during the polymerization step (denoted as polymeric membrane);
- Explore the possibility of using the polymeric membrane in the activated persulfate oxidation of the selected MPs;
- Evaluation of the effect of the water matrix on the proposed treatment technology, by preparing model solutions containing the three MPs under study in two different water matrices, namely ultrapure (UP) water and surface water (SW).

1.3. Presentation of the host institution

This project was carried out in the "Catalysis and Carbon Materials" Group of Associate Laboratory LSRE-LCM, which is a partnership between LSRE - Laboratory of Separation and Reaction Engineering, and LCM - Laboratory of Catalysis and Materials. The main location of LSRE-LCM is the Department of Chemical Engineering at FEUP - Faculdade de Engenharia da Universidade do Porto.

1.4. Contributions of the Work

The work I have done for this dissertation falls within the framework of Project InSpeCt - *Identifying and interrupting micropollutants of EU concern by using Smart Carbon materials* (Principal Investigator: Professor Adrián M.T. Silva). At an early stage, graphite oxide was provided by Marta Pedrosa. I used it to prepare the N-doped reduced graphene oxide material (rGO-M) needed to perform preliminary tests for membrane optimization (amount of rGO-M,

and thickness of polymeric membranes). Afterwards, I prepared graphite oxide, rGO-M, and two types of metal-free carbon membranes (supported and polymeric). I have also assisted in the assembly of the installation used to perform the experiments in continuous mode, and I determined the calibration curves of the peristaltic pump and those for all the analytical techniques employed. Then, I performed the non-catalytic (batch-mode), and adsorption and activated persulfate oxidation experiments (continuous mode). I collected samples for the determination of MPs and sodium persulfate (SPS) concentrations during all the experiments, and I performed permeate water flux (J_W) measurements during the experiments performed in continuous mode. I analyzed all the data obtained by ultra-high-performance liquid chromatography (UHPLC) in order to determine the concentration of MPs in each sample. In this case, the UHPLC method was previously developed and optimized by Dr. Ana Rita Lado Ribeiro, who provided all subsequent technical support together with Dr. Alexandra Maia and Marta O. Barbosa. The colorimetric method for SPS quantification was previously developed and optimized by Marta Pedrosa and my co-supervisor, Dr. Rui S. Ribeiro. Routine SPS measurements were also performed with the help of my co-supervisor. Surface water (SW) was provided by Ana M. Gorito. Regarding characterization techniques, I followed up the water contact-angle measurements that were performed in order to evaluate the hydrophobicity/hydrophilicity of the metal-free carbon membranes.

1.5. Organization of the thesis

A general overview of the methods employed in the literature for peroxymonosulfate and persulfate activation, i.e. for the formation of $SO_4^{\bullet-}$ radicals, is provided in Chapter 2 with focus on carbon-based materials. The relevance of the selected MPs is also discussed in this chapter.

The materials and methods for preparing the graphene derivatives (graphite oxide, N-doped reduced graphene oxide and respective supported and polymeric membranes) are described in Chapter 3, as well as the experimental set-up for activated persulfate experiments and the contact angle measurements for the characterization of the prepared membranes. In addition, a brief explanation of the analytical methods used for determination of MPs and persulfate concentration is included in this chapter.

The results are presented and discussed in Chapter 4, in terms of the performance of the AOT employed when testing different types of metal-free carbon membranes, aqueous matrices, and initial concentrations of MPs, also assessing the formation of reaction by-products and the stability of one type of membrane.

The conclusions are summarized in Chapter 5. Finally, the advantages and limitations of the work done are evaluated in Chapter 6, proposing steps for future developments.

2. Context and State of the art

The decision on the best technology (e.g., tertiary treatment) to minimize the release of MPs into the environment depends on the required effluent quality and on the current performance of the conventional treatment performed in the WWTP [1]. An extensive review of the literature on consolidated (e.g., adsorption on activated carbon, ozonation and filtration) and new advanced treatment methods (e.g., photocatalysis, electrochemical oxidation, sonolysis) for the removal of MPs from urban wastewater is provided by Rizzo et al. (2019) [1]. These technologies can be also considered in the future for processing surface water collected by drinking water treatment plants (DWTPs). In spite of all the efforts done, more cost-effective technological solutions are still needed [1], and this is also the case for activated persulfate oxidation. This AOT is based on the action of $SO_4^{\bullet-}$ radicals, which present high reactivity with organic contaminants and high selectivity in complex environmental matrices [12]. Peroxymonosulfate and persulfate are both typically used as source of $SO_4^{\bullet-}$ radicals. Different strategies can be employed to obtain these radials, often denoted as activation methods [8].

2.1. Activation methods

Peroxymonosulfate and persulfate can be decomposed via formation of $SO_4^{\bullet-}$ radicals (i.e., activated) through a variety of methods, such as thermal, alkaline, radiation (including ultraviolet, gamma ray and ultrasonic activation), and using metals (e.g., transition metals or metal oxides, in homogenous or heterogeneous systems) or carbon materials. A general overview of these activation approaches is given in Table 1.

$SO_4^{\bullet-}$ radicals have similar or even higher redox potential than other radicals (e.g., hydroxyl radicals, chorine radicals, superoxide radicals, carbonate radicals and perhydroxyl radicals) [8]. Moreover, carbon materials appear as a promising alternative for traditional metal catalysts [10, 11]. It has already been shown that heterogeneous activation of the peroxide precursors is effective when using nanostructured carbon materials in powder form, due to their catalytic activity, stability, large specific surface area, controllable structure, reusability, and convenient methods for catalyst recovery [12]. Carbon nanomaterials with different dimensionalities, such as fullerenes, carbon nanotubes, and graphene-based materials have been studied in the activated persulfate oxidation organic contaminants [12-14]. However, only few studies have applied these materials in the form of membranes, graphene derivatives representing a potential solution in this field of research [11, 15].

Table 1. Activation methods typically used to promote the formation of $SO_4^{\bullet-}$ radicals from the decomposition of peroxymonosulfate and persulfate.

Activation methods	Advantages	Drawbacks	References
Thermal	• Effective for the degradation of the organic contaminants; • High temperature may increase the solubility of the organic pollutants;	• High energy input is required; • Not suitable for large-scale applications;	[8]
Alkaline	• Simultaneous action of $SO_4^{\bullet-}$ radicals (primary reactive species at acidic conditions) and hydroxyl radicals (secondary reactive species at neutral to alkaline conditions); • Has been used for in situ chemical oxidation (ISCO);	• High demand of HO^- to achieve and maintain alkaline conditions; • The high pH may affect the existing form of the organic contaminants;	[8, 16]
Radiation	• Ultraviolet radiation is considered as benign and cost-effective technology (solar radiation can be implemented); • Ultrasounds can enhance the formation of $SO_4^{\bullet-}$ radicals due to cavitation effects;	• In most of the cases, the ultraviolet fraction employed (> 350 nm) is unable, by itself, to promote high degradation of many organic contaminants; • High energy input is required; • Not suitable for large-scale applications;	[8]
Metals	• Good performances at low to moderate operating temperatures; • Negligible mass transfer limitations when using homogeneous systems; • Metal oxides are easier to recover from the treated water (heterogeneous system);	• Metal ions are difficult to recover from the treated water; • The efficiency of the homogeneous process is highly influenced by the operating pH; • Leaching of metal species when metal oxides are used;	[8, 11]
Carbon materials	• High specific surface area, which facilitates the adsorption of organic compounds and provides more exposed active sites for surface catalytic reactions; • The surface chemistry can be tailored to improve the catalytic performance; • No metal leaching; • High stability.	• Carbon materials may undergo deactivation phenomena, due to different reasons; • Additional studies are required to investigate the performance of metal-free carbon materials for the removal of several organic MPs simultaneously.	[8, 10-12]

2.2. Activated persulfate oxidation with graphene-based materials

Graphene-based materials have been employed as catalysts for several applications (e.g. chemical, electrochemical and photochemical), including activated persulfate oxidation [8, 11, 14, 15, 17, 18]. The main mechanism for the activation of the persulfate anion ($S_2O_8^{2-}$) by carbonaceous materials is based on a one-electron transfer, through the reaction described by Eq. 1 [8, 12]. Hydroxyl radicals ($HO^{\bullet}$) can also be formed through the reaction described by Eq. 2 [8, 12]. In both cases, the radicals are the responsible species for the oxidation of the organic compounds [8]. The active sites at the surface of carbon materials are usually electron-rich regions, such as the sp^2 covalent carbon network, zigzag edges and oxygen functional groups (i.e. carboxyl and carbonyl groups) [10, 18, 19]. Non-radical pathways can also occur, involving electron transfer from the organic pollutant to persulfate, and/or the generation of singlet oxygen ($^1O_2$) [8, 12].

$$S_2O_8^{2-} + e^- \rightarrow SO_4^{\bullet-} + SO_4^{2-} \quad \textbf{(1)}$$

$$SO_4^{\bullet-} + OH^- \rightarrow SO_4^{2-} + HO^{\bullet} \quad \textbf{(2)}$$

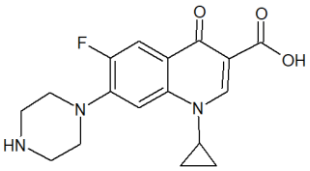
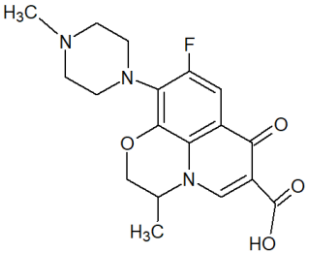
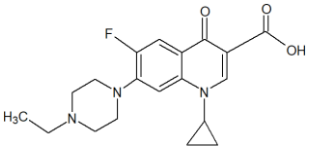
Surface modification methods, such as heteroatom doping (e.g., N, P, S or B), can be employed to increase the availability of active sites and thus enhance the performance of a carbon-based catalyst [8, 11-13, 15, 17]. This was the case of the study on activated persulfate oxidation with N-doped reduced graphene oxide (rGO-M) catalysts recently reported by Pedrosa et al. (2019) [11]. Among the different nitrogen precursors employed, melamine allowed obtaining the highest nitrogen content (23.78 wt.%) and thus the highest catalytic activity for the degradation of phenol in aqueous solution [11]. In this case, experiments performed in continuous mode allowed concluding that the loss of catalytic activity of the membranes was related to the decrease of N-pyridinic groups at the surface of rGO-M [11].

