

Investigating PPCP Removal from Wastewater by Powdered Activated Carbon/Ultrafiltration

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Abstract Powdered activated carbon/ultrafiltration (PAC/UF) hybrid process was investigated for removing from wastewater five pharmaceutical and personal care products (PPCPs): 1-H-benzotriazole, DEET, chlorophene, 3-methylindole and nortriptyline-HCl. Adsorption, UF and PAC/UF experiments were performed, focusing on PPCP adsorption as a function of PPCP characteristics and organic matter (EfOM) competition. Two water matrices and two fine-particle PACs were studied, differing on EfOM nature and concentration and on PAC microporosity. Neutral PPCP uptake by the positively charged, meso- and microporous PACs followed PPCP hydrophobicity expressed by $\log K_{ow}$. The uptake of the positively charged nortriptyline exceeded the expected from $\log D$ due to its high aromaticity and the background ions, which partially shielded PAC-nortriptyline electrostatic repulsions. Adsorption capacity depended on PPCP hydrophobicity whereas the kinetics further depended on PPCP charge. Hydrophobic EfOM was preferentially adsorbed and a

stronger competitor, particularly for PPCPs with $\log K_{ow} < 2.6$. The highly microporous PAC better adsorbed these PPCPs and the hydrophobic EfOM, and it attenuated the EfOM competition. For all waters, PAC had no effect on UF-flux, and it significantly improved PPCP and EfOM removal by PAC/UF over standalone PAC and UF. For all conditions and microcontaminants, PPCP uptake exhibited a sigmoid curve with $\log K_{ow}$, with a turning point at 2.2–2.6. In real applications, meso- and highly microporous PACs are recommended, and the dose should target the PPCPs with $\log K_{ow} < 2.6$.

Keywords PPCPs · PAC/UF hybrid process · Adsorption · Membrane · Hydrophobicity · EfOM

1 Introduction

Municipal wastewater reclamation is a promising solution to overcome the growing pressure on water resources, but it may also hold potential health risk in terms of pathogenic disease and toxic effects due to microcontaminants, such as pharmaceutical and personal care products (PPCPs). Personal care products are used to maintain hygiene and general well-being, including cleansing products, fragrances and protective products, such as insect repellents and antimicrobials. Due to the growth in PPCP industries and to improved analytical methods, the number of PPCPs being detected in wastewater treatment plants (WWTPs) is increasing,

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making WWTPs key barriers against PPCP toxicological effects on the environment and on the human health.

Five PPCPs are addressed in this study since they have different common uses and have been scarce studied. The PPCPs selected were earlier used in advanced oxidation studies (Benitez et al. 2013a, b) and include (i) 1H-benzotriazole (BZ), an anticorrosive agent used in dishwasher detergents, aircraft deicing and antifreeze fluid of motor vehicles; (ii) N,N-diethyl-m-toluamide or DEET, an active ingredient of most commercial insect repellent products; (iii) chlorophene (CP), a biocide used as cosmetic preservative and for general cleaning and disinfection in hospitals and households; (iv) 3-methylindole (ML), a fragrance widely used in perfumes, herbicides, fungicides, dyes, antihypertensive and anticancer medicines; and (v) the antidepressant nortriptyline hydrochloride or nortriptyline-HCL (NH). These PPCPs are frequently found in European wastewaters (Loos et al. 2013; Smital et al. 2011; Baker and Kasprzyk-Hordern 2013), the highest concentrations being reported for benzotriazole and DEET, respectively, $2.7 \mu\text{g L}^{-1}$ and 196 ng L^{-1} average concentrations, and 221 and $15.8 \mu\text{g L}^{-1}$ maximum values. Margot et al. (2013) also found high concentrations ($>5 \mu\text{g L}^{-1}$) of benzotriazole and methylbenzotriazole during a long-term campaign in a Swiss WWTP. DEET was found to be recalcitrant to conventional wastewater treatment (Snyder et al. 2007; Yang et al. 2011). These are poorly studied compounds that partially or totally resist the conventional wastewater treatment; some are recalcitrant even to advanced oxidation, as it was found for Benitez et al. (2013a, b) and Acero et al. (2013, 2015). Acero's et al. (2015) batch lab studies also showed benzotriazole to be poorly removed by a combination of advanced oxidation and high pressure (20 bar) nanofiltration.

