

Carbon Membranes For Water Treatment

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Abstract

In the last years, new advanced oxidation processes (AOPs) have been receiving increasing attention because of the huge potential capacity for the removal of organic and inorganic micropollutants (MPs). However, these processes do not yet find application at full scale. Sulphate radicals ($\text{SO}_4^{\bullet-}$) based AOPs (SR-AOPs) have been widely investigated in recent years, being an alternative to eliminate pollutants from environmental water matrixes. Persulfate (PS) acts as precursor of $\text{SO}_4^{\bullet-}$ and can be activated by non-metal catalysts. Metal-free carbonaceous materials such as carbon nanotubes (CNTs) have attracted a lot of interest as heterogeneous catalysts, because of their chemical and physical properties. Considering that a large volume of the waste produced worldwide is composed by polymers from plastics (e.g., low-density polyethylene (LDPE), high-density polyethylene (HDPE), polypropylene (PP) and polyethylene terephthalate (PET)), the use of plastic polymers as carbonaceous feedstock to produce CNTs has been recently proposed. Moreover, with the sudden progress made in chemistry and material sciences, some researchers have switched towards the fabrication and application of membranes from 1D materials, such as CNTs.

CNTs synthesized by chemical vapor deposition (CVD) using LDPE (CNT-LDPE), HDPE (CNT-HDPE), and PP (CNT-PP) as carbon source, were tested in batch mode, to assess which type of CNTs reveals the best catalytic performance in the activation of persulfate and removal of venlafaxine (VFX) from ultrapure water, bottled water, and surface water. Characterization of the textural properties of the CNTs was performed, and the presence of metals in the CNTs studied. Composite polymeric membranes were fabricated considering 1.6 wt.% of the best performing CNTs (CNT-LDPE and CNT-HDPE). These membranes were tested in continuous mode to remove 21 MPs from SW samples spiked with each at a concentration of $50 \mu\text{g L}^{-1}$.

Keywords (theme): carbon nanotubes, activated persulfate, venlafaxine, composite polymeric membranes, micropollutants

Resumo

Nos últimos anos, novos processos de oxidação avançada (AOPs) têm recebido cada vez mais atenção devido ao grande potencial para a remoção de micropoluentes (MPs) orgânicos e inorgânicos. Contudo, estes processos não encontram ainda aplicação a grande escala. AOPs baseados em radicais sulfato ($\text{SO}_4^{\bullet-}$; SR-AOPs) têm sido amplamente estudados, sendo uma alternativa para a eliminação de poluentes de matrizes ambientais aquosas. O persulfato (PS) age como precursor de $\text{SO}_4^{\bullet-}$ e pode ser ativado por catalisadores não-metálicos. Materiais de carbono sem metais, como os nanotubos de carbono (CNTs), têm atraído muito interesse como catalisadores heterogêneos, devido às suas propriedades físicas e químicas. Polímeros de resíduos plásticos como por exemplo, polietileno de baixa densidade (LDPE), polietileno de alta densidade (HDPE), polipropileno (PP) e polietileno tereftalato (PET), são uma grande fração dos resíduos produzidos globalmente e recentemente, têm sido proposta a utilização de polímeros plásticos como fonte de carbono para a produção de CNTs. Além disso, o progresso na área da química e da ciência dos materiais, assim como estudos recentes, tem promovido a fabricação e aplicação de membranas a partir de materiais 1D, como os CNTs.

CNTs sintetizados por deposição química de vapor (CVD) usando LDPE (CNT-LDPE), HDPE (CNT-HDPE), e PP (CNT-PP) como fonte de carbono, foram testados em modo descontínuo, de forma a avaliar qual o tipo de CNTs que apresenta o melhor desempenho na remoção catalítica da venlafaxina (VFX) presente em água ultrapura, água engarrafada, e água superficial. Para uma melhor compreensão relativamente às características físicas, bem como às diferenças de rendimento entre CNTs testados no âmbito desta dissertação, foi realizada a caracterização das propriedades texturais dos CNTs e um estudo relativo há presença de metais nas amostras. Selecionados os CNTs que evidenciaram melhor desempenho nas experiências em modo descontínuo, membranas poliméricas compostas foram fabricadas considerando 1.6 wt.% desses mesmos CNTs nos materiais que formam as membranas. Estas membranas, foram testadas em modo contínuo, para remover 21 MPs de amostras de SW dopadas com cada composto com uma concentração de $50 \mu\text{g L}^{-1}$.

Palavras-chave (tema): nanotubos de carbono, ativação de persulfato
venlafaxina, membranas poliméricas
compostas, micropoluentes

Declaration

I hereby declare, under word of honor, that this work is original and that all non-original contributions is indicated, and due reference is given to the author and source

Leo Rinto Fernando Azedo
20/09/2021

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Notation and Glossary

		SI	Units Used
C	Concentration	kg m^{-3}	$\mu\text{g L}^{-1}$
C_0	Initial concentration	kg m^{-3}	$\mu\text{g L}^{-1}$
C/C_0	Normalized concentration	*	*
$d_{\text{Removal}}(\%)$	Difference between the removal (%) of VFX by catalysis and its removal (%) by adsorption.	*	*
m_i	Initial mass of CNTs	kg	g
m_f	the mass of CNTs recovered after the purification process	kg	g
p	Pressure	Pa	atm
p_0	Atmospheric pressure	Pa	atm
p/p_0	Normalized pressure	*	*
S_{BET}	Specific surface area	$\text{m}^2 \text{kg}^{-1}$	$\text{m}^2 \text{g}^{-1}$
t	Time	s	min or h
$V_{\text{ads, PTN}}$	Adsorbed volume of N_2 in PTN conditions	$\text{m}^3 \text{kg}^{-1}$	$\text{cm}^3 \text{g}^{-1}$
V_{Total}	Total pore volume	$\text{m}^2 \text{kg}^{-1}$	$\text{cm}^3 \text{g}^{-1}$

Indexes

* Dimensionless values

List of Acronyms

ACN	Acetonitrile
AOPs	Advanced oxidation processes
BW	Bottled water
CECs	Contaminants of emerging concern
CNTs	Carbon nanotubes
CNT-LDPE	CNTs synthesized by CVD of LDPE
CNT-LDPE-PVDF	Composite polymeric membranes fabricated with CNT-LDPE
CNT-HDPE	CNTs synthesized by CVD of HDPE
CNT-HDPE-PVDF	Composite polymeric membranes fabricated with CNT-HDPE
CNT-PP	CNTs synthesized by CVD of PP

CVD	Chemical vapor deposition
dH ₂ O	Distilled water
EtOH	Ethanol
H ⁺	Hydrogen cation
HDPE	High-density polyethylene
HO [•]	Hydroxyl radicals
OH [−]	Hydroxide
H ₂ O	Water
HO ₂ [−]	Perhydroxyl radicals
H ₂ SO ₄	Sulphuric acid
ICP—OES	Inductively Coupled Plasma — Optical Emission Spectrometry
K ₂ S ₂ O ₈	Potassium persulfate
LOD	Limit of detection
LOQ	Limit of quantification
M ⁿ	Metal ions and metal oxide
MPs	Micropollutants
MWCNTs	Multi-walled CNTs
NMP	1-methyl-2-pyrrolidone
O ₂ ^{•−}	Superoxide radical
O-VFX	O-desmethylvenlafaxine
PET	Polyethylene terephthalate
PhACs	Pharmaceutically active compounds
PMS	Peroxymonosulfate
PP	Polypropylene
PS, S ₂ O ₈ ^{2−}	Persulfate
PVDF	Poly(vinylidene fluoride)
PVP	Polyvinylpyrrolidone
RSD	Relative standard deviation
SPS, Na ₂ S ₂ O ₈	Sodium persulfate
SR-AOPs	SO ₄ ^{•−} based AOPs
SO ₄ ^{2−}	Sulphate anion
SW	Surface water
SWCNTs	Single-walled CNTs

UHPLC—FD	Ultra-High-Performance Liquid Chromatography – Fluorescence Detection
UHPLC—MS/MS	UHPLC – tandem Mass Spectrometry
UP	Ultrapure water
UWWTPs	Urban wastewater treatment plants
VFX	Venlafaxine
wt. %	Total weight in percentage
wt. % _l	Total weight loss of CNTs in percentage

1. Introduction

1.1. Framing and presentation of the work

Water is a particularly important resource for humans, being also indispensable for all ecosystems. Water crisis is a profoundly serious issue in some regions of the world. This problem tends to worsen in years to come. Water crisis is spreading worldwide as result of the increasing water consumption and wasting, the climate changes, the irregular water world distribution, and the growing number of anthropogenic activities (Sousa *et al.* 2018).

In general, urban wastewater treatment plants (UWWTPs) are among the main anthropogenic sources in the environment of pharmaceuticals, hormones, and personal care products (Barbosa *et al.* 2016), which may cause adverse effects on aquatic organisms and human health (Krzeminski *et al.* 2019; Li and Zhang 2011; Rizzo *et al.* 2015). Conventional UWWTPs comprising only secondary treatment (*e.g.*, activated sludge) are not effective in the elimination of organic micropollutants (MPs), including contaminants of emerging concern (CECs), since these plants are not originally designed to remove them.

In the last years, new advanced oxidation processes (AOPs) have been receiving increasing attention because of their potential capacity for the removal of organic and inorganic MPs. However, these processes have not yet found application at full scale (Byrne, Subramanian, and Pillai 2018; Ferro *et al.* 2015; Gogate and Pandit 2004; Klammerth *et al.* 2013). Carbon materials have been extensively studied as catalysts in AOPs and more recently few studies have been employing carbon materials in the form of membranes for the activation of persulfate (PS) oxidation, which is an alternative that enables continuous mode operation and overcomes the drawbacks related to the use of suspended powder catalysts (Vieira *et al.* 2022).

Current technologies are unable to promote a proper relation between reusing and recycling of plastic wastes so, the worldwide production of plastics has been increasing over the years (Miranda, Silva, and Pereira 2020; Vieira *et al.* 2022; WWF 2019).

