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Pilot Studies and Cost Analysis of Hybrid Powdered Activated Carbon/Ceramic Microfiltration for Controlling Pharmaceutical Compounds and Organic Matter in Water Reclamation

Rui M. C. Viegas *[ID]**, Elsa Mesquita, Margarida Campinas and Maria João Rosa**

Water Quality and Treatment Laboratory, Urban Water Unit, Hydraulics and Environment Department, LNEC—National Civil Engineering Laboratory, 1700-066 Lisbon, Portugal; emesquita@lnec.pt (E.M.); mcampinas@lnec.pt (M.C.); mjrosa@lnec.pt (M.J.R.)
* Correspondence: rviegas@lnec.pt

Abstract: This paper addresses the enhanced removal of pharmaceutical compounds (PhCs), a family of contaminants of emerging concern, and effluent organic matter (EfOM) in water reclamation by powdered activated carbon/coagulation/ceramic microfiltration (PAC/cMF). Four chemically diverse PhCs are targeted: ibuprofen (IBP), carbamazepine (CBZ), sulfamethoxazole (SMX) and atenolol (ATN). Pilot assays (100 L/(m^2 h), 10 mg Fe/L) run with PhC-spiked sand-filtered secondary effluent and 15 mg/L PAC dosed in-line or to a 15-min contactor. They showed no PAC-driven membrane fouling and +15 to +18% added removal with PAC contactor, reaching significant removals of CBZ and ATN (59%–60%), SMX (50%), colour (48%), A254 (35%) and dissolved organic carbon (DOC, 28%). Earlier long-term demo tests with the same pilot proved PAC/cMF to consistently produce highly clarified (monthly median < 0.1 NTU) and bacteria-free water, regardless of the severe variations in its intake. A detailed cost analysis points to total production costs of 0.21 €/m^3 for 50,000 m^3/day and 20 years membrane lifespan, mainly associated to equipment/membranes replacement, capital and reagents.

Keywords: ceramic membranes; contaminants of emerging concern; cost analysis; hybrid membrane processes; microfiltration; pharmaceutical compounds; water reclamation

1. Introduction

Across the European Union, water shortages and droughts have increased dramatically over the past 30 years and, due to climate change and increasing population, those events are likely to become more frequent and more severe, earnestly demanding more efficient water management. Around the Mediterranean already over 50% of the population is affected by water stress in summer but water scarcity is no longer confined to a few corners of Europe, probably affecting half of Europe's river basins by 2030 [1].

Although water reuse is an important tool for extending the water life cycle and in full compliance with the circular economy objectives, water reuse in the European Union has not yet been seriously tackled and is far below its potential. Nevertheless, in the context of adapting to climate change, a credible momentum to drive changes has been created in the last five years, confirmed by new international strategies such as those of the International Organization for Standardization (ISO/TC 282 Water Reuse) and, at an European level, the targeting of a substantial increase in recycling and safe reuse globally by 2030 (United Nations (UN) Sustainable Development Goal on Water, SDG 6), the establishment of water reuse as a top priority area (Strategic Implementation Plan of the European

Innovation Partnership on Water) and the specific objective of water reuse maximization (Blueprint to safeguard Europe's water resources) [2]. Coherently, the European Commission proposed in May 2018 new rules to stimulate and facilitate water reuse in the EU for agricultural irrigation and, in Portugal, brand new legislation, the Decree-law 119/2019 [3], establishes the legal regime for producing water to be reused, obtained from wastewater treatment.

In many new regulations, including the Portuguese DL 119/2019, water reuse is supported by a fit-for-purpose approach, based on risk assessment and achieving risk minimization through multi-barrier criteria, including water-treatment barriers and physical barriers to limit contact. Pilot treatment studies are, therefore, important to give an insight into treatment technologies reliability and "safety credits", providing guidance about reliable and safe barriers in treatment trains of wastewater treatment plants (WWTPs) and supporting risk assessment studies. Cost analysis is also fundamental to ensure a cost-effective treatment and to promote benchmarking between treatment alternatives.

Up to now, the main human health concern for water reuse has been set on confirmed risks, mostly connected with microbiological parameters. Contaminants of emerging concern, such as pharmaceutical compounds (PhCs), are under vigilance as there is a lack of knowledge or there are poorly documented issues about the potential problems they could cause. PhCs, although not yet regulated, have been receiving increased attention, namely from the European Union regulation, through the watch lists of the Water Framework Directive [4,5], and may be candidates for future regulation once environmental and human health relevance has been established. They may pose a hazard associated with potential toxic, mutagenic and/or endocrine-disrupting action and may lead to the development of antibiotic-resistant bacteria. They are effective at low concentrations, in the ng/L range, and many PhCs are resistant to conventional treatment in WWTPs due to their low biodegradability and chemical resistance. Organic matter (EfOM) control in the treated water brings significant benefits, namely by decreasing colour, odour and synthetic organic compounds. EfOM is an important precursor of undesirable oxidation by-products (e.g., trihalomethanes, haloacetic acids) that should be minimised when post-chlorination is required for water reuse. Therefore, an enhanced EfOM control reduces the chlorine demand, the by-products formation potential and the biofilm growth in water distribution networks.