2.3. Model system of micropollutants of EU concern

In most studies, the performance of carbon-based materials in activated persulfate oxidation is evaluated based on the degradation of one contaminant only, although several organic contaminants co-exist in real water matrices [8]. In the present study, the performance of the different catalytic membranes in activated persulfate oxidation was evaluated using aqueous solutions containing three MPs simultaneously. Moreover, a real water matrix (cf. Section 3.2) was used in addition to studies with UP water, in order to achieve conditions closer to the reality.

The MPs selected for this study are compounds of the chemical class of fluoroquinolone antibiotics, namely ofloxacin (Oflo), ciprofloxacin (Cipro) and enrofloxacin (Enro), which are briefly characterized in Table 2. Enro is used in veterinary practice, and was one of the MPs detected with higher concentration in a previous study of the LSRE-LCM research group on the occurrence of MPs in Portuguese rivers [20]. Oflo and Cipro are used in humans, and they have also been found in several environmental samples [9]. Indeed, Cipro was recently included in the Watch List of CECs for which additional monitoring/impact studies are required, as defined in the Commission Decision 2018/840/EU [5].

Table 2. Model pollutants selected from the chemical class of the fluoroquinolone antibiotics.

Name CAS number	Molecular formula M_w	pK_a	Chemical structure	References
Ciprofloxacin [85721-33-1]	$C_{17}H_{18}FN_3O_3$ 331.35	6.09		[21, 22]
Ofloxacin [82419-36-1]	$C_{18}H_{20}FN_3O_4$ 361.37	5.97		[23]
Enrofloxacin [93106-60-6]	$C_{19}H_{22}FN_3O_3$ 359.40	6.21		[24]

3. Materials and Methods

3.1. Reagents

Synthetic graphite (particle size < 20 μm; catalog number 282863), melamine (99 wt.%), polyvinylpyrrolidone (PVP; MW: 40.000 g mol^{-1}), 1-methyl-2-pyrrolidone (NMP; 99.5 wt.%), poly(vinylidene fluoride) (PVDF; MW: 275.000 g mol^{-1}), ciprofloxacin hydrochloride (EP Reference Standard), and enrofloxacin (98 wt.%) were purchased from Sigma-Aldrich. Sulphuric acid (H_2SO_4; 95 wt.%), ofloxacin (98 wt.%), disodium hydrogen phosphate (Na_2HPO_4; 99 wt.%), monosodium phosphate (NaH_2PO_4; 99 wt.%), and N, N-Dietyl-p-plenylenediamine sulfate (DPD; 99 wt.%) were obtained from Fluka. Sodium nitrate ($NaNO_3$; 99wt.%), formic acid (99 wt.%), potassium permanganate ($KMnO_4$; 99.5 wt.%), and absolute ethanol were obtained from VWR. Hydrogen peroxide (H_2O_2; 30 wt.%) and methanol (HPLC grade) were supplied by Panreac and Fisher, respectively. Sodium persulfate (SPS; MW: 238.110 g mol^{-1}, 99 wt.%) was supplied by Riedel-de Haen. Ultrapure (UP) water was produced in a Milli-Q® water purification system (Merck, Darmstadt, Germany).

3.2. Water matrices

Solutions containing the MPs under study were prepared in (i) ultrapure water (UP; pH = 5.9) and (ii) surface water (SW; pH = 7.3; 4.0 mg L^{-1} total organic carbon; 125 mg L^{-1} total dissolved solids; 13.3 mg L^{-1} chlorides; 3.6 mg L^{-1} nitrates; 22.5 mg L^{-1} sulphates; < 0.05 mg L^{-1} phosphates; 11.1 mg L^{-1} sodium; 25.2 mg L^{-1} calcium; 5.1 mg L^{-1} magnesium) collected on November 19, 2018, nearby the admission point of a drinking water treatment plant located in the district of Porto.

3.3. Preparation of graphene derivatives

3.3.1. Graphite oxide

Graphite oxide was prepared by a modified Hummers' method, as described by Pedrosa et al. (2018) [25]. Briefly, 240 mL of concentrated H_2SO_4 was added gradually under stirring (300 rpm) to a 2 L glass beaker containing 5 g of graphite and immersed in an ice bath to avoid overheating. Then, 5 g of $NaNO_3$ was slowly added to the mixture, followed by adding 30 g of $KMnO_4$. The mixture was stirred for 5 to 10 min prior to the addition of each reagent. In the next step, the mixture was removed from the ice bath and placed in an oil bath at 35 ºC under stirring (300 rpm) for 12 h. After that period, the mixture was allowed to cool down in an ice bath under stringing (400 rpm), diluted with 1250 mL of distilled water, and 35 mL of H_2O_2 (30 wt.%) was added. The mixture was then centrifuged during 30 min at 3000 rpm, to remove

the excess of acid. The resulting paste was filtered, washed with distilled water until reaching pH 5 in the rinsing waters, and dried overnight at 60 °C to obtain graphite oxide (cf. Figure A.1).

3.3.2. N-doped reduced graphene oxide (rGO-M)

Nitrogen-doped reduced graphene oxide (rGO-M) was obtained by pyrolysis of graphite oxide in the presence of melamine, as described previously by Li et al. (2017) [26]. In this procedure, 0.5 g of graphite oxide and 0.4 g of melamine (M) were added to 30 mL of absolute ethanol. After being maintained in an ultrasonic bath for 30 min, the mixture was distributed into two crucibles and dried at 60 ºC (cf. Figure A.2). The resulting material was then subjected to thermal treatment at 350 ºC for 30 min in a muffle furnace under static air (Nabertherm P330), defining a heating rate of 5 ºC min^{-1}. Once cooled down to room temperature, the obtained black powder was washed with 1 L of distilled water under vacuum filtration and dried overnight at 60 ºC, resulting in the rGO-M materials.

3.3.3. Polymeric membranes

Polymeric membranes were fabricated by adapting the procedure previously described by Ayyaru and Ahn (2017) [27]. Briefly, 0.464 g of rGO-M was added to a solution containing 0.070 g of PVP in 6.0 mL of NMP, the resulting mixture being placed in an ultrasonic bath for 3 h at room temperature. 1.07 g of PVDF was then added to the mixture, and the polymerization was allowed to proceed at 40 ºC for 48 h, using an oil bath. Afterwards, the polymer solution was left unstirred overnight at room temperature to allow bubbles to escape. The last step was to use the knife cast technique, as shown in Figure A.3. For that purpose, the polymer solution was placed in a glass plate and spread using a casting knife. This apparatus allows selecting the thickness of the membrane (ca. 50 µm), which was obtained after immersion of the cast polymer solution in distilled water. After complete coagulation, a flat membrane sheet was removed from the glass plate, cut as desired (1.64 cm of inner diameter; 2.10 cm^2 of effective area), and stored in distilled water until further use. One membrane was dried overnight at 60 ºC, and then weighted. The effective mass was 23 mg. Considering that the fraction of rGO-M in the membrane forming materials was 6.4 wt.%, it is assumed that the mass of rGO-M in the polymeric membrane is ca. 1.5 mg.

3.3.4. Supported membranes

Supported membranes were manufactured by adapting the procedure previously described by Pedrosa et al. (2019) [11]. For that purpose, 15 mg rGO-M was dispersed in 30 mL of NMP, homogenized in an ultrasonic bath for 1 h, and then vacuum filtered into a Millipore JGWP PTFE substrate (0.2 µm pore size; 1.64 cm of inner diameter; 2.10 cm^2 of effective area), as shown

in Figure A.4. The resulting membrane was washed with distilled water (15 + 15 mL) prior to final application.