Since the discovery of carbon nanotubes (CNTs) in 1991 by Iijima, using arc-discharge soot materials (Monthieux and Kuznetsov 2006), they have created a widespread interest in most domains of science and engineering due to their

astonishing physical and chemical properties (Jafari 2018; Oriňáková and Oriňák 2011; Paradise and Goswami 2007; Popov 2004; Tsukagoshi *et al.* 2002).

1.2. Objectives

The main objectives of this dissertation are to: (i) compare the efficiency of the three samples of CNTs in the activation of PS and degradation of organic MPs in batch mode, (ii) evaluate the best performing concentration of sodium persulfate (SPS), and (iii) study the effect of different water matrices on the catalytic performance. Another goal is to (iv) to study the properties of the CNTs by applying characterization techniques. The final goals are to (v) fabricate membranes with the best performing CNT samples and (vi) carry out experiments in continuous mode of operation.

1.3. Contribution of the author to the work

The author was responsible for all the experimental work carried throughout this dissertation, except for the synthesis of the CNTs, Inductively Coupled Plasma – Optical Emission Spectrometry (ICP–OES) analysis, the Ultra-High-Performance Liquid Chromatography – tandem Mass Spectrometry (UHPLC–MS/MS) method development and analysis, and the development of the UHPLC – Fluorescence Detection (FD) method used for the determination of venlafaxine (VFX). Nevertheless, the author performed the UHPLC-FD method's calibration and conducted routine sample analysis.

1.4. Organization of the dissertation

This dissertation has six chapters and one annex. Chapter 1 provides a brief introduction of the thematic addressed in this dissertation, including its main objectives and the author's contribution.

Chapter 2 presents in detail the themes addressed throughout this work.

In chapter 3, it is described the methodology used in this work, including the list of reagents used, the experimental approach carried out, as well as the analytical methods applied.

Chapter 4 presents the obtained results and their discussion.

In chapter 5, the main conclusions of the study developed under this dissertation are presented.

The chapter 6 provides a critical assessment of the work, namely the analysis of the objectives achieved and a personal assessment of the work done.

2. Context and State-of-the-Art

2.1. Problematic Scenario

The occurrence of organic pollutants at trace concentrations (*i.e.*, ng L^{-1} to $\mu\text{g L}^{-1}$, known as MPs) is one of the major causes of the deterioration of aquatic compartments. Their discharge, even at residual levels, contributes to their accumulation, with potentially detrimental effects on human and on aquatic ecosystems (Gorito *et al.* 2017; Radovic *et al.* 2015; Ribeiro, Ribeiro, and Tiritan 2016; Stuart *et al.* 2012; Vasquez *et al.* 2014). The organic MPs found in the aquatic environment result from uncountable sources, such as: (i) agriculture (*e.g.*, pesticides); (ii) industry (*e.g.*, industrial chemicals such as flame retardants, plasticizers, or food additives); and (iii) medicine (*e.g.*, pharmaceutically active compounds, PhACs) (Carlsson *et al.* 2006; Kolpin *et al.* 2002). Many of these MPs are considered CECs, a group that includes: new synthetic compounds; substances known for their occurrence in the environment for a long time (*e.g.*, hormones), but not recognized before as potentially hazardous for organisms; and compounds that, despite occurring in the environment for a long time, were only detected recently due to the most recent advances in analytical techniques (Sousa *et al.* 2018). A large amount of these CECs is non-biodegradable and pseudo-persistent, and might cause toxic effects (Wang and Wang 2018).

PhACs reach UWWTPs through the sewage network (He *et al.* 2015), due to the excretion as unchanged compounds or as metabolites, in urine and/or faeces (Sousa *et al.* 2018). Beyond pharmaceuticals and hormones, personal care products, pesticides, and industrial chemicals may be discharged into toilet sinks or as solid waste that, consequently, reach the UWWTPs (Malaj *et al.* 2014). As an example, when industrial effluents are discharged into UWWTPs without any treatment, most MPs are poorly removed (Deblonde, Cossu-Leguille, and Hartemann 2011). Drinking water treatment plants are also not particularly designed to eliminate organic MPs, which highlights the importance of developing optimized and new technologies for the degradation of CECs in the environment.

2.2. Advanced oxidation processes (AOPs)

$\text{SO}_4^{\bullet-}$ based AOPs (SR-AOPs) have been widely investigated in recent years. These radicals, in comparison to hydroxyl radicals ($\text{HO}^\bullet$), have some unique features that are expected to make them present similar or better to promote the elimination of CECs (Huang and Huang 2009; Wang and Wang 2018), namely (i) equal or even higher redox potential (+ 2.5 to + 3.1 V) based on the activation methods (Ghauch and Tuqan 2012); (ii) higher selectivity; (iii) longer half-life (generally between 30 and 40 μs for $\text{SO}_4^{\bullet-}$ and less than 1 μs for $\text{HO}^\bullet$); and (iv) the ability to react with organic compounds under a wide range of pH (2 - 8).

PS and peroxymonosulfate (PMS) act as precursors of $\text{SO}_4^{\bullet-}$, and there are several activation modes: (i) radiation; (ii) heat; (iii) microwaves; (iv) ultrasounds; (v) transition metals; (vi) alkaline; and (vii) non-metal catalysts (Shao *et al.* 2017). The mechanism of thermal activation of PS is represented in Eq. (1) (Wang and Wang 2018). For alkaline activation of PS, a nucleophilic attack on the O–O bond is the main mechanism as shown in Eq. (2) and (3) (Wang and Wang 2018). Due to alkali conditions, $\text{SO}_4^{\bullet-}$ originates $\text{HO}^\bullet$ through Eq. 4 (Wang and Wang 2018). For the activation of PS by metal ions and metal oxides, the mechanism is the reduction, as described in Eq. (5) (Wang and Wang 2018). PS is a white crystal that has high stability (bond energy is 140 kJ mol^{-1}); can be easily dissolved in water (solubility of 730 g L^{-1}) (Liang *et al.* 2010); has symmetrical structure, with a distance O–O of 1.497 Å; and is a strong oxidizer (redox potential of 2.01 V). Sodium PS ($\text{Na}_2\text{S}_2\text{O}_8$) and potassium PS ($\text{K}_2\text{S}_2\text{O}_8$) are the most common, and the PS aqueous solution is acidic. PS is generally preferred over PMS as precursor of $\text{SO}_4^{\bullet-}$ for decontamination applications because it is more stable and water soluble (Liang *et al.* 2010). The properties of PS and PMS are listed in Table 1.



Table 1 – Properties of PS and PMS.

Properties	Sodium PS	PMS*
Formula	$\text{Na}_2\text{S}_2\text{O}_8$	$\text{H}_3\text{K}_5\text{O}_{18}\text{S}_4$
CAS number	7775-27-1	10058-23-8
Molecular weight	238.1 g mol^{-1}	614.7 g mol^{-1}
Solubility**	556 g L^{-1}	$> 250 \text{ g L}^{-1}$
Redox potential	+ 2.01 V	+ 1.82 V

* PMS refers to Oxone

** Solubility is based on the data at 20 °C
(Wang and Wang 2018)

Metal-free carbonaceous materials have attracted a lot of interest as heterogeneous catalysts because of their chemical and physical properties. They have many advantages in comparison to metal-based catalysts, such as (i) chemical stability at different pHs, and (ii) easy to tune the pore structure and surface chemistry (Zhao *et al.* 2017). Moreover, carbonaceous materials like fullerenes, CNTs, and graphene derivatives act as metal-free catalysts for several applications (Dai *et al.* 2015).

2.3. Plastic wastes

For years, researchers have been looking for several ways to overcome the pollution caused by plastic waste and, recently, some researchers have suggested using plastic polymers as the carbonaceous feedstock to produce CNTs (Bazargan and McKay 2012). In 2019, the global production of plastics reached approximately 370 million metric tonnes, and only in Europe, approximately 58.1 million metric tonnes of these materials were produced (PlasticsEurope 2020). Following this increase over the years, recent estimates are that by 2050, the cumulative plastic waste generation will be over 25,000 million tonnes. It is expected that 36.4% of these plastic wastes will be discarded in landfills or in the environment, 36.4% would be incinerated, and only 27.2% will be recycled (Geyer, Jambeck, and Law 2017). Due to the large volume of plastic wastes generated worldwide, all the natural ecosystems are being increasingly contaminated affecting all living species (Miranda, Silva, and Pereira 2020). To mitigate this worldwide problem, it is important the adoption of preventive strategies and measures. However, the recycling of plastic materials has been limited by the lack of economic attractiveness in the resulting products from the recycling of plastic wastes (Miranda, Silva, and Pereira 2020).

Using plastic wastes as feedstock to produce added-value materials and/or products has been proposed to increase the attractiveness of plastics recycling. The

interest in carbon materials has been growing due to their unique properties, such as high surface area, electronic conductivity, porosity, structural stability at high temperatures, and rich/tailorable surface chemistry (Figueiredo 2013; Zhang *et al.* 2016). Being these carbon materials so unique, they have been increasingly employed in very different fields, such as environmental (Lalovic *et al.* 2017), energy (Yun *et al.* 2014), biomedicine (Lin *et al.* 2004), and analytical (Agui, Yanez-Sedeno, and Pingarron 2008) applications. A large fraction of the waste produced worldwide is composed by polymers from plastic wastes such as low-density polyethylene (LDPE) or high-density polyethylene (HDPE), polypropylene (PP), polyethylene terephthalate (PET) (Bazargan and McKay 2012).

2.4. CNTs

Elemental carbon in sp^2 hybridization can form a variety of structures, such as (i) fullerenes (0D), (ii) carbon nanotubes (CNTs, 1D), (iii) graphene (2D) and (iv) graphite (3D) (Hou, Liu, and Cheng 2008). CNTs may consist of one (single-walled CNTs, SWCNTs) or up to dozens and hundreds (multi-walled CNTs, MWCNTs) seamless graphene cylinders stacked with a layer spacing of approximately 0.34 nm (Hou, Liu, and Cheng 2008).