Powdered activated carbon (PAC) adsorption is considered a cost-efficient recommended technology [6,7] and has proven to be effective for PhC and EfOM removal from water and wastewater [8–11], with its performance depending on the interactions established with the contaminants, namely hydrophobic or electrostatic. Thus, besides the PAC properties (hydrophobicity, charge and pore volume and its distribution), the contaminant properties, namely their size, charge and hydrophobic/hydrophilic character determine their removal.

PAC dosing to a WWTP usually requires a mixing tank and a downstream particle retention process such as sedimentation and granular media filtration (typically sand filter) or membrane filtration (e.g., low pressure membranes as microfiltration (MF) or ultrafiltration). MF with pore size below 0.1 μm typically operates at pressures below 1 bar and is a safe barrier against protozoa and turbidity. Low-pressure ceramic membranes are emerging for safe water reclamation for unrestricted uses given its high effectiveness for suspended solids and bacteria (the latter for membrane pore sizes below 0.1 μm), and mechanical and chemical robustness with operational and subsequent cost-efficiency advantages over polymeric membranes [12–16]. The hybrid powdered activated carbon/ceramic microfiltration (PAC/MF) technology is regarded as a new process [7] and integrates the advantages of both processes. On the one hand, the ceramic membranes resist to PAC particle abrasion and those with 0.1 μm (or less) pore size are absolute barriers against the fine-PAC particles which often go through the conventional solid–liquid separation in WWTP. On the other hand, by adsorbing organic matter which otherwise could adsorb onto the membrane surface and/or block the membrane pores, creating and additional resistance to water transport across the membrane, PAC may also contribute to minimise membrane fouling [17], which is the main phenomenon affecting the membrane productivity and its technical-economic feasibility [18].

In previous studies with the same pilot [16], one-year 24/7 demonstration of coagulation-ceramic MF (0.1 μm) was developed in Portugal in two WWTPs in the Lisbon metropolitan area. The results obtained demonstrated the technology's effectiveness, reliability and efficiency towards water quality, with the process consistently producing highly clarified (monthly median < 0.1 NTU) and bacteria-free water, regardless of the severe variations in its intake. Further studies were then developed aiming at enhancing the removal of organics by PAC dosing.

In this study, four chemically different and widely used PhCs were targeted, as well as EfOM. This paper presents operational and quality results obtained and a cost analysis of the process.

2. Materials and Methods

2.1. Powdered Activated Carbon/Microfiltration (PAC/MF) Pilot

The reclamation scheme comprised sand filtration of the WWTP secondary effluent (pilot intake) followed by a polishing step of coagulation and PAC/MF. PAC and ferric chloride coagulant dosing and the membrane pilot (containerised) were fully automated, remote controlled and with in-line monitoring of pressure, flow rate, temperature, pH and turbidity. A scheme of the PAC/MF process, highlighting the PAC dosing alternatives, is depicted in Figure 1. The MF membrane and module (Metawater, Japan) specifications are given in Table 1.
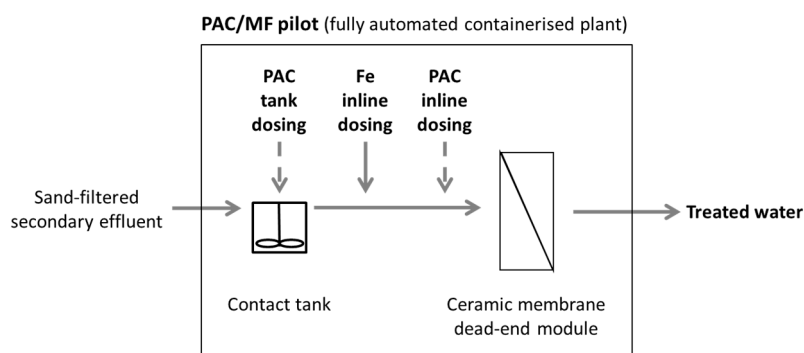

Figure 1. Scheme of the powdered activated carbon/microfiltration (PAC/MF) process.

Table 1. Membrane specifications.

Pore Size	Material	No. of Channels	Channel Diameter	Module Length/Diameter	Membrane Area Per Module	Total Membrane Area
0.1 μm	Al_2O_3	55	2.5 mm	1 m/30 mm	0.4 m^2	0.8 m^2

The PAC/MF pilot was fed using a submersible pump located in the sand-filtered effluent tank of the WWTP. The pilot contained a stirred contact tank of 20 L, to where the intake water was pumped, and to where PAC slurry was also continuously dosed with a peristaltic pump during the PAC tank dosing periods. After the contact tank, coagulant was continuously dosed inline with a peristaltic pump and the water was pressurized (with the main centrifugal pump) to enter the microfiltration module. During the periods with PAC inline dosing, the PAC slurry was dosed continuously to a static mixing tube just before pressurizing the water. The membrane module operated in a continuous dead-end mode with constant permeate flow rate, during a set of filtration cycles. Each filtration cycle was followed by a backwash with pressurised air and permeate to remove the accumulated solids. Further details of the pilot facility and of its operation can be found in Viegas et al. [16].