3.4. Activated persulfate experiments

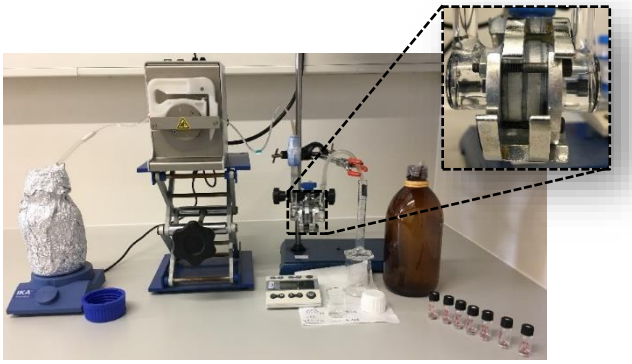
Activated persulfate experiments were carried out using the experimental set-up shown in Figure 1. The performance of two distinct metal-free carbon membranes (polymeric and supported) was evaluated in activated persulfate experiments performed at room temperature (22 ± 2°C), and considering $[Enro]_0 = [Oflo]_0 = [Cipro]_0 = 100$ μg L^{-1}. In these experiments, each aqueous solution to be treated was prepared by adding a known amount of a stock solution containing the three MPs under study (11 mg L^{-1} each) to 250 mL of the aqueous matrix (UP water or SW). Then, a known amount of a SPS stock solution (1302.85 mg L^{-1}) was added in order to obtain the desired SPS concentration (25 mg L^{-1}), that moment being considered t = 0 min. In routine experiments, the solution containing the MPs under study and the desired amount of SPS was fed in continuous mode to the membrane cell (at a flow rate of 0.10 mL min^{-1}, previously determined according to the calibration curve of the peristaltic pump shown in Figure A.7), the treated water being collected in a glass bottle. Appropriate samples were withdrawn periodically (0.0, 1.0, 1.5, 2.0, 4.0, 6.0, 8.0 and 24 h), and immediately refrigerated at 5 °C prior to analysis. An excess of methanol (300 μL) was added to these samples (1 mL) for detection of MPs by florescence, while 500 μL samples were used for SPS determination. Permeate water flux (J_w) measurements were performed with the same frequency, by application of Eq. 3 according to the volume (V) and time register (Δt) of the samples collected into a graduated cylinder (Figure 1).

$$J_w = \frac{V}{A\,\Delta t} \quad \textbf{(3)}$$

Pure adsorption tests were performed in the absence of SPS. Non-catalytic experiments were specifically performed in batch mode, in order to evaluate the stability of the selected MPs in the presence of SPS. All the experiments were performed without pH conditioning, i.e., with the inherent pH of the solution to be treated. The performance of the activated persulfate treatment was also evaluated considering the MPs at other concentrations (in the range 10 – 1000 μg L^{-1}). Long-term experiments were performed to evaluate the stability of the metal-free carbon supported membranes. In this case, the first 6 h were devoted to pure adsorption, followed by 90 h of activated persulfate oxidation in which the micropollutant solution was replaced daily. After the oxidation experiments, the pH of the treated water was measured (pH_{UP} = 5.9; pH_{SW} = 7.3), and the used membranes were stored for future characterization (cf. Figure A.5). Most experiments were performed in duplicate, the average values of MPs conversions being reported together with the corresponding standard deviation

whenever possible. In the case of SPS, selected experiments were performed in duplicate. The standard deviation of SPS conversion was always below 6%.

(a)



(b)

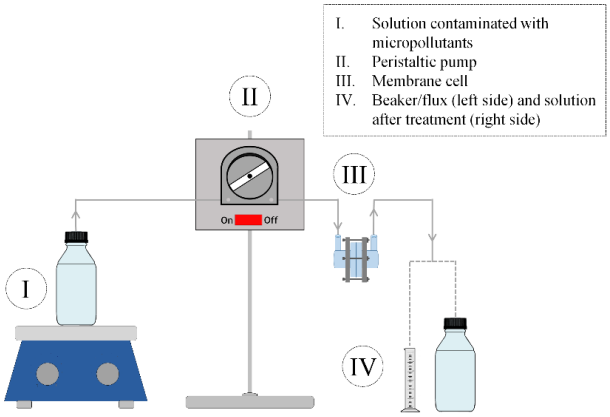


Figure 1. Experimental set-up used for the experiments: (a) front view and (b) schematic representation. Inset of (a): front view of the membrane cell.

3.5. Analytical methods

3.5.1. Micropollutants determination

The concentrations of Enro, Oflo and Cipro were determined by ultra-high-performance liquid chromatography (UHPLC), using a Shimadzu Corporation apparatus (Tokyo, Japan) consisting of an Autosampler (SIL-30AC), a Degasser (DGU-20A5), an Oven (CTO-20AC), two Pumps (LC-30AD), a Fluorescence Detector (FD; RF-20AXS), and a System Controller (CBM-20 A Lite). Chromatographic separation was optimized using a Kinetex™ 1.7 µm XB-C18 100 Å column (100 × 2.1 mm i.d.) supplied by Phenomenex, Inc. (California, USA), set at 40 °C. A mixture of (A) 0.1% aqueous formic acid and (B) methanol was used as mobile phase (total flow rate of 0.3 mL min^{-1}), delivered as follows: 25% of B for 0.5 min, a linear gradient from 25% to 65% during 9 min (kept during 0.5 min), a linear gradient from 65% to 25% in 0.5 min and finally an equilibration time of 7.5 min, corresponding to a total run time of 18 min. The autosampler temperature was kept at 15 °C, and the injection volume was 30 µL. The excitation wavelength of the FD was 290 nm and the emission wavelength was 460 nm.

Duplicate measurements were performed to determine the calibration curves shown in Figures A.8 and A.9. Standard solutions were prepared in UP water and SW in the range 1 - 120 μg L^{-1}, in the presence of methanol.

3.5.2. Persulfate determination

The SPS concentration was determined by the N,N-Dietyl-p-plenylenediamine sulfate (DPD) method, by adapting the colorimetric procedure previously reported by Gokulakrishnan et al. (2016) [28]. This method is based on the oxidation of DPD by SPS, leading to pink colored solutions with a maximum absorbance peak at a wavelength of 551 nm (cf. Figure A.10).

Firstly, two working solutions were prepared: (i) phosphate buffer (100 mmol L^{-1}, pH 7, 50 mL), prepared by adding 0.4144 g of Na_2HPO_4 and 0.2569 g of NaH_2PO_4; and (ii) DPD solution (25 mmol L^{-1}, 10 mL), prepared by dissolving 0.0655 g of DPD in H_2SO_4 (0.05 mol L^{-1}). For stability purposes, the DPD solution was stored in an amber bottle at 5 ºC for no more than one week.

In each measurement, 500 μL of sample was added to 2.5 mL of phosphate buffer, and diluted with 1.5 mL of UP water. 500 μL of the DPD solution was then added, the color being allowed to develop during 10 min at room temperature. Next, absorbance was recorded at 551 nm against a blank prepared by replacing the sample by UP water, using a JASCO V-570 UV/VIS spectrophotometer.

A series of standard solutions containing SPS (in the range 1 – 30 mg L^{-1}; cf. Figure A.6) were prepared by successive dilutions of a stock solution (1303 mg L^{-1}) in UP water. Triplicate measurements were performed to determine the calibration curve shown in Figure A.10.

3.6. Characterization techniques

3.6.1. Water contact-angle measurements

The hydrophobicity/hydrophilicity of the metal-free carbon membranes was estimated by water contact-angle measurements using the sessile-drop method [29]. An Attention optical tensiometer (model Theta) allowed image acquisition and data analysis. The measurements with water were performed on a dry polymeric membrane and on rGO-M in the form of a pressed pellet. In either case, the contact-angle was obtained from triplicate measurements performed in different locations of the sample.

4. Results and discussion

4.1. Characterization

rGO-M was characterized in a previous publication - Pedrosa et al. (2019) [11]. In order to complement the characterization data, the water contact-angle of rGO-M was determined using the sessile-drop method [30]. Similar measurements were also made with polymeric membranes, as shown in Figure 2. This allows estimating the hydrophilicity/hydrophobicity of the materials. The water contact-angles obtained were 28.1 ± 3.2º for rGO-M (measured in the form of a pressed pellet), and 69.1 ± 2.5º for the polymeric membrane. This allows concluding that the polymeric membrane is more hydrophobic than the supported membrane only containing rGO-M.

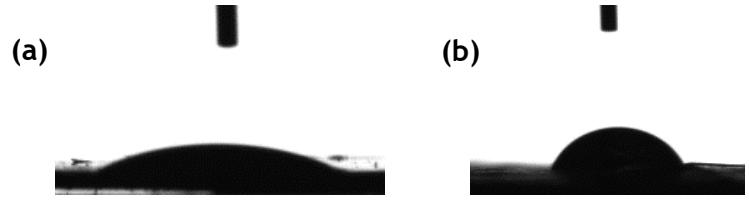


Figure 2. Water droplet dropped on the surface of (a) rGO-M in the form of a pressed pellet, and (b) polymeric membrane.

4.2. Activated persulfate oxidation

4.2.1. Metal-free carbon membranes: supported vs. polymeric

Initial experiments were performed in continuous mode in order to evaluate the performance of the two types of metal-free carbon membranes (supported and polymeric) in the activated persulfate oxidation of aqueous solutions containing the three MPs under study. Adsorption runs were also performed. An UP water matrix was used for that purpose. As observed in Figures 2a and 3a, the adsorption of MPs on both membranes is low at the end of the experiments (i.e., the membranes are saturated after a certain period). In the case of supported membranes, the adsorption of the 3 MPs is actually null after 24 h. Regarding the results obtained in the activated persulfate oxidation tests performed with supported and polymeric membranes (cf. Figures 3b and 4b, respectively), a good performance was achieved, corresponding to conversions of the target MPs in the range 83 - 90% at the end of the experiments (some unexpected increase/decrease of the MPs concentrations being observed with the polymeric membranes between 4 and 8 h). Thus, it is concluded that both catalytic membranes are effective for the degradation of MPs by activated persulfate oxidation.

In addition, there is more consumption of SPS at the beginning of the experiment with the polymeric membrane. In the other hand, the consumption of SPS remained approximately constant during the experiment with the supported membrane. Although polymeric membranes are more hydrophobic, no significant differences were obtained in values of the water permeate flux (J_W) obtained in the experiments performed with the two types of membranes.