Some of the current existing methods for CNT production are catalytic chemical vapor deposition (CVD), electric arc discharge method, flame synthesis, laser ablation method, and the solar energy route (Bazargan and McKay 2012). Among these methods, CVD seems to be the most promising for large-scale production (10,000 tons of CNTs per annum) (Cheng *et al.* 2013; Dasgupta *et al.* 2007; Manawi *et al.* 2018). Considering that the above-mentioned methods for CNT production are energy and resource demanding, researchers have been seeking to develop alternative, more cost-effective, routes to produce CNTs at large scale. Chemical recycling through valorization of plastic waste as a low-cost feedstock for production of carbon nanotubes is an attractive strategy (Modekwe *et al.* 2021).

2.5. Membrane Technologies

Membranes are used in water purification, air filtration, biomedical and food industry, and energy storage applications (Luo, Abdu, and Wessling 2018; Ulbricht 2020; Wang and Lin 2019). Moreover, membrane technologies can be coupled with catalytic oxidation for water treatment by using a catalytic membrane with a dual role: filtration and catalysis (Li *et al.* 2021). The two major advantages of this approach are related to the simultaneous degradation of the pollutants that in turn allows the

self-cleaning of the membrane and avoids fouling (Li *et al.* 2021). CNTs membranes have been studied as a highly efficient solution to be applied as catalytic membranes in water and wastewater treatment (Li *et al.* 2020). In fact, CNTs have received an increasing attention for environmental catalysis due to their unique properties, namely their high surface area and chemical stability, as well as their good mechanical properties and electronic conductivity (Ahmad Zulkifli, Yazid, and Jani 2021).

2.6. Legislation

The presence of pharmaceuticals in urban wastewaters, and in the water intended for consumption, is not legislated in Portugal; however, there is a Commission Implementing Decision (EU) - 2020/1161 of 4 August 2020 - that establishes a watch list of substances for Union-wide monitoring in the field of water policy pursuant to Directive 2008/105/EC of the European Parliament and of the Council.

Regarding the current regulation on urban wastewater, Directive 91/271/EEC of the European Council, of 21 May 1991, commonly referred to as Urban Wastewater Directive, aims to protect the environment from the harmful effects of urban wastewater discharges. In Portugal, the treatment of urban wastewaters is legislated by Decreto-Lei n.º 152/97, which transposes the above mentioned Directive 91/271/CEE, and adopts the provisions applicable to the collection, treatment, and discharge of urban wastewaters into the aquatic environment as well as the list of identification of sensitive areas and less sensible areas for the continental territory. In 2020, the new review of sensitive areas was completed, pending only the publication of the respective legal legislation. The rejection of urban wastewaters is carried out considering principles like precaution, prevention and correction referred in Decreto-Lei n.º 226-A/2007.

The current regulation on water quality for human consumption in Portugal is set by Decreto-Lei n.º 306/2007. The revision of Directive 2020/2184 of 16 December 2020, of the European Parliament and of the Council, on water quality intended for human consumption was adopted. The Directive entered into force on 12 January 2021 and now Member-States have two years to transpose it into national law.

2.7. Target CEC: Venlafaxine

VFX was selected as model compound representing MPs, because this PhAC is one of those included in the watch list of substances for Union-wide monitoring in the field of water policy (Decision (EU) 2020/1161 of 4 August 2020). VFX, an antidepressant, and its active metabolite O-desmethylvenlafaxine (O-VFX), belong to a group of drugs called selective serotonin and norepinephrine reuptake and weak dopamine reuptake inhibitors. The concentrations of both (VFX and O-VFX) in UWWTP effluents, and in the aquatic environments receiving the treated effluents discharged from UWWTPs, are higher than the concentrations detected for other antidepressant drugs (Metcalf *et al.* 2010; Schultz and Furlong 2008). VFX and O-VFX have been detected in discharged UWWTPs effluents at concentrations ranging from 808 to 2,050 ng L⁻¹ and from 1,637 to 1,927 ng L⁻¹, respectively (Arlos *et al.* 2015; Mehdi *et al.* 2019; Metcalfe *et al.* 2010; Schultz and Furlong 2008). Similar concentrations of these compounds have been found in surface water (SW), *e.g.*, in Grand River (Southern Ontario, Canada) concentrations of VFX ranging from 61 to 901 ng L⁻¹ and of O-VFX ranging from 167 to 1,472 ng L⁻¹ were detected (Metcalf *et al.* 2010). In Portugal, the presence of VFX in SW receiving discharges of UWWTP effluents was also reported, *e.g.*, in Lis River, where VFX reached an average concentration of 182 ng L⁻¹ (Paiga *et al.* 2016). Despite the relatively high concentrations found, it is worthy to mention that the effects of this PhAC on aquatic species are relatively unknown (Mehdi *et al.* 2019). The properties of VFX are listed in Table 2.

Table 2 – VFX physical-chemical properties.

Properties	VFX
Molecular formula	C ₁₇ H ₂₇ NO ₂
CAS number	93413-69-5
Molecular weight	277.4 g mol ⁻¹
Solubility (at 25 °C)	267 mg L ⁻¹

3. Materials and methods

3.1. Chemicals and materials

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), alachlor (MW: 269.77 g mol⁻¹), acetamiprid (MW: 208.85 g mol⁻¹), atenolol (MW: 266.34 g mol⁻¹), atrazine (MW: 215.88 g mol⁻¹), bezafibrate (MW: 361.82 g mol⁻¹), carbamazepine (MW: 236.27 g mol⁻¹), clofibric acid (MW: 214.65 g mol⁻¹), diclofenac sodium (MW: 318.14 g mol⁻¹), diphenhydramine hydrochloride (MW: 291.82 g mol⁻¹), enrofloxacin (MW: 359.39 g mol⁻¹), isoproturom (MW: 206.28 g mol⁻¹), ketoprofen (MW: 254.28 g mol⁻¹), methiocarb (MW: 225.31 g mol⁻¹), metoprolol tartrate (MW: 684.8 g mol⁻¹), ofloxacin (MW: 361.37 g mol⁻¹), propranolol hydrochloride (MW: 295.80 g mol⁻¹), thiachloprid (MW: 252.72 g mol⁻¹), thiamethoxam (MW: 291.71 g mol⁻¹), tramadol hydrochloride (MW: 299.84 g mol⁻¹), venlafaxine hydrochloride (MW: 313.86 g mol⁻¹), warfarin (MW: 308.33 g mol⁻¹), iron (II) chloride tetrahydrate (MW: 198.81 g mol⁻¹, 98 wt.%), aluminium nitrate nonahydrate (MW: 375.13 g mol⁻¹, 98.5 wt.%) were purchased from Sigma-Aldrich. Sulphuric acid (H₂SO₄; 95 wt.%), acetonitrile HPLC and MS grade (ACN; MW: 41.05 g mol⁻¹, 99.95 wt.%), formic acid (99 wt.%), and hydrochloric acid (37 wt.%) were obtained from VWR. Nitric acid (MW: 63.01 g mol⁻¹) was obtained from Fluka. Sodium persulfate (SPS; MW: 238.110 g mol⁻¹, 99 wt.%) was supplied by Riedel-de Haën. All chemicals were used as received, without further purification. GN-6 paper filter (0,45 µm; 47 mm) were distributed by Pall Corporation (Michigan, USA). Ultrapure water (UP) was produced in a Milli-Q® water purification system (Merck, Darmstadt, Germany), distilled water (dH₂O) was produced in a distillation unit assembled at FEUP, the bottled water (BW) used was from the brand Fastio® (Chamoim, Terras de Bouro, Portugal), and SW was collected in Fradelos – Vila Nova de Famalicão, Braga, Portugal. *Aqua regia* is a mixture of pure nitric acid and hydrochloric acid, with a volume ratio of 1:3.

3.2. Purification of the CNTs

The CNTs used in this research work (CNT-LDPE, CNT-HDPE, and CNT-PP) were prepared and synthesized by Lucas Fenato (Annex A) at the Polytechnic Institute of Bragança, within the project PLASTIC_TO_FUEL&MAT, and were kindly provided for the development of the present dissertation.

Regarding the purification step, 1.1 g of each sample of CNTs (CNT-LDPE, CNT-HDPE, and CNT-PP) was dispersed in 55 mL of dH₂O, after which 55 mL of H₂SO₄ (95 wt.%) was added. The oxidation occurred over 3 h at 140 °C, in a round bottom flask equipped with a condenser, which was immersed in an oil bath under stirring (240 rpm). The purification experimental set-up is shown in Fig. 1. Once completed the oxidation process, the dispersion was vacuum filtered using GN-6 paper filter and the retained material was washed with 2.25 L of dH₂O, aiming at obtaining high-quality CNTs. After this washing step, the filtered CNTs were recovered from the paper filter using a micro-spatula and dried overnight in an oven at 100 °C.

The total weight loss of CNTs, in percentage, (wt.%_l) after the purification step was estimated from Eq. (6).

$$\text{wt.\%}_l = \left(\frac{m_i - m_f}{m_i} \right) \times 100\% \quad (6)$$

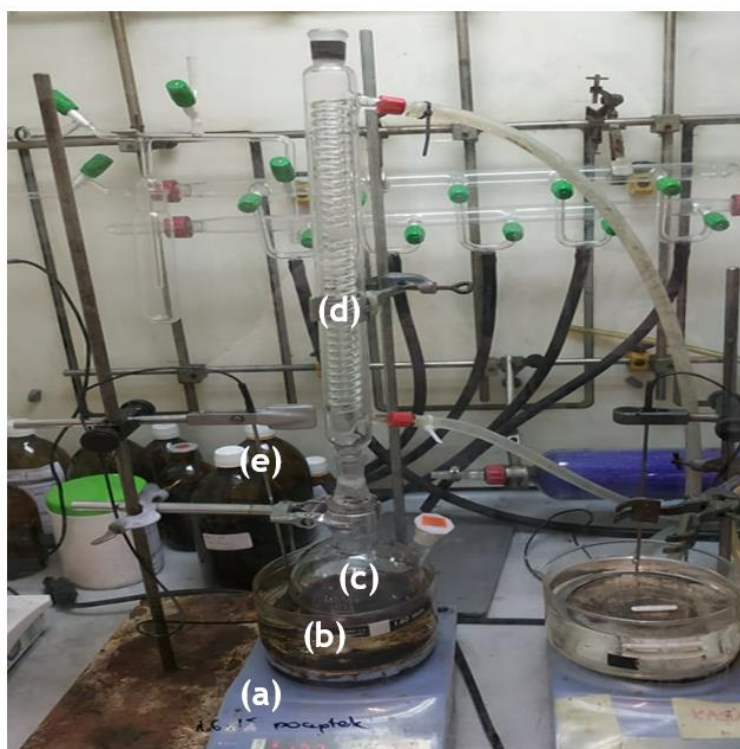


Fig. 1 — Experimental set-up used for the purification of CNT: (a) stirring and heating plate; (b) oil bath; (c) reactor; (d) condenser; and (e) thermocouple.