2.2. PAC/MF Operational Conditions and Procedure

After the previous operational optimisation performed [16], the tests were conducted in dead-end mode, at a constant flux (100 L/(m^2 h), in short lmh), dosing FeCl$_3$ coagulant (10 mg Fe/L) and PAC

(15 mg/L, Norit SAE Super, Cabot), and 60-min filtration time followed by backwash. Besides the backwash, the cleaning strategies also included chemically enhanced backwashing (CEB), with two CEBs per day, one with sulfuric acid and one with sodium hypochlorite.

The tests were carried out during 35 days, comprising a period with only inline coagulant dosing and no PAC addition (30 days) followed by a period with PAC dosing (5 days). During the whole time, for assessing the operational performance, the membrane flux and the inlet and outlet pressure were monitored. The transmembrane pressure (TMP, in bar), the fouling rate, i.e., the TMP increase (in bar) during a filtration cycle, required to keep the constant flux, in mbar/h and the specific flux (or permeability, in L/(m^2 h bar)) were computed. For each of the testing periods average values were calculated. The water recovery rate (*R*) was also assessed according to:

$$R = \frac{V_p - V_{BW} - V_{CEB}}{V_p} \times 100 \tag{1}$$

where V_p is the permeate volume produced, and V_{BW} and V_{CEB} are the permeate volumes used in backwash and CEB procedures, respectively.

On the first day of the second period, inline spiking of a cocktail of PhCs was conducted (Section 2.3) and three different configurations were assessed consecutively: (i) inline coagulant dosing and no PAC addition (Fe/MF configuration); (ii) inline coagulant dosing followed by inline PAC dosing (Fe/PAC in-line/MF); (iii) PAC dosing to a 15 min contact tank, followed by inline coagulant dosing (PAC tank/Fe/MF). Each configuration comprised a 1 h-filtration cycle for stabilization and a 1 h-filtration cycle for sampling (1 L grab samples), at 20, 40 and 58 min of the filtration cycle. The grab samples were analysed for EfOM while composite samples, prepared by mixing 500 mL aliquots of each grab sample, were analysed for PhCs. The removal efficiencies were computed as follows:

$$Removal = \left(1 - \frac{C_P}{C_f}\right) \times 100 \tag{2}$$

where C_p and C_f are the concentrations in the permeate and in the feed, respectively.
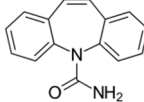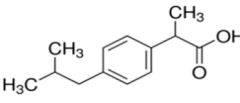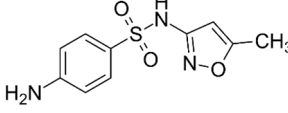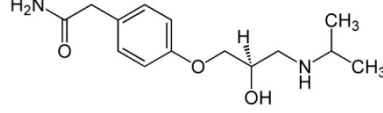
After the tests, the PAC tank dosing was kept for 4 more days to assess the operational performance of the pilot.

2.3. Pharmaceutical Compounds Targeted

Four pharmaceutical compounds with different physical-chemical properties were selected for the studies: ibuprofen (IBP, anionic and relatively hydrophobic), carbamazepine (CBZ, neutral hydrophobic), sulfamethoxazole (SMX, anionic hydrophilic) and atenolol (ATN, cationic hydrophilic). Their chemical structures, molar mass and octanol-water distribution coefficient (log D, a measure of the compound hydrophobicity at a given pH) and charge at pH 7.4 are depicted in Table 2. Charge was predicted with Chemicalize [19], developed by ChemAxon, and logD was predicted using the ACD/Labs Percepta Platform. Both properties were retrieved from ChemSpider [20] database.

The above campaigns were performed with inline PhC spiking to the intake water, supplementing about 2 μg/L of each PhC, corresponding to 10 nM of IBP and 8 nM for CBZ, SMX and ATN). The PhCs from pilot intake and treated wastewater samples were quantified by solid-phase extraction-liquid chromatography–tandem mass spectrometry (SPE-LC–MS/MS Waters, Milford, MA), USA) as described in Gaffney et al. [21].

Table 2. Chemical structure and physico-chemical properties of the target pharmaceuticals.