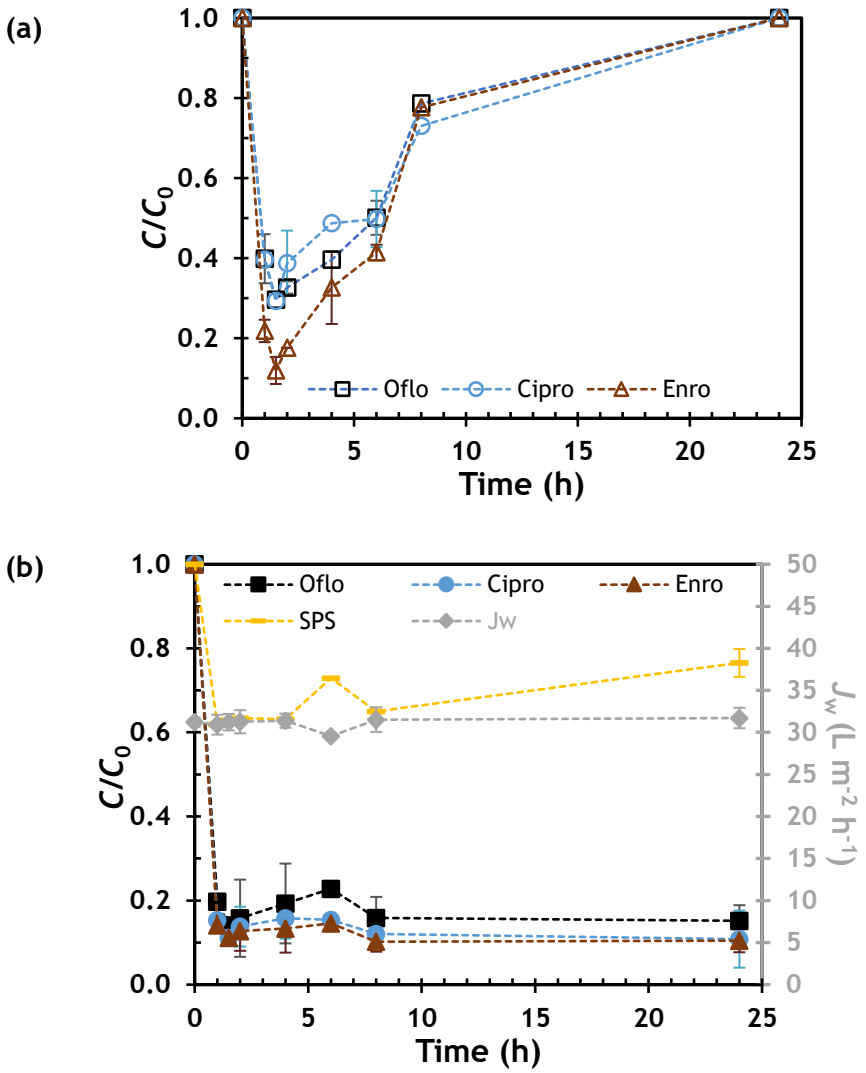


Figure 3. Removal of Oflo, Cipro and Enro obtained in (a) adsorption, and (b) activated persulfate oxidation experiments performed in UP water, with supported membranes. Water permeate flux (J_w) and conversion of SPS are also shown in (b). Experimental conditions: $[MPs]_0$ = 100 µg L^{-1} each; [SPS] = 25 mg L^{-1}; pH_0 = 5.3 (inherent pH); Q = 0.1 mL min^{-1} (continuous mode); and T = 22 ± 2 ºC.

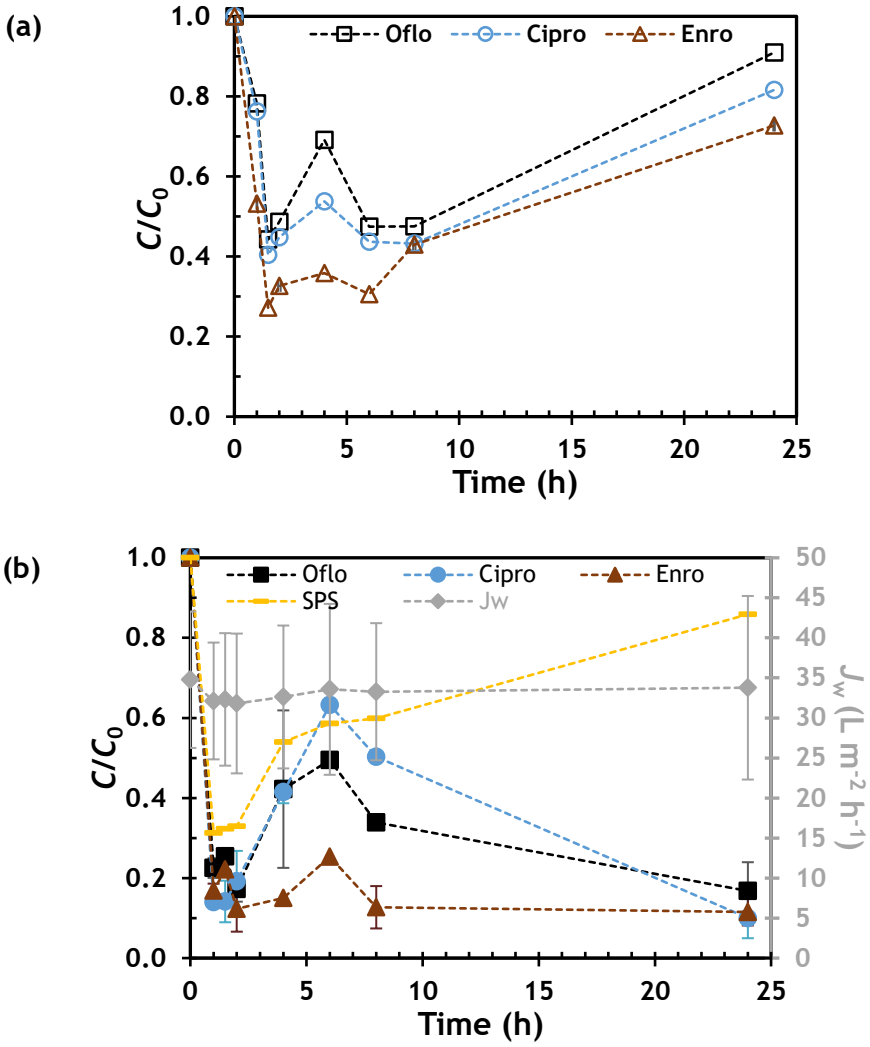


Figure 4. Removal of Oflo, Cipro and Enro obtained in (a) adsorption, and (b) activated persulfate oxidation experiments performed in UP water, with polymeric membranes. J_w and conversion of SPS are also shown in (b). Experimental conditions as given in Figure 3, except that pH_0 = 5.3 (inherent pH).

4.2.2. Effect of water matrix

The effect of water matrix was then evaluated, by using SW instead of UP water. SW contains many ions and some organic matter that may interfere in activated persulfate oxidation, as detailed in Section 3.2. In this case, a non-catalytic experiment was performed in batch mode to evaluate the possible oxidation of the MPs by SPS alone. After 24 h, the degradation of Oflo, Cipro and Enro was ca. 0, 2 and 5%, respectively. This result allows concluding that SPS is unable to degrade the MPs under study just by itself. As previously observed when a UP water matrix was employed, the adsorption of MPs on both membranes is negligible after a certain period (cf. Figures 5a and 6a, with supported and polymeric membranes, respectively). Regarding activated persulfate oxidation, the removal of Enro is ca. 22 and 12% after 24 h, respectively

in the experiments performed with supported and polymeric membranes, whereas the removal of Cipro is ca. 10% with both membranes, and no removal of Oflo is observed (cf. Figures 5b and 6b). Less consumption of SPS is also observed under these conditions, when compared to that obtained with the UP water matrix.