3.3. Water Matrices

A standard solution of VFX at 10 mg L^{-1} was prepared in UP and stored at 4°C . This solution was used to obtain working solutions containing $250 \text{ }\mu\text{g L}^{-1}$ of VFX in: (i) UP ($\text{pH} = 6.2$); (ii) BW ($\text{pH} = 7.1$; $1.0 \pm 0.2 \text{ mg L}^{-1}$ of sulphates; $1.3 \pm 0.3 \text{ mg L}^{-1}$ of calcium; $9.6 \pm 2.0 \text{ mg L}^{-1}$ of silicon; $4.2 \pm 0.4 \text{ mg L}^{-1}$ of chlorides; $4.1 \pm 0.4 \text{ mg L}^{-1}$ of sodium; $0.6 \pm 0.1 \text{ mg L}^{-1}$ of potassium); and (iii) SW ($\text{pH} = 7.3$) collected from Ave River, nearby the discharge point of the effluent treated by Agra UWWTP in Fradelos - Vila Nova de Famalicão, district of Braga, Portugal. SW was vacuum filtered using GN-6 paper filter to remove suspended solids that would interfere in analytical steps. The filtrated SW was kept at 4°C until further use.

For continuous experiments, a standard solution containing 21 MPs (alachlor, acetamiprid, atenolol, atrazine, bezafibrate, carbamazepine, clofibric acid, diclofenac, diphenhydramine, enrofloxacin, isoproturon, ketoprofen, methiocarb, metoprolol, ofloxacin, propranolol, thiachlopid, thiamethoxam, tramadol, venlafaxine, and warfarin) at 25 mg L^{-1} was prepared in acetonitrile and stored at -20°C . This solution was used to prepare working solutions containing $50 \text{ }\mu\text{g L}^{-1}$ of the target MPs in SW. For that, the volume of solution was added into a volumetric flask and the solvent was evaporated using a gentle nitrogen stream prior to the addition and homogenization of the SW.

3.4. CNT-HDPE-PVDF and CNT-LDPE-PVDF membranes

The fabrication of composite polymeric membranes was done by adapting a procedure described elsewhere (Ayyaru and Ahn 2017), considering 1.6 wt.% of CNTs in the membrane forming materials. For composite polymeric membranes fabricated with CNT-HDPE (CNT-HDPE-PVDF), 0.4641 g of CNT-HDPE was added to a solution containing 0.2812 g of PVP and 24 mL of NMP. The resulting mixture was sonicated for 3.5 h at room temperature and then 4.2846 g of PVDF was added. The polymerization proceeded at 40°C for 48 h, under magnetic stirring at 450 rpm. After polymerization, the solution was left overnight at room temperature without stirring to remove air bubbles. Afterwards, this solution was placed in a glass plate and spread using the knife cast technique (Fig. 2). The casting film applicator used was a Elcometer 3580 (Warren, MI) that allows selecting the thickness of the cast polymeric solution ($50 \text{ }\mu\text{m}$), which was then immersed in dH_2O to accomplish the final coagulation. The resulting flat membrane sheet of CNT-HDPE-PVDF was removed from the glass plate, cut to obtain a membrane of 1.64 cm of inner diameter (2.10 cm^2 of effective area), and

stored in dH₂O until further use. A similar procedure was followed for the preparation of composite polymeric membranes fabricated with CNT-LDPE (CNT-LDPE-PVDF), except that the amounts of CNTs and reagents were reduced proportionally (0.2320 g of CNT-LDPE, 0.1410 g of PVP, 12 mL of NMP, and 2.1400 g of PVDF).

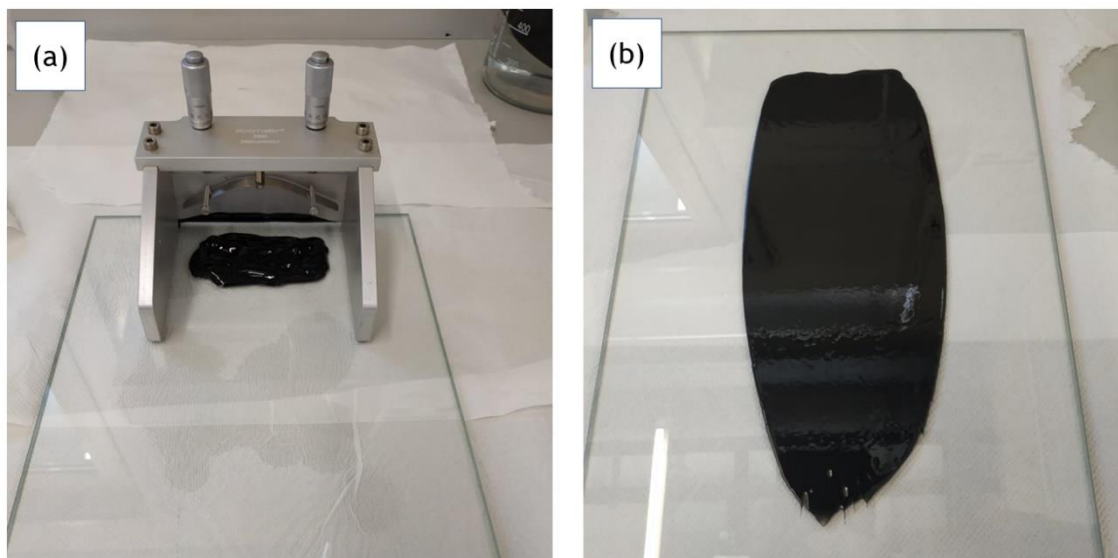


Fig. 2 – Application of knife cast technique: (a) placement of the polymeric solution in a glass plate, which was (b) spread using the knife casting technique.

3.5. Activated Persulfate Experiments

3.5.1. Batch experiments

Activated PS experiments in batch mode were carried out at room temperature (22 ± 2 °C). For catalytic experiments, 50 mL of a solution containing VFX ($250 \mu\text{g L}^{-1}$) in UP was treated in a 100 mL glass cylindrical amber reactor to which the selected amount of SPS (25 or 250 mg L^{-1}) was added, followed by the selected amount of CNTs (50 mg L^{-1}). The initial sample ($t = "0"$ min) was collected from the batch reactor after adding SPS to the solution containing VFX, and the time of experiment started after the addition of the CNTs. Adsorption experiments were performed in the absence of SPS, and in these experiments the initial sample was collected before adding the CNTs to the solution. Control (non-catalytic) experiments were also performed to evaluate the stability of VFX in the presence of SPS, and in these experiments the initial sample was collected before adding SPS to the solution. The batch reactor was covered with aluminium foil to avoid light activation of SPS, whereas the room temperature was maintained with the air conditioner system of the laboratory to avoid major temperature variations. Sample aliquots of 0.2 mL were collected from the batch reactor using a syringe and transferred to chromatographic vials. In the case of

adsorption and catalytic experiments, the samples collected were filtered with PTFE syringe filters (13 mm; 0.2 μm pore diameter) after collection due to the presence of the suspended solids (CNTs) that could interfere in subsequent analytical analysis. The following sampling periods were considered: 0; 5; 10; 15; 30; 45; 60; 75; 90; and 120 min. All samples were frozen until analysis for determination of VFX concentration by UHPLC–FD. All experiments were conducted without pH adjustments, with the inherent pH of UP (pH = 6.2), BW (pH = 7.1), or SW (pH = 7.3). The difference removal in % (d_{Removal} (%)) is determined by the difference between the removal (%) of VFX by catalysis and the removal (%) of VFX by adsorption, this value being obtained for each one of the samples of CNTs.

3.5.2. Continuous mode experiments

Activated PS experiments in continuous mode were conducted at room temperature (22 ± 2 °C) as performed in batch mode. The solution containing the target MPs and the selected amount of SPS (25 mg L^{-1}) was fed in continuous mode to the membrane cell (0.11 mL min^{-1}) using a peristaltic pump, the treated water being collected in a glass bottle. A graduated cylinder was used for flow rate monitoring purposes. Each composite polymeric membrane fabricated for this purpose was tested during 48 h and permeated aliquots (0.2 mL) were collected using a 2 mL syringe with needle, following by transfer to chromatographic vials. In the first 24 h, the adsorption test was performed in the absence of SPS. The initial sample ($t = \text{"0"} \text{ h}$) was collected from the feeding bottle, after the feeding system was filled, corresponding to the beginning of the experiment. After 24 h, the feeding bottle was replaced by another one with the same composition of MPs, but with the difference that SPS was added (to start the catalytic test), and the feeding line was filled with this solution ($t = \text{"0"} \text{ h}$). Control experiments were performed at the same time in batch mode, *i.e.* in the feeding bottle, to assess the stability of the target MPs in the presence of SPS, whereas the catalytic experiments occurred in the membrane cell simultaneously. The feeding bottle was covered with aluminium foil in all experiments to avoid light activation of SPS, and the inherent pH of SW (pH = 7.3) was used without pH adjustments. All samples were frozen until analysis.

3.6. Characterization techniques

The textural properties of the CNTs were determined from N₂ adsorption-desorption isotherms obtained at $-196\text{ }^{\circ}\text{C}$ (Quantachrome NOVA 4200e adsorption analyser). Before the analysis, the samples were outgassed during 6 h at $130\text{ }^{\circ}\text{C}$. By applying the Brunauer-Emmett-Teller equation, the specific surface area of the CNTs was determined, and by considering the amount of N₂ adsorbed at a relative pressure (p/p^0) close to 1, the total pore volume was determined.