Pharmaceutical Compound	Chemical Structure	Molar Mass (g/mol)	Log D (pH 7.4)	Net Charge (pH 7.4)
Carbamazepine		236.3	2.3	0
Ibuprofen		206.3	0.5	−1
Sulfamethoxazole		253.3	−0.56	−1
Atenolol		266.3	−1.85	1

2.4. Wastewater Characterisation

The intake water inorganic and dissolved organic matrices were characterised (Table 3) in grab samples. pH and electrical conductivity (EC) were measured with a multiparametric potentiometer (Consort, C863T) and turbidity was measured with a turbidity meter (WTW Turb 555) using standard methods of analysis [22]. Dissolved organic matter (EfOM) in the pilot intake and treated water was assessed in filtered samples (0.45 μm, polypropylene membrane, GH Polypro Pall Corporation) by measuring: (i) dissolved organic carbon (DOC) by the ultraviolet (UV)/persulphate chemical oxidation method (EN1484:1997) using a TOC analyser (Teledyne, TOC Fusion), (ii) ultraviolet–visible (UV–Vis) absorbance of water samples at 436 nm (A436) and at 254 nm (A254), representing, respectively, colour and organic compounds with aromatic rings and double C-C bonds (UV–Vis spectrophotometer, Jasco, V630 and 50 mm optical path quartz cells) and (iii) specific UV absorbance at 254 nm (SUVA) calculated as A254/DOC.

Table 3. Intake water quality of the pilot tests conducted with Fe/MF, PAC tank/Fe/MF and Fe/PAC inline/MF processes.

Intake Water Quality	Fe/MF			PAC Tank/Fe/MF Fe/PAC In-Line/MF		
	(30 days, *n* = 12)			(5 days, *n* = 3)		
	Average	P25	P75	Average	min	max
pH	6.7	6.7	6.8	6.7	6.7	6.8
EC (mS/cm)	0.84	0.68	0.90	0.79	0.74	0.81
Turbidity (NTU)	2.0	1.7	2.2	2.2	2.1	2.3
TSS (mg/L) [1]	3.3	3.0	3.3	3	-	-
Faecal coliforms (CFU/100 mL) [2]	9.9×10^3	8.0×10^3	1.5×10^4	8.8×10^3	4.9×10^3	1.3×10^4
COD (mg O_2/L) [1]	31	30	31	30	-	-
DOC (mg C/L)	5.0	4.5	5.8	5.3	4.8	5.9
A254 (cm^{-1})	0.14	0.14	0.15	0.15	0.15	0.15
A436 (m^{-1})	1.3	1.2	1.5	1.3	1.2	1.5
SUVA (L/(mg C m))	2.8	2.6	3.1	2.8	2.5	3.1

[1] Total Suspended Solids (TSS) and Chemical Oxygen Demand (COD) were analysed in 4 samples for the Fe/MF configuration and in one sample during the PAC dosing configurations; [2] Faecal coliforms were analysed in 7 samples for the Fe/MF configuration and in 2 samples during the PAC dosing configurations.

2.5. PAC Characterisation

Based on earlier tests, a good performing commercial PAC of renewable source was selected-Norit SAE Super (Cabot). The PAC textural properties were characterised by an external laboratory (Table 4), namely BET specific surface area and the total pore volume (meso- and micropore volumes) through the α_S method, based on N_2 adsorption isotherms at -196 °C. The density functional theory was applied for determining the PAC pore size distribution. The point of zero charge (pH_{pzc}), i.e., the pH at which the PAC presents as many positively as negatively charged surface groups, was also determined following the method proposed by Moreno-Castilla et al. [23]. Results show that the tested PAC has high specific surface area (A_{BET}) with similar volumes of micropores (0.7 nm $\leq$ width $\leq$ 2 nm) and of mesopores (2 nm < width < 50 nm). The water pH was lower than the pH_{pzc} of the PAC in all experiments; hence, the PAC net surface charge was always positive.

Table 4. PAC textural characteristics and pH_{pzc}.

Particle Diameter (μm)	S_{BET} (m^2 g^{-1})	V_{total} [1] (cm^3 g^{-1})	V_{meso} [2] (cm^3 g^{-1})	$V_{total\ micro}$ [3] (cm^3 g^{-1})	$V_{supermicro}$ [4] (cm^3 g^{-1})	$V_{ultramicro}$ [5] (cm^3 g^{-1})	pH_{pzc}
15	1093	0.79	0.39	0.40	0.40	0.00	9.9

[1] Evaluated at $p/p^0 = 0.975$ in the N_2 adsorption isotherms at -196 °C; [2] V_{meso}: mesopore volume (2 nm < width < 50 nm), given by the difference between V_{total} and $V_{total\ micro}$; [3] $V_{total\ micro}$: total micropore volume (width $\leq$ 2 nm); [4] $V_{supermicro}$: supermicropore volume (0.7 nm $\leq$ width $\leq$ 2 nm); [5] $V_{ultramicro}$: ultramicropore volume (width < 0.7 nm).

2.6. Statistical Methods

The statistical significance of differences in inlet and outlet concentrations of EfOM and in their removal efficiencies in the three different configurations tested was assessed through one-way analysis of variance (ANOVA) *p*-value. Using this method, for *p*-value greater than 0.05 (corresponding to 95% confidence), there is no statistically significant difference between the group means being compared, while for *p*-values below 0.05 a significant difference exists.