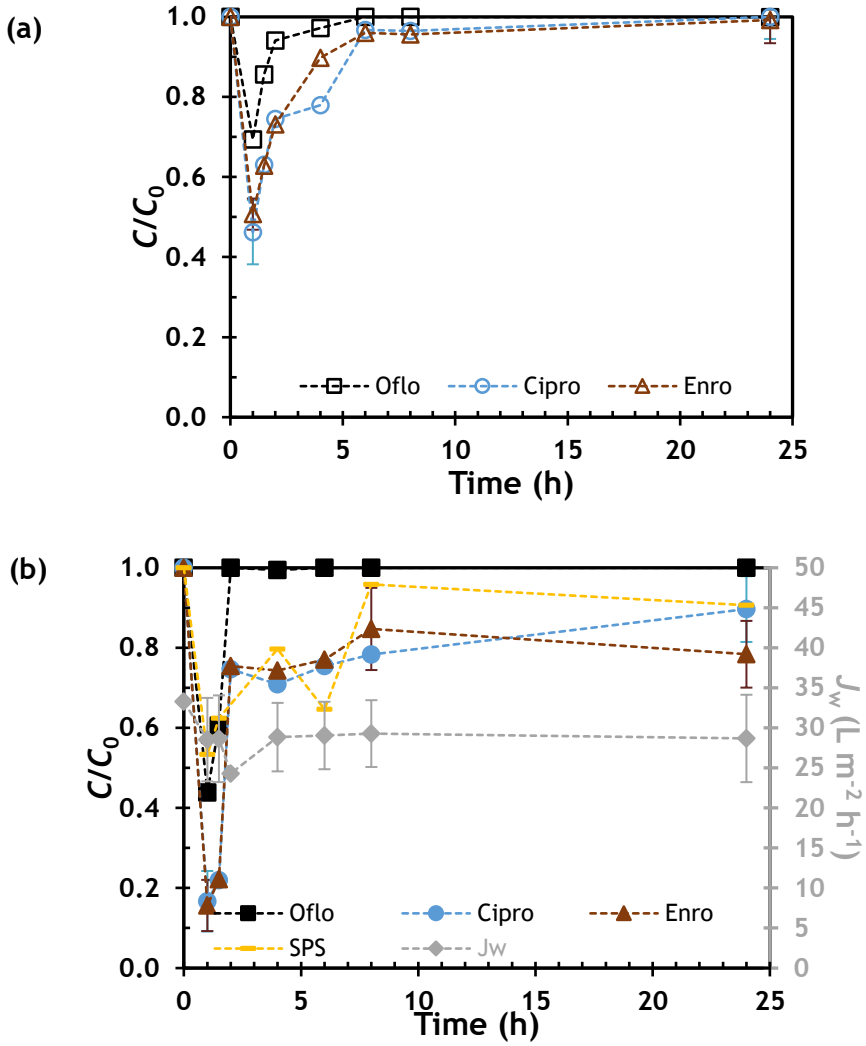


Figure 5. Removal of Oflo, Cipro and Enro obtained in (a) adsorption, and (b) activated persulfate oxidation experiments performed in SW, with supported membranes. J_w and conversion of SPS are also shown in (b). Experimental conditions as given in Figure 3, except that pH_0 = 7.6 (inherent pH).

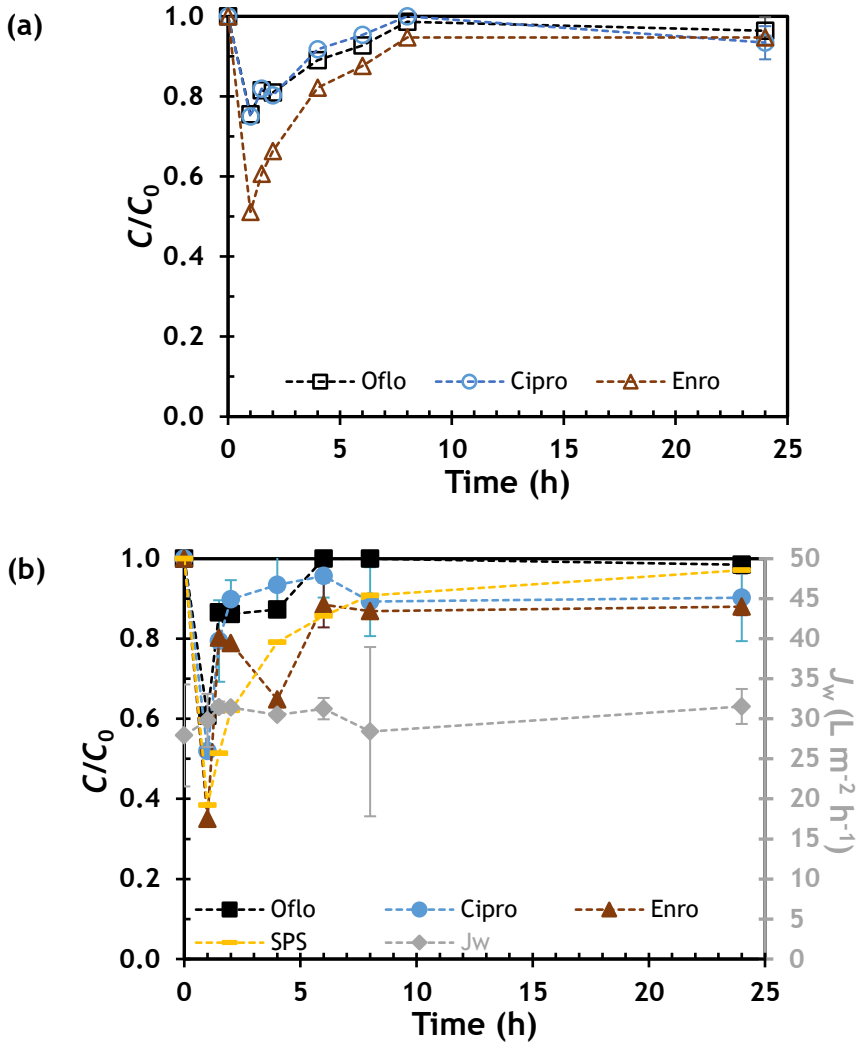


Figure 6. Removal of Oflo, Cipro and Enro obtained in (a) adsorption, and (b) activated persulfate oxidation experiments performed in SW, with polymeric membranes. J_w and conversion of SPS are also shown in (b). Experimental conditions as given in Figure 3, except that pH_0 =7.6 (inherent pH).

Several studies report that the efficiency of the treatment processes can decrease considerably when real water matrices are used instead of simulated ones [6, 31]. The results summarized in Figure 7 confirm this trend. The lower conversion of SPS observed in SW suggests that less $SO_4^{\bullet-}$ radicals may be formed due to presence of ions and/or natural organic matter, thus affecting the performance of the treatment. Since many factors can dictate the efficiency of activated persulfate oxidation, experiments should be performed considering realistic conditions [32, 33]. Nevertheless, more studies on the optimization of SPS concentration and operating pH are required.

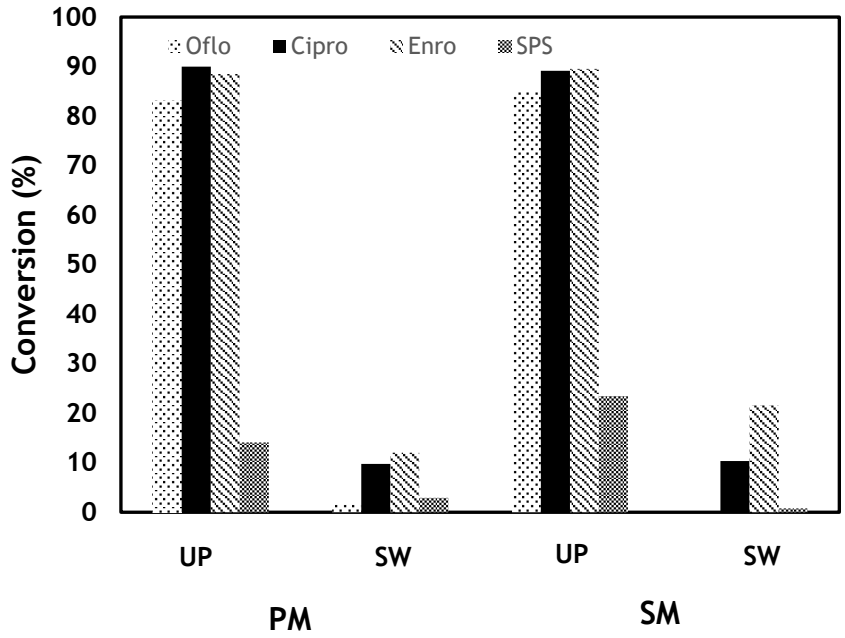


Figure 7. Conversion of Oflo, Cipro, Enro and SPS obtained after 24h in activated persulfate oxidation experiments performed with polymeric (PM) and supported membranes (SM). The effect of UP and SW matrices is also shown. Experimental conditions as given in Figures 3-6.

4.2.3. Effect of MPs concentration

The response of the activated persulfate oxidation treatment to variations in the initial concentration of the selected MPs was assessed in the range 10 – 1000 μg L^{-1}. As observed in Figure 8, the degradation of the MPs under study is higher at concentrations of 100 μg L^{-1} when UP water is employed (more studies are needed for interpretation of these results). When SW is used, no significant changes are observed (cf. Figure 9).

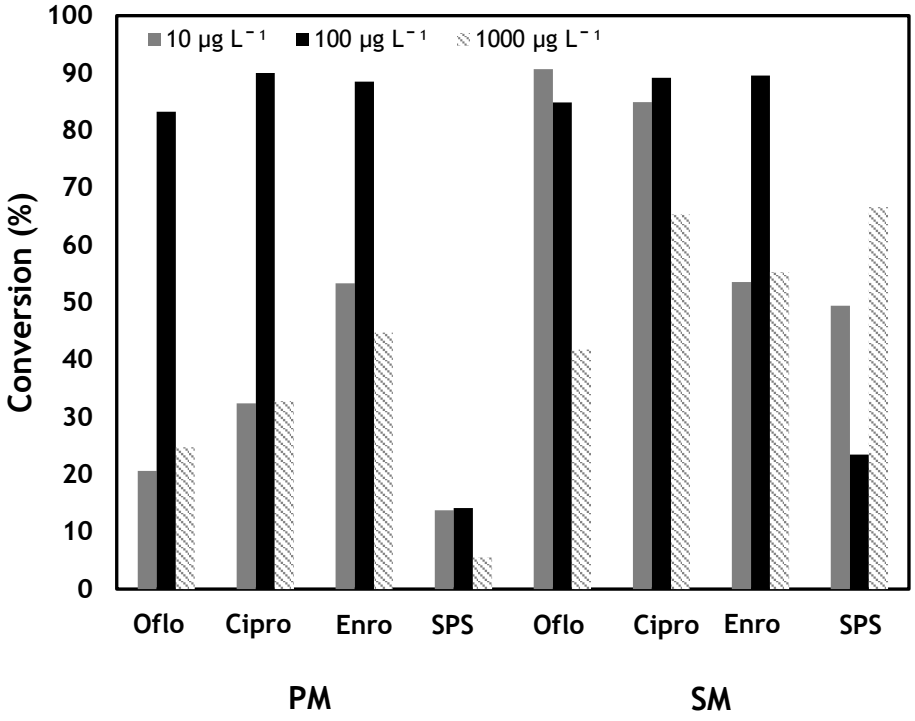


Figure 8. Conversion of Oflo, Cipro, Enro and SPS obtained after 24 h in activated persulfate oxidation experiments performed in UP water, with polymeric (PM) and supported membranes (SM). Experimental conditions as given in Figure 3, except that $[MPs]_0$ = 10, 100 and 1000 μg L^{-1} each.