3.7. Analytical methods

3.7.1. Ultra-High-Performance Liquid Chromatography – Fluorescence Detection (UHPLC–FD)

The concentration of VFX was determined by UHPLC–FD, using a Shimadzu Corporation equipment consisting of an autosampler (SIL-30AC), a degasser (DGU-20A5R), an oven (CTO-20AC), a pump (LC-30AD), and a fluorescence detector (RF-20AXS). Chromatographic separation was optimized and conducted in isocratic mode in a Kinetex™ 1.7 μm XBC18 100 Å (100 x 2.1 mm i.d.), set at $30\text{ }^{\circ}\text{C}$. A mixture of (A) aqueous formic acid 0.1 % (V/V) and (B) acetonitrile was used as mobile phase (total flow rate of 0.25 mL min^{-1}), and delivered as follows: 77% of A and 23% of B. The total run time was 10 min. The autosampler temperature was kept at $15\text{ }^{\circ}\text{C}$, and the injection volume was 20 μL . The excitation wavelength of the FD was 230 nm, and the emission wavelength was 300 nm.

3.7.2. Ultra-High-Performance Liquid Chromatography – Tandem Mass Spectrometry (UHPLC–MS/MS)

The concentrations of the target MPs were determined by UHPLC–MS/MS using a Shimadzu Corporation equipment consisting of an autosampler (SIL-30AC), a degasser (DGU-20A5), an oven (CTO-20AC), two pumps (LC-30 AD), and a triple quadrupole mass spectrometer (LCMS-8040 – Shimadzu Corporation equipment). Chromatographic separation was optimized and conducted in isocratic mode using a Kinetex™ 1.7 μm XBC18 100 Å (100 x 2.1 mm i.d.), set at $40\text{ }^{\circ}\text{C}$. A mixture of (A) ultrapure water and (B) acetonitrile acidified with formic acid (0.1 %, V/V) was used as mobile phase at a flow rate of 0.2 mL min^{-1} , and delivered as follows: 85% of A and 15% of B. The total running time was 33 min. The autosampler temperature was kept at $15\text{ }^{\circ}\text{C}$ and the injection volume was 10 μL .

3.7.3. Inductively Coupled Plasma – Optical Emission Spectrometry (ICP–OES)

The acid digestion of the CNTs was performed to evaluate the remaining overall content of iron (Fe) and aluminium (Al) in the CNTs, after the purification step. It was performed by dispersing each sample in dH₂O (1 mg mL⁻¹) and adding 6 mL of *aqua regia* to 6 mL of the resulting dispersion, which was heated at 40 °C for 48 h to promote the sample digestion. After reaching the room temperature, the digested samples were filtered with a red rim syringe filter (FP 30 /0.2 CA filter unit, 0.2 µm pore diameter).

The filtered digested samples (10 mL) were analysed in an ICP–OES ICAP 7000 SERIES (Thermo Scientific) equipped with a nebulizing system, an autosampler (ASX-520), a water chiller (Smart H150-1500S), a peristaltic pump, and using optical emission spectrometer for detection. The quantification of metals present in each liquid phase obtained and collected was quantified considering calibration curves for each metal to be analysed (Al and Fe).

4. Results and discussion

4.1. Characterization Techniques

Most of the as-prepared CNTs contain a certain amount of impurities such as (i) metal catalyst particles, and (ii) carbonaceous impurities (e.g. amorphous carbon, fullerenes and carbon nanoparticles), resulting from the synthesis process of the CNTs (Hou, Liu, and Cheng 2008). Thus, a purification step was required to obtain CNTs with higher quality. Therefore, before testing the three samples of CNTs under study, liquid-phase oxidation was performed to remove the amorphous carbon, metals (resulting from the catalyst used in the synthesis of the CNTs by CVD), and other possible impurities. The initial mass of CNTs (m_i), the mass of CNTs recovered after the purification process (m_f), and the total weight loss of CNTs in percentage (wt.%) after the purification step, was estimated by using Eq. (6). The results are presented in Table 3.

Table 3 – Total mass of CNTs available for this dissertation: (m_i), mass of CNTs recovered after the purification process (m_f), and total weight loss of CNTs in percentage (wt.%), arising from the purification process.

	m_i (g)	m_f (g)	wt.% _l
CNT-LDPE	1.103	0.6381	42.15%
CNT-HDPE	1.101	0.6386	42.00%
CNT-PP	1.101	0.6542	40.58%

According to the literature (Hou, Liu, and Cheng 2008), the values of wt.%_l obtained are within the expected range (30 – 50%).

The textural properties of the CNTs were determined from the N₂ adsorption-desorption isotherms obtained at – 196 °C. This information is useful to understand the differences in the performances observed for the CNTs tested in the degradation of VFX. The results obtained are presented in Fig. 3 and the textural properties of the CNTs are summarized in Table 4.

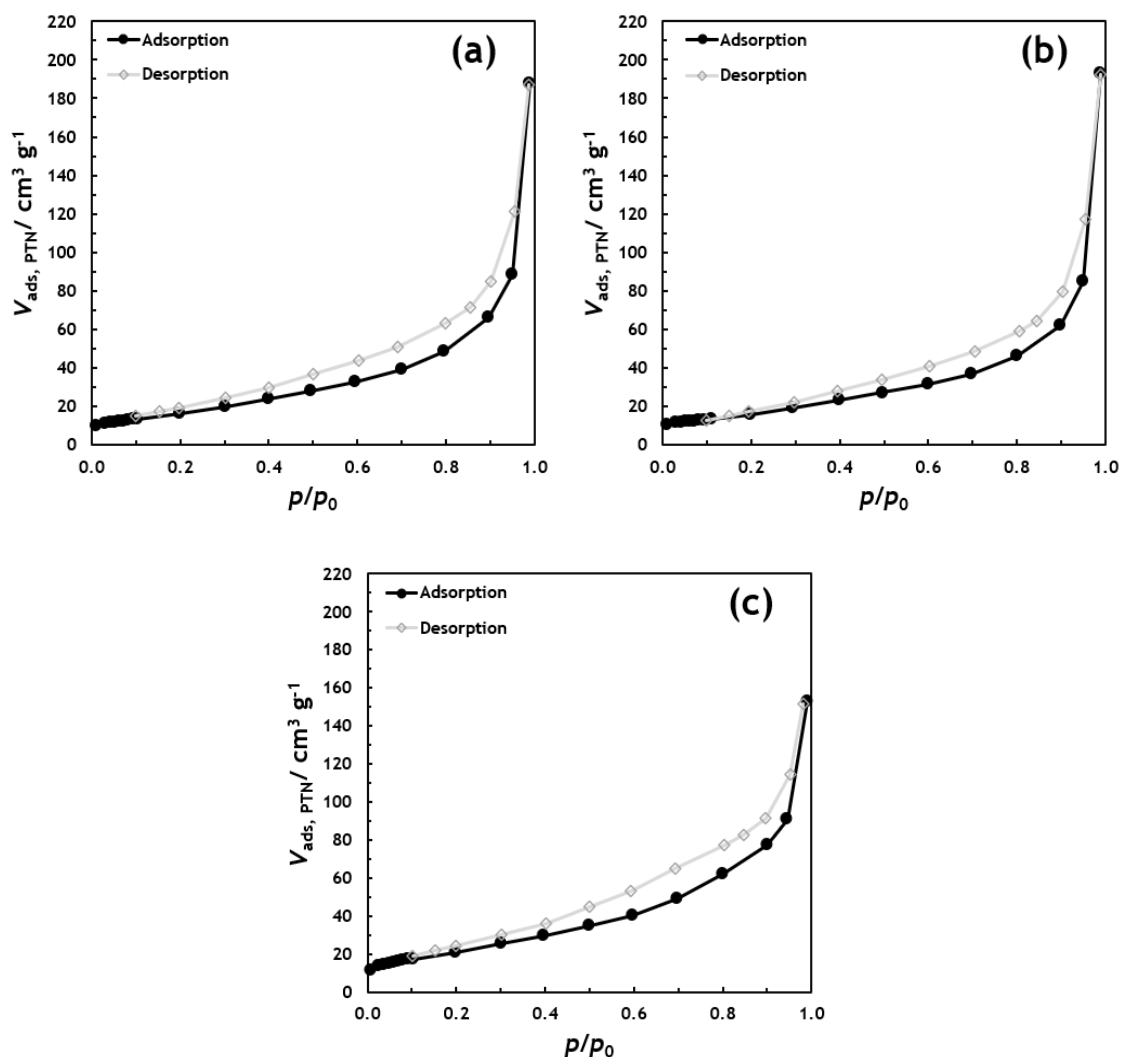


Fig. 3 – N_2 adsorption-desorption isotherms at -196°C , obtained in a Quantachrome NOVA 4200e adsorption analyser for (a) CNT-LDPE, (b) CNT-HDPE, and (c) CNT-PP.

Table 4 – Textural properties of the CNTs.

	S_{BET} ($\text{m}^2 \text{g}^{-1}$)	V_{Total} ($\text{cm}^3 \text{g}^{-1}$)
CNT-LDPE	55	0.290
CNT-HDPE	52	0.298
CNT-PP	73	0.236

Analysing the physisorption data (Fig. 3), it is possible to verify that the desorption does not follow the adsorption. It is assumed that, in the adsorption isotherm, the surface coating is done homogeneously, layer by layer. This means that N_2 molecules do not overlap until a layer is fully filled. After the completion of the filling (adsorption), the desorption isotherm was obtained. The difference between the

adsorption isotherm and the desorption isotherm is called hysteresis and it was expected to occur due to the capillary condensation. This condensation takes place because N₂ presses the walls of the carbon materials and they compact the N₂ which leads to capillary condensation (*i.e.*, gaseous N₂ becomes liquid N₂). The calculations necessary for the characterization of the textural properties of the CNTs can only be done until the hysteresis starts to occur because then, the method loses validity. At this temperature (– 196 °C) it is fair to assume that chemical reactions do not occur, so the adsorption is entirely due to physisorption.