Prior to conducting the ANOVA, the homogeneity of variance of the data sets to be compared was assessed through the Hartley's Fmax test: an observed Fmax value lower than the critical value, for a level of significance of 0.05, evidences that the variances are homogeneous and that the ANOVA can be performed.

3. Results and Discussion

3.1. Membrane Pilot Results

3.1.1. Operational Results

The pilot testing allowed assessing the performance and obtaining the key design parameters [24] of the configurations tested. Table 5 presents the average values for the Fe/MF and for the PAC dosing testing periods, the latter comprising both Fe/PAC in-line/MF and PAC tank/Fe/MF configurations, since the same PAC and PAC dose (15 mg/L) were used.

Table 5. Performance and key design parameters of Fe/MF and PAC dosing configurations (average values for each testing period).

Parameter	Fe/MF	Fe/PAC In-Line/MF PAC Tank/Fe/MF
	(30 days)	(5 days)
Water recovery rate (%)	98	98
Inlet pressure (bar)	0.43	0.46
Transmembrane pressure (TMP, bar)	0.37	0.40
Fouling rate (mbar/h)	139	116
Specific flux (lmh/bar)	296	261

Similar transmembrane pressure and fouling rate were observed for Fe/MF and for the PAC dosing configurations, namely 0.37 bar and 139 mbar/h for Fe/MF vs. 0.40 bar and 116 mbar/h when dosing PAC. Considering that the dissolved organic matter content of the wastewater during both demonstration periods was similar (Table 3), the results allowed it to be concluded that no PAC-driven membrane fouling or pore blocking occurred.

3.1.2. Pharmaceutical Compound (PhC) and Effluent Organic Matter (EfOM) Removals

Table 6 shows the inlet and outlet concentrations measured in the three grab samples collected during the 1 h filtration cycles and the corresponding removals of DOC, A254 and A436. The PhC and EfOM cycle-averaged inlet and outlet concentrations and removals obtained in the three configurations tested are presented in Figures 2 and 3, respectively. Major water-quality enhancement was observed when dosing PAC. With Fe/MF no PhC removals were observed and EfOM removals (DOC, A254 and A436) were ~12%, whereas PAC dosing (in-line and tank) yielded significant removal of PhCs. With PAC in-line addition (15 mg/L) average removals between 19% and 38% were obtained, CBZ and ATN being the best adsorbed compounds and IBP presenting the lower removal. When PAC was dosed to a 15 min contact tank +17% to +18% added removal of PhCs were obtained than with in-line dosing (except for IBP) with the highest removals again being obtained for CBZ and ATN (56%), followed by SMX (47%) and far above IBP removal (15%). CBZ removals were below those obtained by Löwenberg et al. [25] in a pressurized PAC/ultrafiltration pilot with PAC addition to a contact tank (ca. 75%–88% average), but SMX were rather similar (35%–55%). The lower CBZ removal may be justified by the slightly lower PAC dose in the present study (15 mg/L vs. 20 mg/L) and PAC contact time (15 min. vs. 2 h).

Table 6. Inlet and outlet concentrations and removal efficiencies of dissolved organic carbon (DOC), A254 and A436.