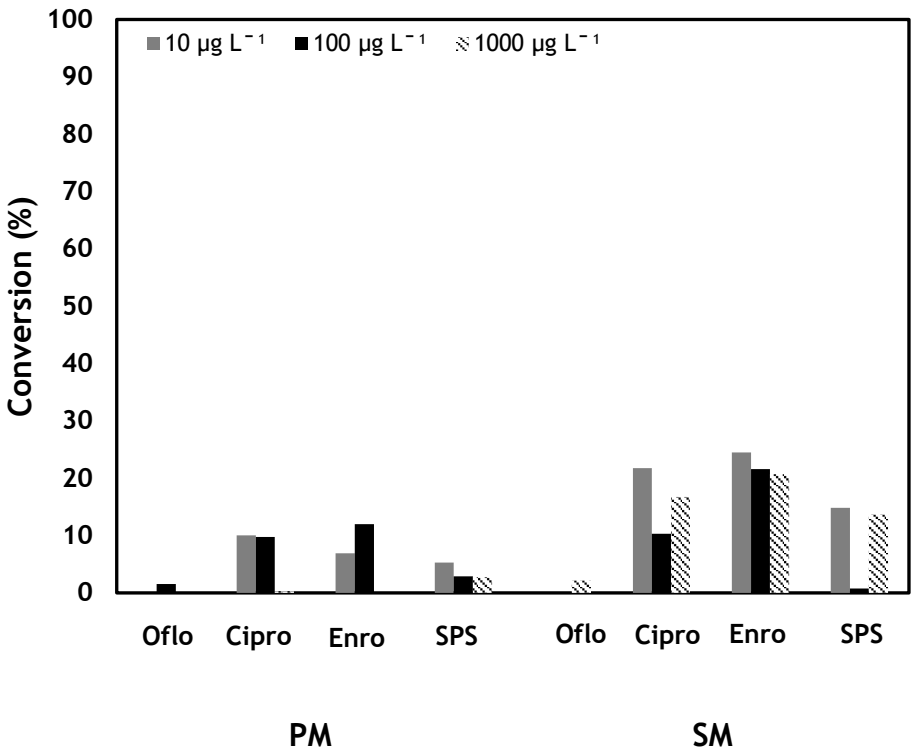


Figure 9. Conversion of Oflo, Cipro, Enro and SPS obtained after 24 h in activated persulfate oxidation experiments performed in SW, with polymeric (PM) and supported membranes (SM). Experimental conditions as given in Figure 5, except that $[MPs]_0$ = 10, 100 and 1000 µg L^{-1} each.

4.2.4. Formation of reaction by-products

Formation of unknown by-products as consequence of MPs oxidation was observed in experiments performed with both types of membranes. At least two by-products were clearly detected in the chromatograms obtained by UHPLC (identified as X and Y in Figure 10). Further studies should be performed in order to identify these by-products. It is important to refer that these by-products might be more toxic and/or persistent than the parent compounds, so toxicological studies are also needed in future studies.

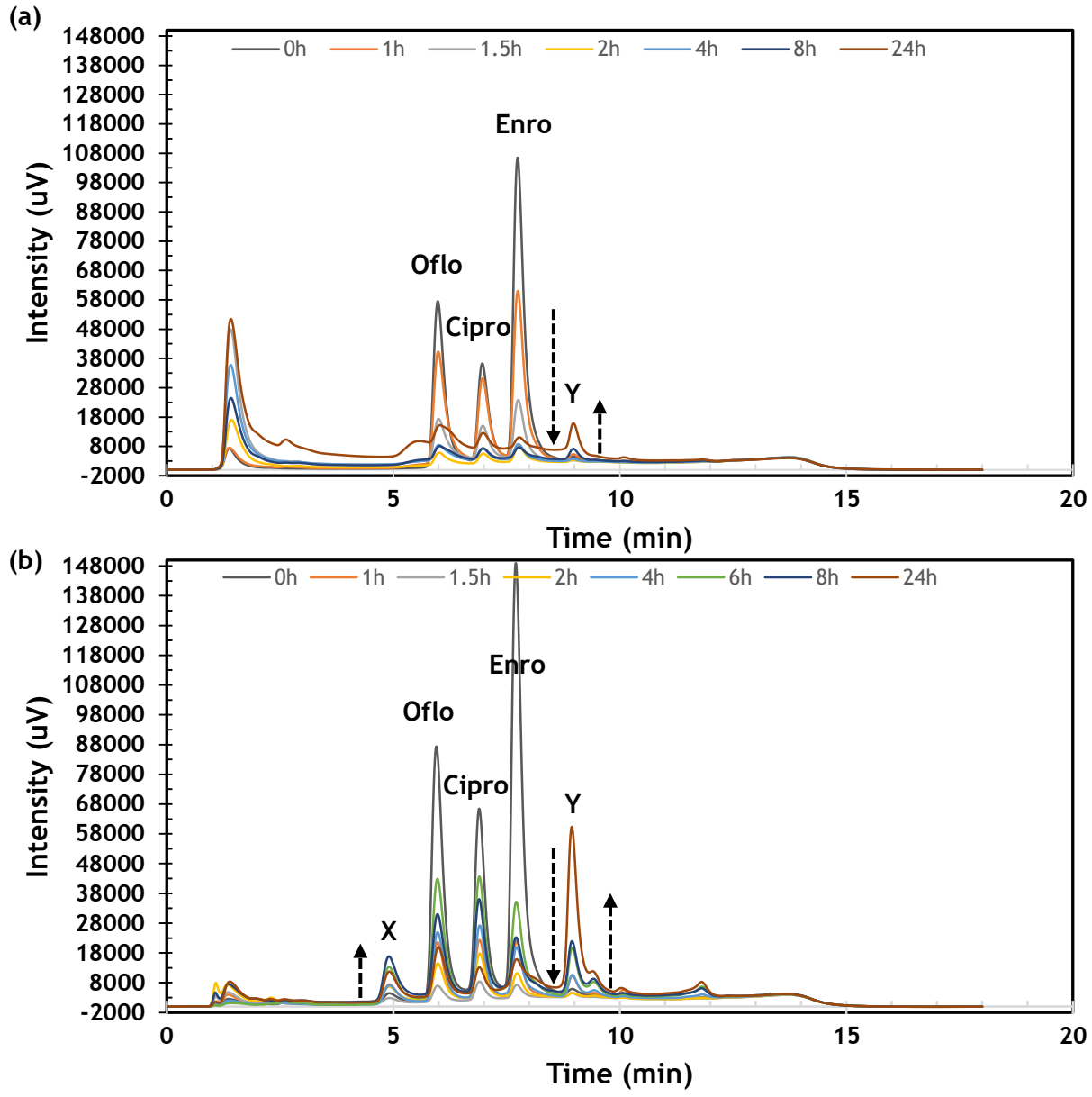


Figure 10. Chromatograms of Oflo, Cipro and Enro, and respective by-products, obtained in the UHPLC system coupled to a fluorescence detector, as described in Section 3.5. Experiments performed with UP water, and (a) supported membranes and (b) polymeric membranes. Experimental conditions as given in Figure 3.

4.2.5. Stability of the metal-free carbon supported membranes

To evaluate the stability of the metal-free carbon supported membrane in UP water, a long-term experiment was performed as described in Section 3.4. In this case, the first 6 h were devoted to adsorption, followed by 90 h of activated persulfate oxidation, in which the solution containing the MPs was replaced daily. The results obtained are given in Figure 11. As observed, the conversions of Cipro and Enro only decrease from ca. 90% and 93% after 22 h, to ca. 70% and 82% after 90 h, respectively. The decrease observed for Oflo removal in the same period is slightly higher, going from ca. 80% to ca. 50%. SPS conversion follows the same trend. Apparently, the fouling of the membrane is negligible, as reflected by the relatively constant value of J_W. This result was expected since UP water was employed in this experiment and since graphene-based materials have antifouling properties, as previously reported when studying ultrafiltration membranes [27]. Although some deactivation occurs, the supported membranes prepared with rGO-M still maintain a considerable catalytic activity for degradation of the target MPs after 90 h of operation in continuous mode.