Analysing the data presented in Table 4, the CNTs with smaller surface area are those with the highest total pore volume. CNT-PP was the carbon material with the highest surface area and the smallest total pore volume. CNT-HDPE presented the smallest surface area and the highest total pore volume, but it is similar to CNT-LDPE because the common deviation of this characterization data is $\pm 5\text{-}10 \text{ m}^2 \text{ g}^{-1}$.

Looking at the isotherm patterns obtained and represented in Fig. 3, and considering that CNTs do not present a microporous structure (Rocha *et al.* 2016; Tessonnier *et al.* 2009), it was possible to affirm that the CNTs, studied under this dissertation, only presented pores in the mesopore range (2-50 nm) (Sotomayor, Cychosz, and Thommes 2018).

4.2. Batch Experiments

The main objective of this dissertation project is to determine which plastic polymer produced the best performing CNTs for the activation of SPS and degradation of VFX. The results presented for batch experiments were obtained as duplicates, triplicates or quadruplicates, depending on the experiment (n is provided in each figure). Figs. 4, 5, and 6 show the results obtained with UP, BW, and SW, respectively, for the removal of VFX by adsorption, non-catalytic conversion, and catalysis. It is also represented the relative standard deviation (RSD), in the series where were considered more than one experiment.

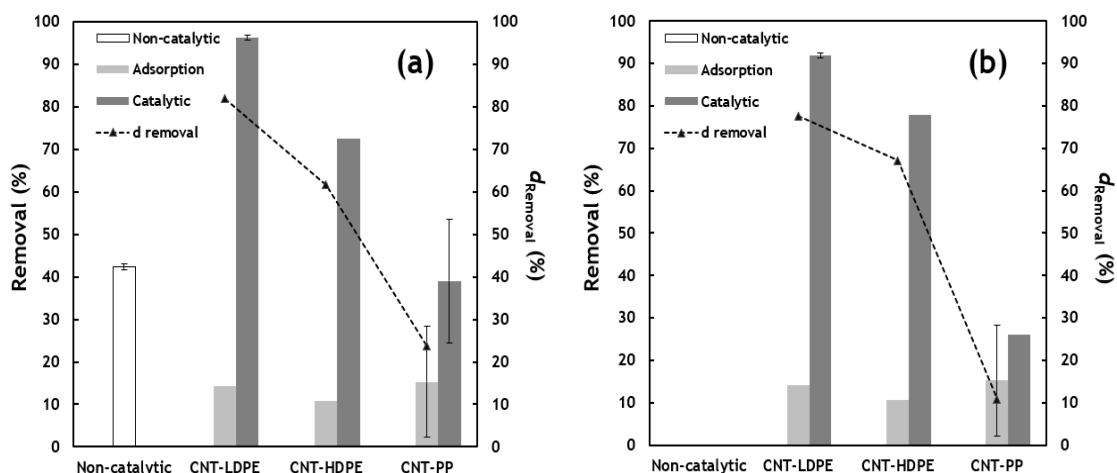


Fig. 4 – Batch experimental results for the removal of VFX ($250 \mu\text{g L}^{-1}$) after 2 h, with different CNTs using (a) $[\text{SPS}] = 250 \text{ mg L}^{-1}$ and (b) $[\text{SPS}] = 25 \text{ mg L}^{-1}$ - UP (pH = 6.2); $22 \pm 2 \text{ }^{\circ}\text{C}$; and $[\text{CNTs}] = 50 \text{ mg L}^{-1}$. $d_{\text{Removal}} (%)$ is the difference between the removal (%) of VFX by catalysis and its removal (%) by adsorption.

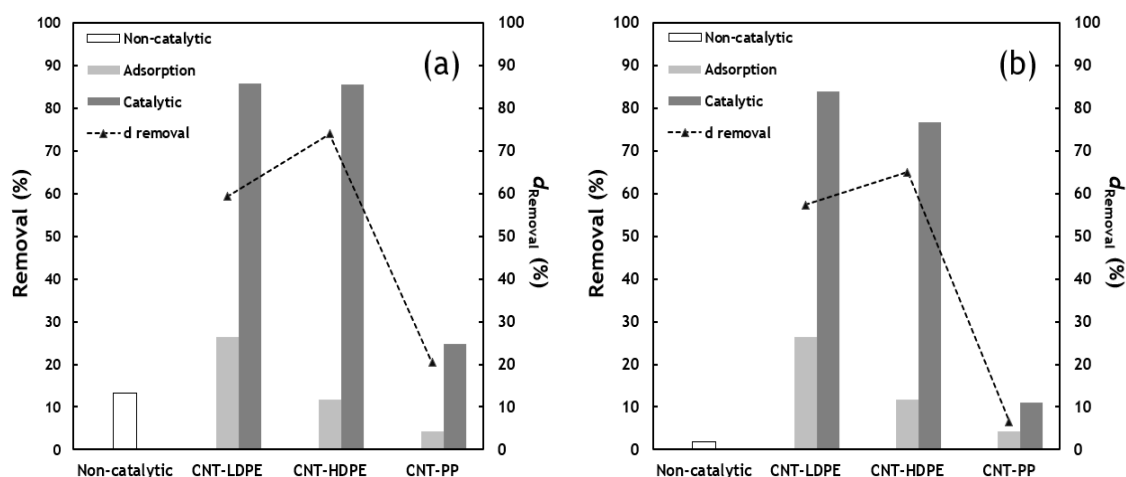


Fig. 5 – Batch experimental results for the removal of VFX (250 µg L⁻¹) after 2 h, with different CNTs using (a) [SPS] = 250 mg L⁻¹ and (b) [SPS] = 25 mg L⁻¹ - BW (pH = 7.1); 22 ± 2 °C; and [CNTs] = 50 mg L⁻¹. d_{Removal} (%) is the difference between the removal (%) of VFX by catalysis and its removal (%) by adsorption.

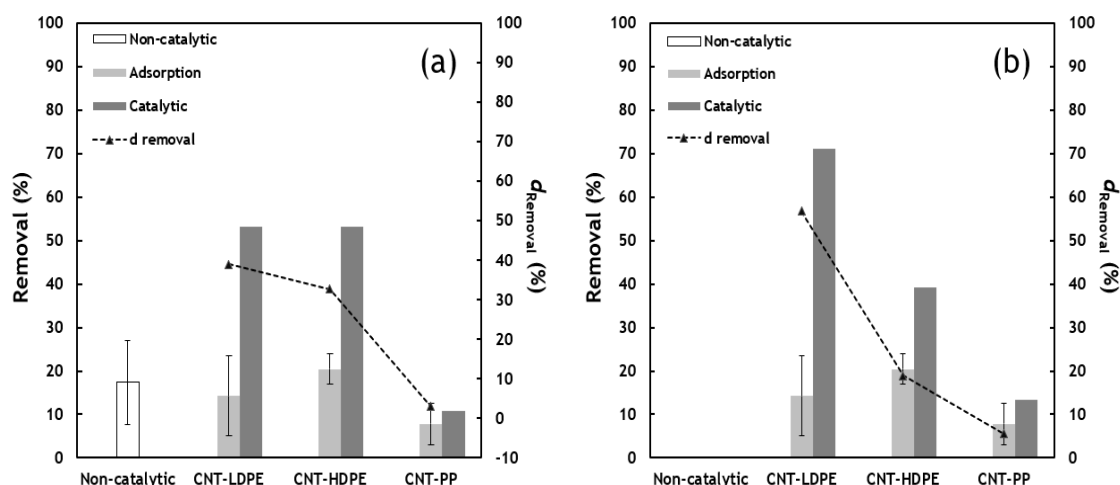


Fig. 6 – Batch experimental results for the removal of VFX (250 µg L⁻¹) after 2 h, with different CNTs using (a) [SPS] = 250 mg L⁻¹ and (b) [SPS] = 25 mg L⁻¹ - SW (pH = 7,3); 22 ± 2 °C; and [CNTs] = 50 mg L⁻¹. d_{Removal} (%) is the difference between the removal (%) of VFX by catalysis and its removal (%) by adsorption.

Analysing the results of non-catalytic experiments in Figs. 4, 5, and 6 (*i.e.* adding SPS only without a carbon material - white bars), it is evident that VFX is less stable in the presence of higher concentrations of SPS because the removal of VFX was always higher when using a SPS concentration of 250 mg L⁻¹ (set of figures “a”), instead of 25 mg L⁻¹ (set of figures “b”), regardless of the aqueous matrix under study (UP, BW or SW). Considering possible explanations for the high non-catalytic conversions obtained when the higher SPS concentration was used, we found a recent study

reporting that PS can be activated even at a room temperature of 22 °C (Zrinyi and Pham 2017). Thus, when the concentration of SPS in solution is higher, more oxidative species are expected, which may consequently react and degrade VFX. Regarding the comparison between different matrices, the pH of the solution can play a role in the decomposition of SPS. Under alkaline conditions, SPS can be decomposed to $\text{SO}_4^{\bullet-}$ and further originate $\text{HO}^\bullet$. At acidic conditions, $\text{SO}_4^{\bullet-}$ is the primary reactive species for the degradation of organic compounds, whereas at alkaline conditions, $\text{SO}_4^{\bullet-}$ has an important role in degradation. Under neutral conditions, both $\text{SO}_4^{\bullet-}$ and $\text{HO}^\bullet$ contribute to the degradation of the organic pollutants (Liang and Su 2009; Wang and Wang 2018). Therefore, one possible explanation for the higher non-catalytic removal of VFX when using UP as matrix, is its lower pH, where the sulphate radicals are the primary reactive species. As expected, the VFX removal is lower in the case of BW and SW, but for these two matrices the values are interestingly similar as the respective pHs, *i.e.* both being around a neutral pH of 7.1 - 7.3. Regarding the catalytic experiments, it was observed that the concentration of SPS had a less pronounced effect on the elimination of VFX; however, in the specific experiments with CNT-LDPE in SW (Figs. 6a and b), the removal of VFX was unexpectedly higher when using the lower SPS concentration (Fig. 6b).