| Configuration	t (min)	DOC			A254			A436		
		Feed (mg/L)	Permeate (mg/L)	Removal (%)	Feed (cm^{-1})	Permeate (cm^{-1})	Removal (%)	Feed (m^{-1})	Permeate (m^{-1})	Removal (%)
Fe/MF	20	5.48	4.69	14	0.150	0.128	15	1.50	0.94	37
	40	5.45	4.77	12	0.149	0.132	11	1.31	1.34	0
	58	5.44	4.62	15	0.148	0.130	12	1.23	1.17	5
Fe/PAC inline/MF	20	5.37	3.98	26	0.147	0.099	33	1.24	0.63	49
	40	5.37	3.96	26	0.147	0.122	17	1.23	1.05	15
	58	5.45	4.11	25	0.152	0.105	31	1.33	0.60	54
PAC tank/Fe/MF	20	5.16	3.80	26	0.144	0.096	33	1.17	0.63	46
	40	5.11	3.72	27	0.146	0.094	36	1.16	0.62	47
	58	5.05	3.64	28	0.143	0.091	36	1.16	0.55	52
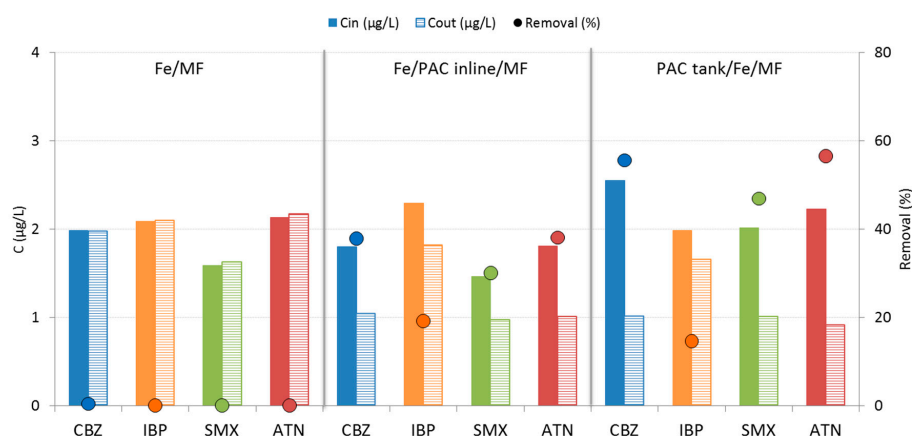
Figure 2. PhC cycle-averaged inlet and outlet concentrations and removal efficiencies by Fe/MF, Fe/PAC in-line/MF and PAC tank/Fe/MF.
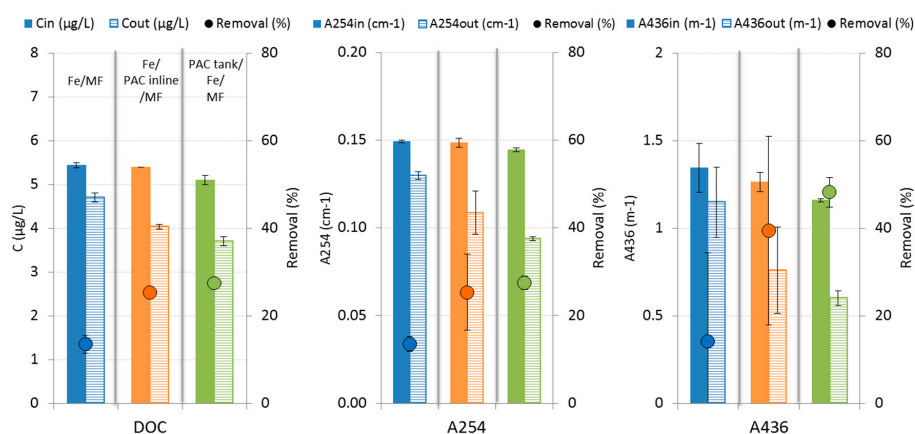
Figure 3. Effluent organic matter (EfOM) cycle-averaged inlet and outlet concentrations and removal efficiencies by Fe/MF, Fe/PAC in-line/MF and PAC tank/Fe/MF.

Overall, the neutral hydrophobic CBZ and the positively charged hydrophilic ATN were better removed with PAC than the negatively charged compounds (the relatively hydrophobic IBP and the hydrophilic SMX). While the higher removals for CBZ can be attributed to hydrophobic interactions with the PAC, for ATN it should be due to PAC–EfOM–ATN interactions [10].

A one-way ANOVA test was conducted to assess the statistical significance of differences in inlet and outlet concentrations of DOC, A254 and A436 and in their removal efficiencies in the three different configurations tested. Its use was first validated with the Hartley's Fmax test with Fmax observed values for comparing inlet and outlet concentrations and for comparing removal efficiencies, both below their critical values (39 and 87.5).

The ANOVA showed the inlet and outlet concentrations to be different (p-value < 0.05) except for A436 in the Fe/MF configuration. As such, the removal efficiencies for DOC, A254 and A436 were calculated and their removals for the three configurations were compared. The results showed no statistically significant difference in the removals between the two PAC dosing configurations for the three parameters (p-value > 0.05) while showing difference in the removals between the Fe/MF and the PAC tank/Fe/MF configuration.

For this latter configuration, the EfOM removals observed, namely 48% for colour, 35% A254 and 27% DOC, are particularly beneficial for water reuse, particularly if a post-chlorination is required, since it is expected that they lessen the chlorine demand and the disinfection by-products formation potential. The post-chlorination is usual for unrestricted irrigation, to provide a disinfectant residual in the reclaimed water distribution network.

3.2. Cost Analysis

For the cost analysis the operational conditions tested and the design parameters presented in Table 5 were used. Given the better removals obtained with PAC dosing to a contact tank, this procedure was selected, and 15 min contact time was considered.

The plant was assumed to operate 24 h per day, 365 days per year. Based on the pilot demo, plant downtime 40 min/day for backwash, 35 min/day for CEB and 18 min/day for routine maintenance and cleaning-in-place were considered and a plant lifespan of 40 years was assumed [26]. A finance rate of 3.2%, the average finance rate of Águas de Portugal group, was considered.

The components and their lifetime considered for calculating the capital expenditure costs (CAPEX) are presented in Table 7 and the operating expenditure costs (OPEX) considered are presented in Table 8. The annualised costs of replacement of equipment were included in OPEX. No costs for land acquisition and for buildings were considered. Further details can be found in [24].

Table 7. Assets and their lifetime considered for calculating the capital expenditure costs (CAPEX).