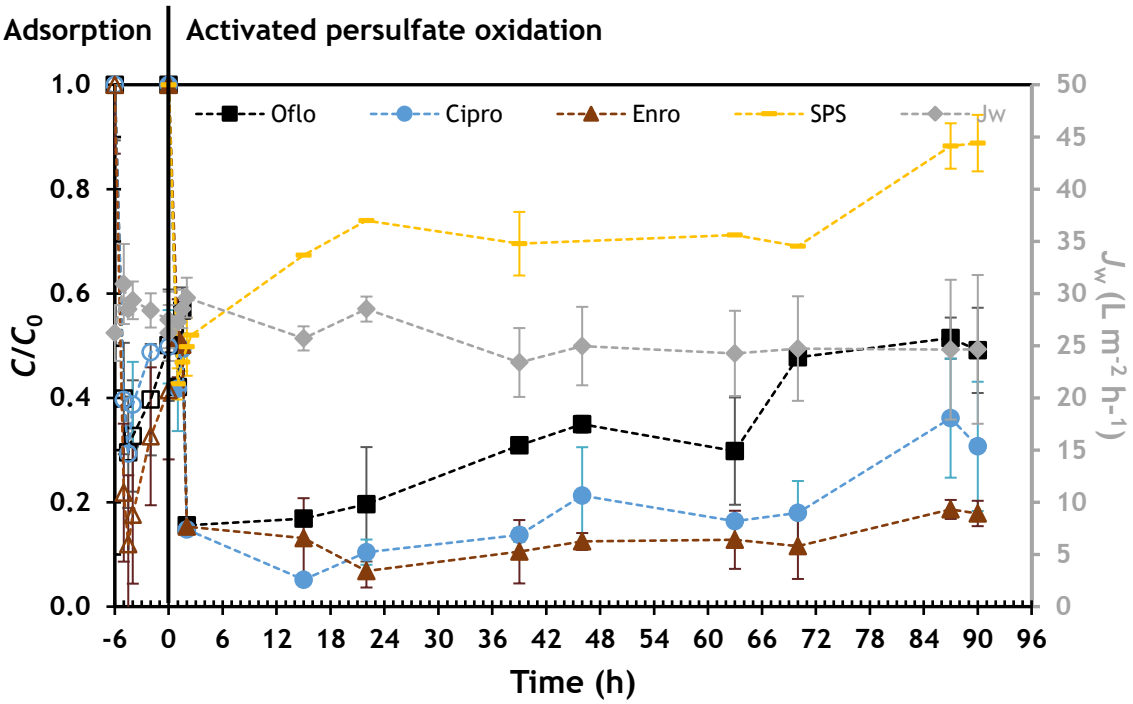


Figure 11. Removal of Oflo, Cipro and Enro obtained during long-term experiments performed with supported membranes and UP water (6 h of adsorption, followed by 90 h of activated persulfate oxidation). J_w and conversion of SPS are also shown. Experimental conditions as given in Figure 3.

5. Conclusions

Activated persulfate oxidation of MPs was successfully performed with metal-free graphene-based catalytic membranes in continuous mode of operation. The results obtained in the activated persulfate oxidation experiments performed with supported and polymeric membranes showed that both catalytic membranes are effective for the degradation of the selected MPs (Oflo, Cipro and Enro) in UP water matrix, corresponding to conversions in the range 83 - 90% after 24 h of operation. Adsorption tests, and a non-catalytic experiment, allowed confirming the catalytic activity of these metal-free membranes.

The effect of the water matrix was also evaluated. The efficiency of the treatment process decreased considerably when SW was used instead of UP water. The removal of Enro was ca. 22 and 12% after 24 h, respectively in the experiments performed with supported and polymeric membranes, while the removal of Cipro was ca. 10% with both membranes, and no removal of Oflo was observed. Moreover, lower consumption of SPS was attained with SW.

The response of the activated persulfate oxidation treatment to variations in the initial concentration of these MPs was also investigated. The higher conversions in the degradation of the MPs under study were obtained for a concentration of 100 μg L^{-1} each (in UP water). Formation of at least two by-products of MPs oxidation was observed in experiments conducted with the both types of membranes.

The stability of the metal-free carbon supported membranes was evaluated. Although some deactivation occurs, the membrane maintains considerable catalytic activity for degradation of the selected MPs after 90 h of operation in continuous mode.

In all cases, no significant variation of the water permeate flux (J_W) was observed along the experiments, suggesting the antifouling properties of graphene-based materials when shaped as membranes.

6. Assessment of the work done

The potential of the smart design of metal-free carbon materials for the activated persulfate oxidation of three fluroquinolone antibiotics was proved in this project for a continuous mode of operation. Two different carbon-based catalytic membranes were successfully prepared with rGO-M, their performance in this AOT being evaluated. Thus, the main goal of the project was achieved. The results obtained showed that both supported and polymeric membranes are effective for the degradation of the selected MPs (with a concentration of 100 μg L^{-1} each) by activated persulfate oxidation in UP water. Nevertheless, it should be mentioned that polymeric membranes are easier to work with, when compared to supported membranes. Polymeric membranes can be conserved in water until use, maintaining the structural stability, while supported membranes should be placed in the membrane cell immediately after fabrication.

All the adsorption and activated persulfate experiments reported in this study were performed in duplicate. However, it was not possible to analyze some samples collected in the last experiments due to technical difficulties with the UHPLC apparatus.

At this stage, some additional results are being obtained, and one manuscript is under preparation for submission to a scientific international journal.

The following tasks should be carried out before any of the membranes considered in this study could be designed as a commercial product:

- Studies on the optimization of SPS concentration and operating pH are required;
- Long-term experiments performed with SW;
- Characterization of the rGO-M collected after long-term experiments performed with supported membranes, in order to understand the causes of the partial catalyst deactivation observed in this study;
- Identification of the by-products formed and toxicological studies;
- Experiments for the degradation of other CECs;
- Analysis of the cost effectiveness of the treatment, especially before moving to the pilot or industrial scale.

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Appendix 1.Photo gallery

(a)  (b) 

Figure A.1. Graphite oxide obtained by the modified Hummers' method: (a) filtration and washing with distilled water, and (b) graphite oxide obtained after drying overnight at 60 °C.

Figure A.2. Graphite oxide impregnated with melamine, after the thermal treatment in the muffle furnace.

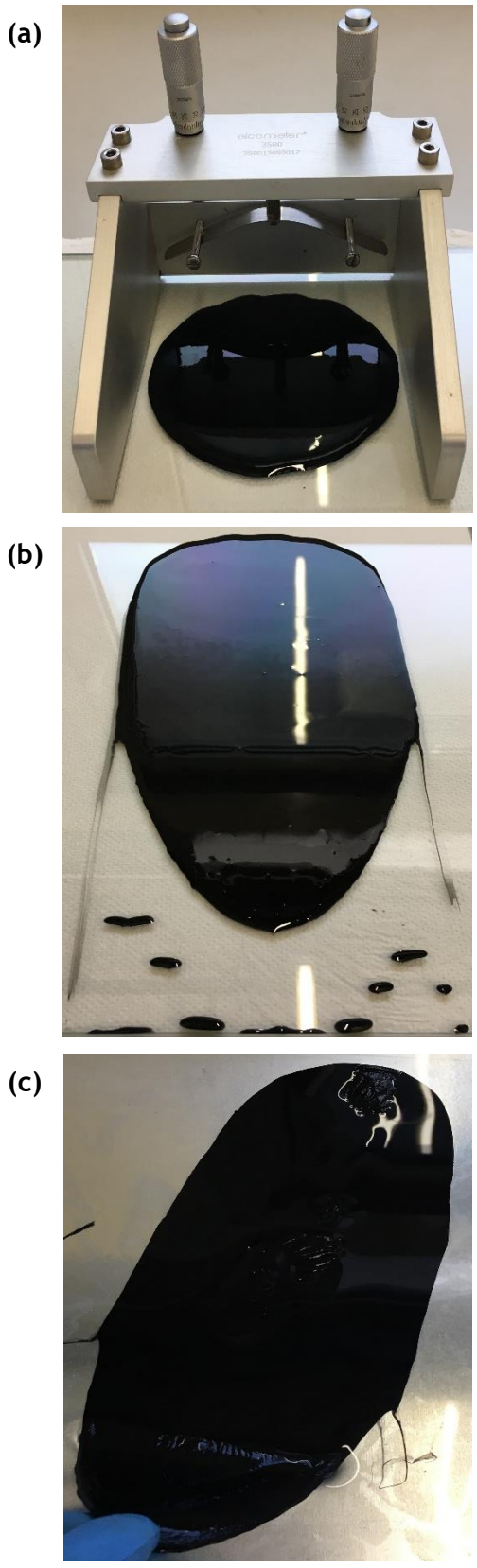

Figure A.3. Application of the knife cast technique: (a) placement of the polymer solution in a glass plate, which was then (b) spread using the casting knife shown in (a); (c) flat membrane sheet obtained after complete coagulation of the solution.

Figure A.4. Vacuum filtration step during the fabrication of supported membranes.

(a) (b)

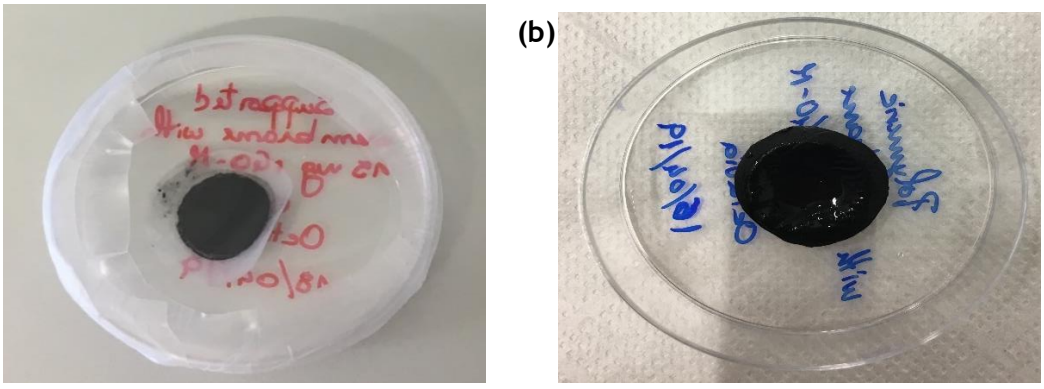

Figure A.5. (a) Polymeric and (b) supported membrane collected after the activated persulfate oxidation experiments.