In adsorption experiments (light grey bars in Figs. 4, 5 and 6), the three types of CNTs under study presented quite similar removal percentages of VFX in UP (Fig. 4), whereas CNT-LDPE presented higher removals in BW (Fig. 5) and CNT-HDPE in SW (Fig. 6). To try to understand these differences, the textural properties of the CNTs (Table 4) were compared. However, it can be concluded that the textural properties of the CNTs cannot be correlated with the adsorption removal of VFX. In fact, the adsorption percentages were approximately similar in UP, the highest removal being obtained when using CNT-PP, whereas the opposite trend was observed in the other two aqueous matrices, *i.e.* CNT-PP was the carbon material with the lowest adsorption. On the other hand, CNT-LDPE and CNT-HDPE were the carbon materials with the highest adsorption percentage in BW and SW, respectively, as referred above. In any case, the removals of VFX obtained by adsorption were always in a narrow range, between 4-27 %.

To assess which CNTs had the best performance as a catalyst (dark grey bars in Figs. 4, 5, and 6), a concentration of SPS equal to 25 mg L⁻¹ was selected, since the non-catalytic conversion of VFX was negligible at this concentration in the matrices studied, meaning that the activation of SPS observed for the removal of VFX was due

to the carbon materials added to the solutions. In particular, the d_{removal} presented in Figs. 4, 5, and 6 is a very important variable for choosing the best performing CNTs, because the difference between the catalytic removal and the adsorption removal of VFX gives an estimate for the catalytic removal provided by the CNTs. Analysing Figs. 3, 4, and 5, CNT-LDPE were the best performing CNTs in the removal of VFX from UP and SW, and CNT-HDPE were the best performing CNTs in the removal of VFX from BW (*i.e.*, slightly better than CNT-LDPE). In the three aqueous matrices in analysis, CNT-PP were the CNTs that had the worst performance in the removal of VFX.

It is known that transition metal ions such as Fe^0 , Fe^{2+} , Cu^{2+} , Co^{2+} , Ag^+ , and metal oxides can activate PS to form $\text{SO}_4^{\bullet-}$ (Wang and Wang 2018). For the activation of PS by metal ions and metal oxides, the mechanism is the reduction as Eq. (5) shows (Wang and Wang 2018). Considering the possibility that the CNTs used in this work were not truly metal-free, since the purification step might not remove all the traces of metal catalysts used in the CNTs synthesis process, a study on metal leaching was performed. Catalytic experiments in batch mode were performed in UP using a $[\text{SPS}] = 25 \text{ mg L}^{-1}$, and a $[\text{CNTs}] = 50 \text{ mg L}^{-1}$ to evaluate the leaching of Al and Fe from the CNTs. The results are presented in Table 5.

Table 5 – Al and Fe leached from the CNTs during 2 h of catalytic experiments performed in batch mode in UP (pH = 6.2), at $22 \pm 2 \text{ }^\circ\text{C}$, using $[\text{SPS}] = 25 \text{ mg L}^{-1}$ and $[\text{CNTs}] = 50 \text{ mg L}^{-1}$.

	Al			Fe		
	LOD ($\mu\text{g L}^{-1}$)	LOQ ($\mu\text{g L}^{-1}$)	Concentration ($\mu\text{g L}^{-1}$)	LOD ($\mu\text{g L}^{-1}$)	LOQ ($\mu\text{g L}^{-1}$)	Concentration ($\mu\text{g L}^{-1}$)
CNT-LDPE			<LOD/<LOQ			2.40
CNT-HDPE	2.52	7.00	<LOD/<LOQ	± 0.00	1.45	<LOD/<LOQ
CNT-PP			<LOD/<LOQ			<LOD/<LOQ

Analysing the data in Table 5, it is possible to verify that only the concentration of Fe that leached from CNT-LDPE, after 2 h of catalytic experiment in UP, was quantifiable ($>\text{LOQ}$), but quite low ($2.40 \mu\text{g L}^{-1}$). Considering this specific result, another catalytic experiment in batch mode was performed in UP using $[\text{SPS}] = 25 \text{ mg L}^{-1}$ and the quantified amount of iron, *i.e.* $[\text{Fe}^{2+}] \approx 2.40 \mu\text{g L}^{-1}$ (Fig. 7). The

objective of this experiment was to evaluate if VFX is removed from the water matrix due to the Fe^{2+} leached from the CNT-LDPE material.

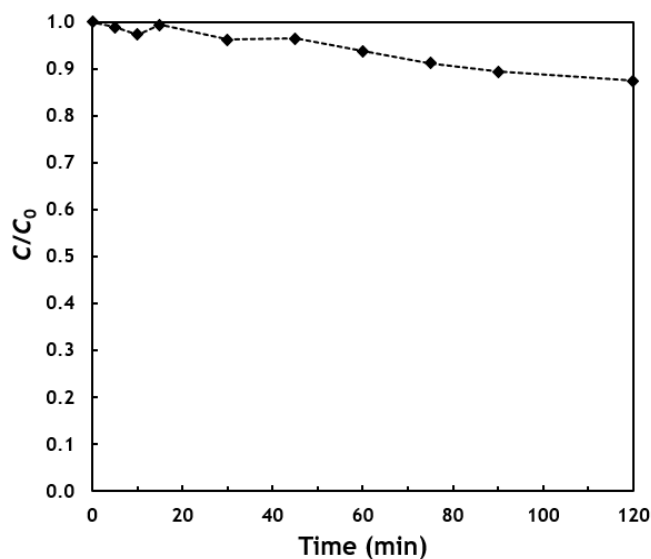


Fig. 7 – Catalytic removal of VFX by Fe^{2+} at $2.40 \mu\text{g L}^{-1}$ during 2 h in batch mode - $[\text{SPS}] = 25 \text{ mg L}^{-1}$; UP (pH = 6.2); and $22 \pm 2^\circ\text{C}$. C/C_0 corresponds to the normalized VFX concentration.

It can be observed that the removal of VFX from UP was low (13%) after 2 h (Fig. 7). By comparing this value with the catalytic removal percentage of VFX from UP with $[\text{SPS}] = 25 \text{ mg L}^{-1}$, and $[\text{CNT-LDPE}] = 50 \text{ mg L}^{-1}$ (i.e. $d_{\text{Removal}} > 70\%$ in Fig. 4b), it is possible to infer that the performance of CNT-LDPE in UP was mostly attributed to the material itself, but there is also some contribution from the iron leached. In fact, by subtracting the effect of the leached iron, CNT-LDPE and CNT-HDPE perform almost equally, with CNT-HDPE slightly surpassing the efficiency of CNT-LDPE ($\approx 2\%$).

Analysing the Al and Fe leached from the samples under the framework of the Portuguese legislation in force (Decreto-Lei n.º 306/2007), the concentrations are lower than the limit defined for the quality of water intended for consumption ($[\text{Al}] \leq 200 \mu\text{g L}^{-1}$; $[\text{Fe}] \leq 200 \mu\text{g L}^{-1}$). The requirements for discharges of effluents from UWWTPs do not include limits for metals (Decreto-Lei n.º 152/97, of June 19).

The acid digestion of the CNTs allowed to quantify the remaining overall content of Fe and Al in the CNTs, after the purification step. Despite most of the concentrations of leached metals were $< \text{LOD/LOQ}$, as shown in Table 5, the numeric values obtained were considered to perform a study on how much of those metals were leached during

catalytic experiments from the overall metal content present in the CNTs. The results are shown in Table 6.

Table 6— Total content of Fe and Al in the CNTs, and respective leaching percentages.

	wt.% of Al in the sample	wt.% of Fe in the sample	wt.% of Al leached	wt.% of Fe leached
CNT-LDPE	0.032	0.70	22.17	0.67
CNT-HDPE	0.028	0.37	13.41	0.22
CNT-PP	0.023	0.52	3.39	0.04

Analysing Table 6, it is possible to verify that the overall content of Al on the structure of the CNTs is smaller than the overall content of Fe. However, Fe was more resistant to the leaching phenomenon in comparison with Al because, from the overall content of Fe and Al present in the CNTs the leaching of Fe was lower than 1%, while the leaching of Al was between 3-23%. The CNTs studied under this dissertation presented a similar remaining content of Al on their structure, after the purification step was applied, because the difference between the wt.% of Al in the samples were lower than 0.01%. CNT-LDPE was the carbon material with the highest content of Fe (0.70 wt.%), and CNT-HDPE was the carbon material with the smallest content of Fe (0.37 wt.%). The leaching of Al and Fe was higher when the overall content of those metals was also higher. The purification step was very effective in the removal of metals (resulting from the catalyst used for its synthesis) from the CNTs because the overall content of Fe and Al on their structure was lower than 1 wt.%. Analysing the overall leaching of metals from the CNTs, CNT-PP was the carbon material more resistant to the leaching of metals because, the wt.% of Al leached was lower than 4%, while for CNT-LDPE and CNT-HDPE was between 13-23%, and the wt.% of Fe leached was lower than 0.05%, while for CNT-LDPE and CNT-HDPE was between 0.20-0.70%.

4.3. Continuous mode experiments

From the results obtained in the experiments performed in batch mode, CNT-LDPE and CNT-HDPE were those showing the best performance to treat the three aqueous matrices tested. Accordingly, composite polymeric membranes were fabricated considering 1.6 wt.% of CNT-LDPE or CNT-HDPE in the membrane forming materials. The reasons behind the fabrication of two types of composite polymeric membranes lied on the fact that these carbon materials were the most promising to activate SPS and thus, to remove VFX from the three matrices.