Component	Lifespan (years) [1]
Membranes	20
Pipes and valves	20
Instrumentation and control	8
Tanks and frames	14
Chemically enhanced backwashing (CEB) skid	15
Feed, backwash, CEB and PAC dosing pumps	10
Miscellaneous equipment [2]	14

[1] Values adapted from [24] and from [15,27] for membrane lifespan; [2] electrical supply and distribution equipment, disinfection facilities, treated water storage and pumping and the wash water recovery system.

Table 8. Operating expenditure (OPEX) costs considered for the cost analysis.

OPEX	Cost
Energy cost for pumping and mixing	0.08 €/kWh [1]
Personnel costs (annual cost)	20 k€/worker [2]
Chemical reagents costs [1]	
PAC	2.95 €/kg
Coagulant	1.4 €/kg Fe
Sodium hypochlorite solution	0.416 €/kg
Sulphuric acid solution	0.130 €/kg
Maintenance	1.5% of the total capital costs

[1] Provided by the water utility; [2] average value of Portuguese WWTPs.

The costs of the components were adapted from the literature or provided from suppliers and are expressed as power type functions of the form:

$$\text{Cost} = a \times \text{variable}^b \tag{3}$$

Table 9 lists the variables and the parameters *a* and *b* per type of cost.

Table 9. Cost functions of the components [24].

Input Cost	Variables; Parameters
Membranes (€) [1]	membrane area (m^2); $a = 756$, $b = 0.97$
Pipes and valves (€) [2]	membrane area (m^2); $a = 5313$, $b = 0.42$
Instruments and controls (€) [2]	membrane area (m^2); $a = 1296$, $b = 0.66$
Tanks and frames (€) [2]	membrane area (m^2); $a = 2732$, $b = 0.53$
Miscellaneous (€) [2]	membrane area (m^2); $a = 7052$, $b = 0.57$
Pumps (€) [3]	power (kW) × safety factor (2): $a = 26011$, $b = 0.354$
Personnel allocation	plant flow rate (m^3/day); $a = 0.0148$, $b = 0.41$

Cost function [1] obtained from costs provided by a membrane supplier on September 2016; [2] adapted from [26]; [3] obtained from costs presented in [28]; adapted from [29] to Portuguese water utilities.

In Figure 4, the OPEX and investment costs (Figure 4a) and the total production costs (Figure 4b) for treating the WWTP sand-filtered secondary effluent studied are plotted as functions of the plant flow rate, for the Fe/MF and PAC/Fe/MF processes.
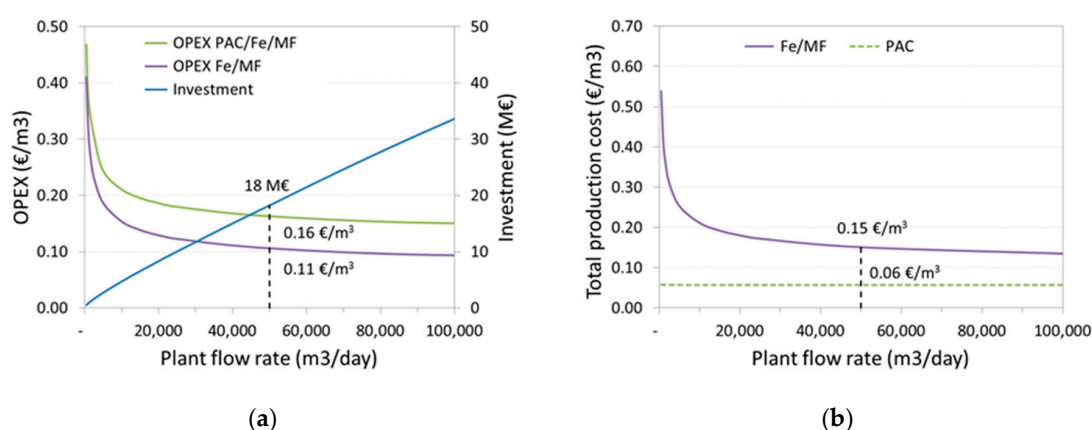
Figure 4. (**a**) Investment and OPEX for Fe/MF and for PAC/Fe/MF and (**b**) total production cost for Fe/MF and for PAC with filtered wastewater treatment plant (WWTP) secondary effluent, highlighting the values for 50,000 m^3/day, the median flow rate of the case study WWTP (15 mg/L PAC; 10 mgFe/L).

It can be observed that the OPEX and the total production costs (€/m^3) are substantially different for very small and big plants, e.g., total production costs of 0.22 €/m^3 for a 50,000 m^3/day plant (the median flow rate of the case study WWTP) and 0.52 €/m^3 for a plant treating 1000 m^3/day. Furthermore, the plant scale is particularly impacting the costs below 20,000 m^3/day, whereas these are fairly constant above 60,000 m^3/day.