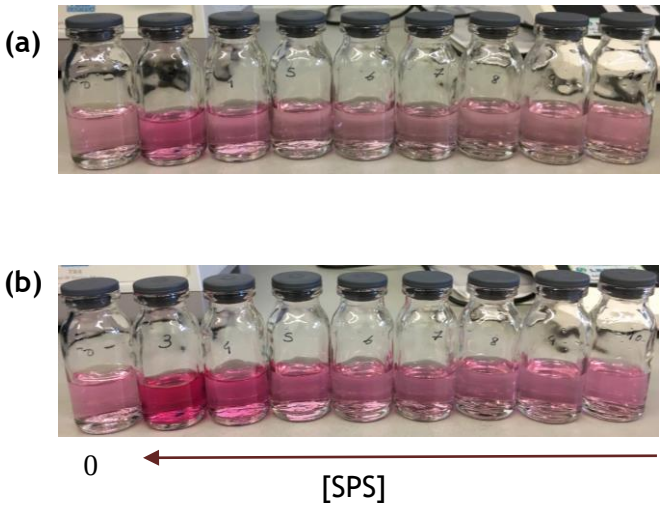

Figure A.6. Oxidative coloration of DPD by standard solutions prepared with different concentrations of SPS: (a) when DPD reagent was added, and (b) after 10 min equilibration.

Appendix 2. Calibration curves

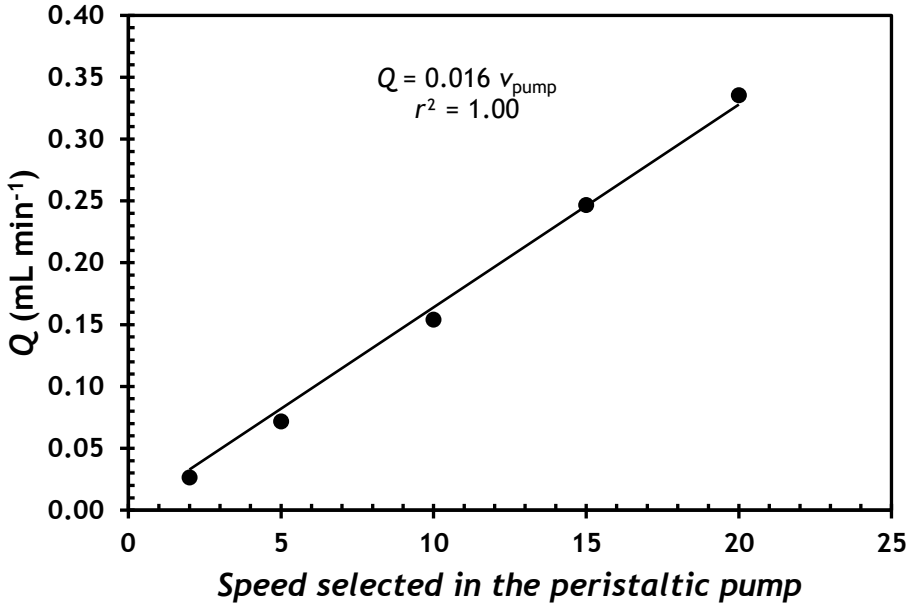

Figure A.7. Calibration curve obtained for the peristaltic pump. Symbols represent experimental data, while the line represents the linear fitting.

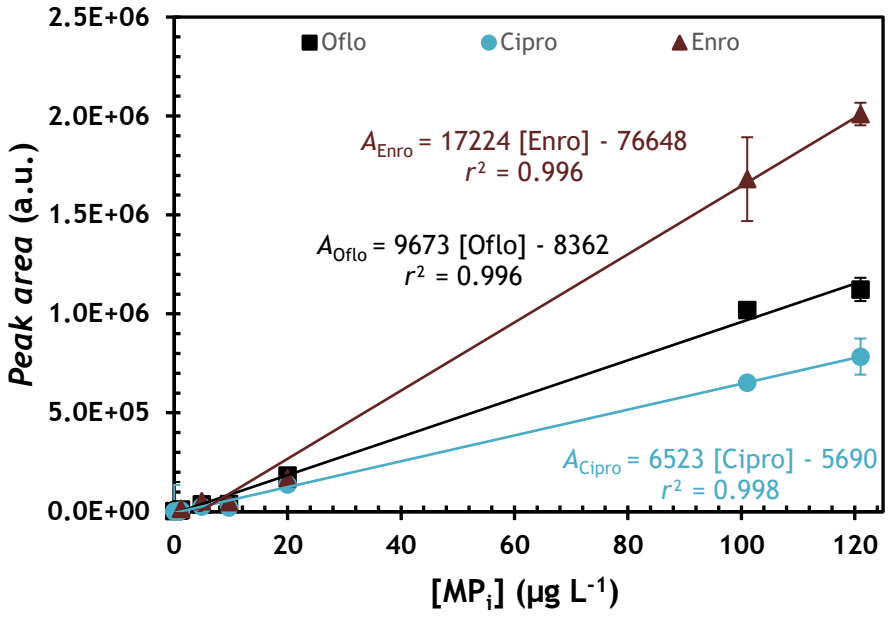

Figure A.8. Calibration curves obtained for the determination of the MPs concentration in UP water, and in the presence of methanol. Symbols represent the mean values obtained in two independent measurements, while the lines represent the linear fittings.

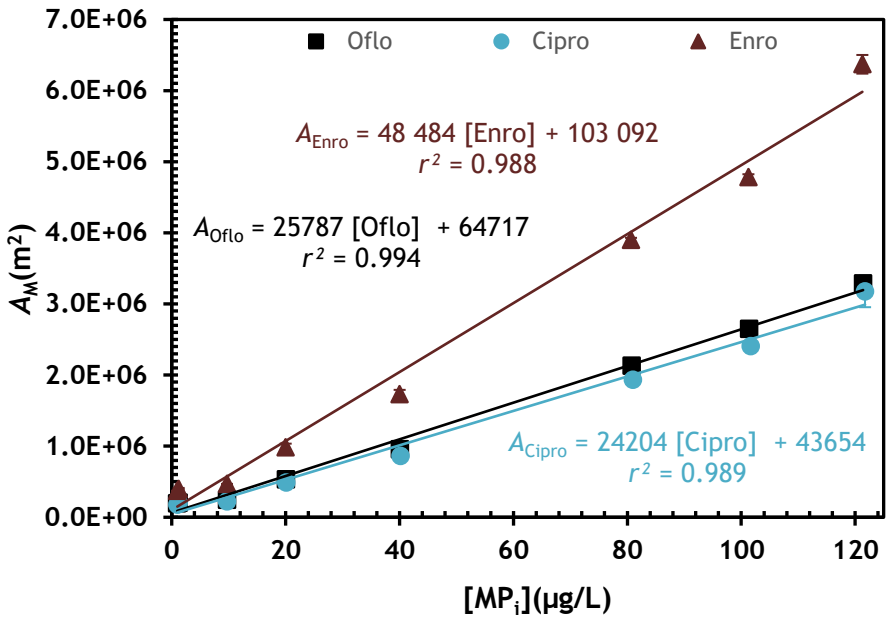

Figure A.9. Calibration curves obtained for the determination of the MPs concentration in SW, and in the presence of methanol. Symbols represent the mean values obtained in two independent measurements, while the lines represent the linear fittings.

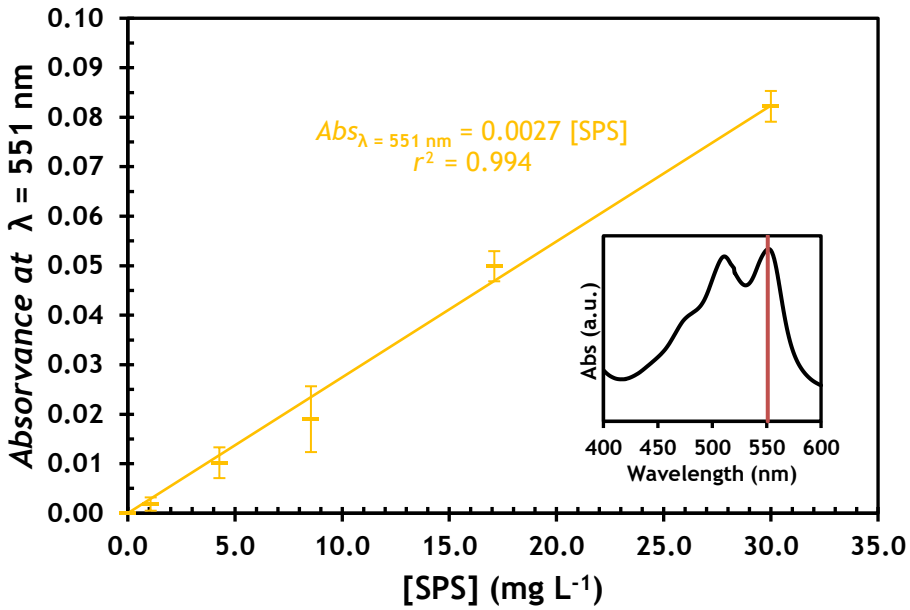

Figure A.10. Calibration curve obtained for the determination of SPS concentration. Inset: absorbance spectrum of SPS in the presence of DPD and phosphate buffer. Symbols represent the mean values obtained in three independent measurements, while the line represents the linear fitting.