Fig. 8 displays the removal of the target MPs under study by using the CNT-HDPE-PVDF and CNT-LDPE-PVDF membranes, and the removal of the same MPs by non-catalytic conversion (*i.e.*, in samples collected from the feeding bottle containing the MPs and SPS), all these results obtained after 48 h. As described in Chapter 3.5.2, the first 24 h corresponded to the adsorption stage in the absence of SPS, with the initial sample being collected from the feeding bottle, after the feeding system was filled. It is worthy to mention that the removal by adsorption of the target MPs was much higher when using the CNT-LDPE-PVDF membrane (but never higher than 92%) than that observed when applying the CNT-HDPE-PVDF membrane (lower than 66%). The second period of 24 h corresponded to a simultaneous evaluation of catalytic (membrane cell) and non-catalytic conversion (feeding bottle), and these results are shown in Fig. 8. Considering the huge amount of data and number of MPs under study, only average removals are presented in this figure, triplicate experiments being needed for the representation of the results obtained for each individual MP and along time. The beginning of this second stage of the experiment corresponded to moment when the system got filled with a new solution with the same composition to which SPS was added. It is also represented the RSD.

The non-catalytic removal of the target MPs did not exceed 40%, except for methiocarb (59%), bezafibrate (64%) and diclofenac (51%).

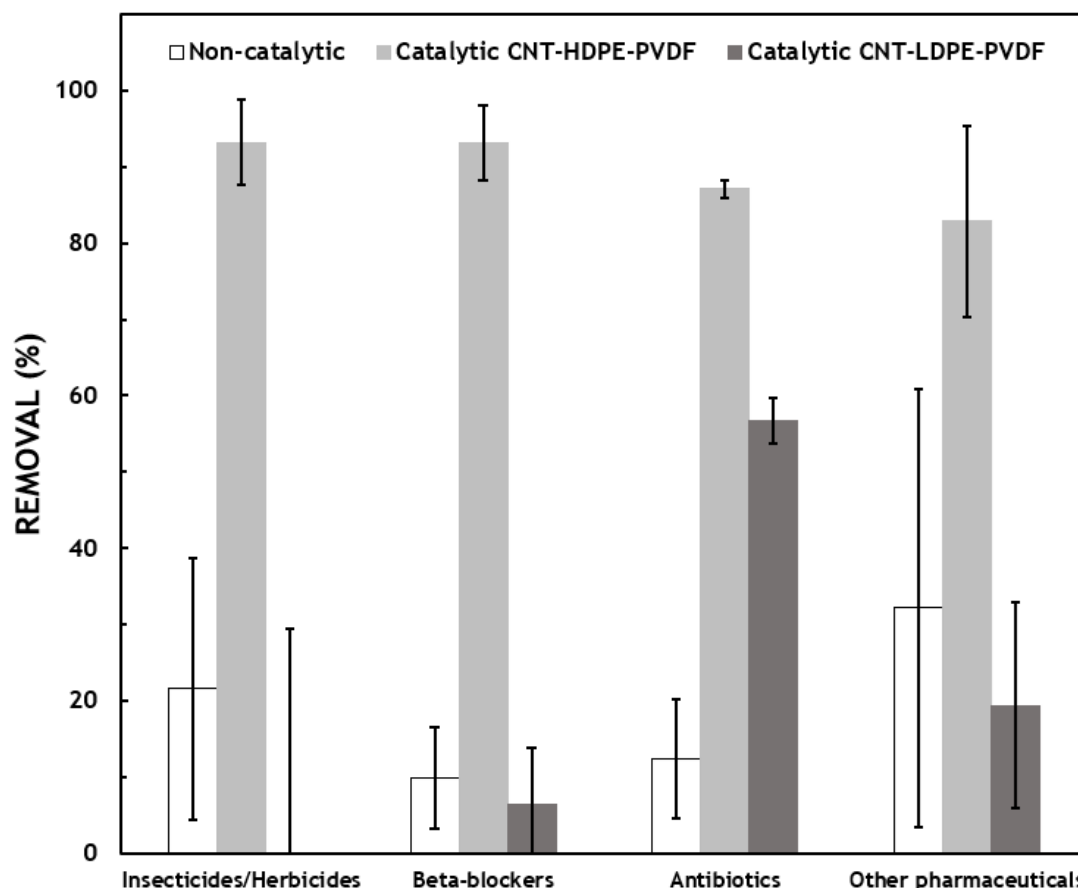


Fig. 8 — Average catalytic removals of insecticides/herbicides, beta-blockers, antibiotics, and other pharmaceuticals ($50 \mu\text{g L}^{-1}$ each MP) from SW ($\text{pH} = 7.3$) in continuous mode experiments ($22 \pm 2^\circ\text{C}$) with the CNT-HDPE-PVDF (light grey bars) and CNT-LDPE-PVDF (dark grey bars) membranes, and non-catalytic conversion (white bars) in the feeding bottle containing these MPs in the presence of $[\text{SPS}] = 25 \text{ mg L}^{-1}$. All the samples shown in this figure were collected after 24 h of catalytic and non-catalytic conversion.

Despite CNT-LDPE had a better efficiency in the activation of SPS for the batch catalytic removal of VFX from SW with $[\text{SPS}] = 25 \text{ mg L}^{-1}$ (Fig. 6b), when using the same experimental conditions under continuous mode (Fig. 8), it was verified that the membrane fabricated with CNT-HDPE showed the best catalytic removal of the target 21 MPs.

The high values of RSD may be ascribed to (i) any impurities in the chromatographic vials due to an incomplete cleaning process that could affect the analysis; (ii) with a problem in the sample/s acquisition, namely impurities that could

be present in the needle or in the syringe; or (iii) any problem related to the conservation of the samples.

5. Conclusions

CNT-PP was the type of CNTs that presented the highest surface area and the smallest total pore volume, whereas CNT-HDPE presented the smallest surface area and the highest total pore volume, but similar to CNT-LDPE.

CNT-PP was the type of CNTs that presented the smallest content of Al resulting from the catalyst used for its synthesis by CVD, followed by CNT-HDPE and CNT-LDPE. CNT-LDPE was the type of CNTs that presented the highest content of Fe, followed by CNT-PP and CNT-HDPE. CNT-PP were the most resistant CNTs in relation to the leaching of Al and Fe, followed by CNT-HDPE and CNT-LDPE.

The lower concentration of SPS tested (25 mg L^{-1}) was selected according to the aim of this work to assess the catalytic activity, since it was observed a marked contribution of SPS at the highest concentration tested (250 mg L^{-1}) for the non-catalytic conversion of VFX. CNT-LDPE was the best performing CNTs in the catalytic removal of VFX from SW, and CNT-HDPE was the best type of CNTs in the removal of VFX from both UP and BW. However, under continuous mode to treat SW spiked with 21 MPs, the CNT-HDPE-PVDF membrane showed a better catalytic efficiency to activate PS than the CNT-LDPE-PVDF membrane and thus, to degrade the 21 target MPs.

6. Assessment of the work done

6.1. Objectives achieved

The objectives of this dissertation described in section 1.2 were mostly attained. In summary:

- CNT-LDPE and CNT-HDPE showed to be promising materials in the activation of PS for the removal of VFX from the three aqueous matrices.
- The best SPS concentration for the catalytic studies was 25 mg L^{-1} , because VFX was more stable in the presence of this concentration of SPS, in comparison to its stability when using a concentration of 250 mg L^{-1} .
- Three aqueous matrices were tested throughout this work (UP, BW, and SW) and the catalytic performance was studied in different water matrices.
- The textural properties of the CNTs, as well as the remaining overall content of metals in the CNTs, were determined to help to better understand the differences in their performance. However, more characterizations should have been performed such as CNTs surface chemistry analysis, and thermogravimetric analysis, allowing to get more insights on the CNTs features and the related differences in the performance. In this case, the goal was partially achieved.
- Composite polymeric membranes were fabricated with CNT-LDPE and CNT-HDPE.
- The last goal of my dissertation was only partially achieved, because both CNT-LDPE-PVDF and CNT-HDPE-PVDF were tested only once, without performing replicates and thus, those results obtained were preliminary and some other experiences should be performed in the continuation of this work.

6.2. Final assessment

Looking back, I can say that the work went very well because many results were obtained and the decisions made within the scope of the study developed under this dissertation were sustained with data.

A huge amount of batch experiments was performed in order to have reproducible data to allow the selection of the best performing CNTs for the activation of PS to remove VFX. By deciding based on solid results, composite polymeric membranes were fabricated with the most promising materials.

Considering the objectives of this work, more time would be required to carry out and apply more characterization techniques for a better understanding of the CNTs features and their performances. More time would be also an asset to perform more

experiments with the fabricated membranes, since the information acquired under continuous mode was only preliminary data and more data is needed by repeating the experiments, to support the choice of the best performing composite polymeric membrane in the activation of SPS for the catalytic removal of the target MPs.

In a conclusion note and considering that many composite polymeric membranes were already fabricated by me with CNT-LDPE and CNT-HDPE, additional assays could be performed in the future with these fabricated membranes, namely adsorption and catalytic experiments (e.g., by extending the duration time of the experiments). Moreover, other techniques should be applied in order to better characterize the membranes.

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Annex A - Synthesis of the CNTs

Synthesis of $\text{Fe}_2\text{O}_3/\text{Al}_2\text{O}_3$

10 mmol $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ was dissolved in 20 mL of ethanol (EtOH), which was heated until boiling and then cooled down until reaching the room temperature. 20 mmol $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ was dissolved in ethylene glycol, which was heated at 60 °C for 5 min, and then cooled down until reaching room temperature. Both solutions were mixed and 6.6 g of Al_2O_3 was added, stirred, and heated at 60 °C for 2h. Then, the temperature was raised and kept at 120 °C until a gel texture was obtained. To evaporate the remaining solvent, the temperature was raised to 210 °C. The obtained powder was heat treated at 300 °C for 12 h and 600 °C for 24 h, under an air atmosphere, resulting in the catalyst $\text{Fe}_2\text{O}_3/\text{Al}_2\text{O}_3$.

CVD

Three samples of CNTs were synthesized by CVD: (i) CNT-LDPE; (ii) CNT-HDPE; and (iii) CNT-PP. Each synthesis consisted in the loading of 5 g of polymer (LDPE, HDPE or PP) in the upper region of a tubular oven and of 1 g of catalyst ($\text{Fe}_2\text{O}_3/\text{Al}_2\text{O}_3$) in the lower region of this oven. After reaching 850 °C in the lower region and 450 °C in the upper region, the oven was kept at these conditions for 1 h, using N_2 as carrier gas.