Table 10 and Figure 5 depicts the cost structure, breakdown in capital, replacement of components, reagents, energy, maintenance and personnel, for the median flow rate of the case study WWTP (50,000 m^3/day), for both Fe/MF and PAC/Fe/MF configurations. For the latter, a PAC dosing of 15 mg/L was assumed and its dosing cost includes the reagent, the required pump(s) and the mixing and pumping energy costs.

The cost structure reveals that when using Fe/ceramic MF, the main costs are associated with replacement of equipment and membranes (50%), capital (30%) and reagents (16%). When PAC is added, i.e., for PAC/Fe/ceramic MF, the cost structure changes, the reagent cost increases and surpasses the replacement costs, representing 39% vs. 36% for the latter; the relative contribution of the capital costs also decreases from 30% to 21%.

Table 10. Cost structure of the Fe/MF and PAC/Fe/MF for a plant flow rate of 50,000 m^3/day, considering 20 years and 10 years of membrane lifespan.

Cost Structure		Costs (€/m^3)	
		Membrane Lifespan	
		20 years	10 years
CAPEX		0.045	
	Membranes	0.034	
	Other equipment	0.011	
OPEX		0.106	0.174
	Membrane replacement	0.034	0.102
	Other equipment replacement	0.041	
	Reagents	0.024	
	Energy	0.002 [2]	
	Maintenance	0.004	
	Personnel	0.001	
TOTAL Fe/MF		0.151	0.219
	PAC [1]	0.057	
TOTAL PAC/Fe/MF		0.208	0.276

[1] including the costs of the reagent, of mixing and pumping energy and of the pumps; [2] corresponding to 0.026 kWh/m^3.
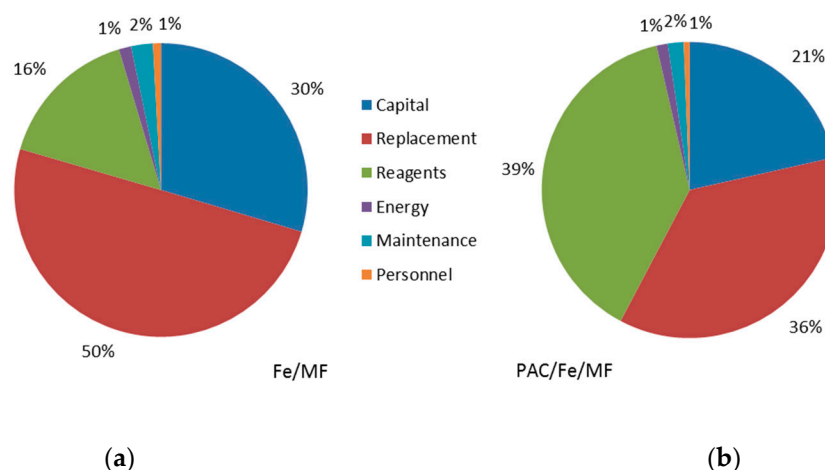
Figure 5. Cost structure of (**a**) Fe/MF and (**b**) PAC/Fe/MF for a plant flow rate of 50,000 m^3/day.

The above costs were calculated assuming a 20-year lifespan of the membranes, as presented in other studies [15,27]. However, as their application in wastewater treatment is fairly new no actual figures exist. Thus, and given the high weight of membranes replacement in the total costs, a more conservative scenario was considered, assuming 10 years lifespan of the membranes. The costs are detailed in Table 10 and show, for the design flow rate, a cost increase of 0.07 €/m^3, corresponding to a 50% increase of the total cost of the Fe/MF configuration with a 20-year lifespan of the membranes. This observation strengths the importance of controlling membrane fouling, through an adequate pretreatment and an effective membrane cleaning, the critical factors for preserving membrane lifetime.

4. Conclusions

The pilot PAC/Fe/ceramic MF tests run with sand-filtered secondary effluent spiked with four chemically different pharmaceutical compounds showed that 15 mg/L PAC did not promote membrane fouling and that PAC dosing to a 15-min contactor performed better than its in-line dosing for these 4 PhCs. In these conditions, PAC promoted significant removals (47%–56%) of three target PhCs, with the highest removals being obtained for carbamazepine and atenolol (56%). While the higher removals for CBZ can be attributed to hydrophobic interactions with the PAC, for ATN it should be due to PAC–EfOM–ATN interactions. Considerable EfOM removal was also achieved, which is beneficial if a further post-chlorination is required for water reuse.

A detailed cost analysis of the process, as a function of the plant flow rate, was performed pointing to total production costs of 0.21 €/m^3 for a 50,000 m^3/day plant and 20 years' membrane lifetime, with a higher share of OPEX (0.17 €/m^3), mainly associated to equipment/membranes replacement and reagents costs than of CAPEX (0.04 €/m^3). The membrane lifespan was shown to be a key factor for the costs.

Conflicts of Interest: The authors declare no conflict of interest. The funder had no role in the design of the study; in the collection, analyses, or interpretation of data; in the writing of the manuscript, or in the decision to publish the results.

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