Investigation on advanced technologies to achieve high-quality standards is therefore needed, and the hybrid process of powdered activated carbon adsorption/ultrafiltration (PAC/UF) arises as an interesting solution. PAC adsorption is considered one of the best available technologies for the removal of microcontaminants, and recently, it has been combined with low-pressure ($<1 \text{ bar}$) membrane processes such as microfiltration or ultrafiltration. Previous experiences with PAC/UF at lab and pilot scale demonstrated that UF is an effective barrier against microbial contaminants and fine PAC particles, whereas PAC is used to effectively improve the removal of microcontaminants while enabling to

control the membrane irreversible fouling (Campinas and Rosa 2010a, b). Compared to the advanced oxidation processes, PAC/UF does not originate the undesirable oxidation by-products (OBPs) and has the potential to control them, either by removing the precursors or the OBPs formed in earlier stages. On the other hand, compared to other membrane processes tested, UF operates at significantly lower pressure and subsequent lower energy demand.

Very recently, some studies were published focusing on the control of pharmaceutical compounds by hybrid PAC/membrane systems; however, they almost exclusively addressed membrane submerged systems and not pressurized ones as in our paper. Submerged and pressurized systems are very different in configuration and in operational conditions (e.g. PAC doses and contact time, cleaning procedures). As compared by Löwenberg et al. (2014), both systems are highly effective allowing a 60–95 % removal of emerging contaminants, including benzotriazole, and the pressurized system, using a polyethersulphone membrane in dead-end mode of operation, is more compact and entails a lower energy demand.

For low molecular weight contaminants ($<300 \text{ Da}$), the adsorption onto activated carbon is the key-step in PAC/UF hybrid process as size exclusion and steric hindrance mechanisms are expected to be negligible due to the high-molecular weight cut-off of the UF membrane (100–300 kDa) compared to their molecular weight. PAC should be tailored according with the time-space needs, i.e. be easily adjustable to specific contaminants and different water qualities. However, comprehensive data for understanding PPCP adsorption in wastewater treatment are relatively scarce, mostly due to the wide spectrum of compounds and chemical properties (size, hydrophobicity, charge, functional groups). In addition, details on PAC chemical and textural properties and their relation with the PPCP adsorption are also insufficient.

Challenges of PAC/UF hybrid systems are the adsorbent's selection and optimisation, the membrane fouling control and the prediction of full-scale process performance (Stoquart et al. 2012), which must fit the contaminant(s) properties and the wastewater matrix characteristics. The time-space diversity of wastewater matrix characteristics highlights the importance of conducting further studies on PPCP-EfOM (effluent organic matter) competitive adsorption. EfOM direct competition for the adsorption sites and/or PAC pore blockage/constriction by EfOM is major adsorption-

limiting phenomena, which depend on PAC pore size distribution, EfOM concentration and composition and competitor/contaminant proportions (Campinas et al. 2013). In a recent study (Margot et al. 2013), a large PAC/UF pilot plant was long tested, and high variations in microcontaminants' removal rate were observed, especially for compounds with lower PAC affinity, which was attributed to EfOM competition.

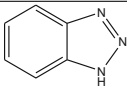
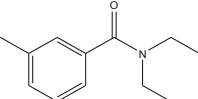
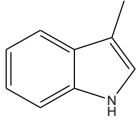
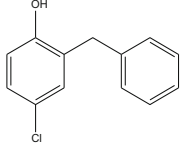
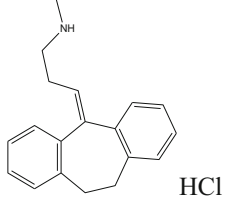
Therefore, a comprehensive study on pressurized PAC/UF was developed to investigate the PPCP adsorption as a function of their characteristics and PPCP-EfOM competitive adsorption. Standalone UF tests and PAC kinetics were also performed to better assess the PAC effect on PPCP removal by PAC/UF hybrid processes. A widely used membrane (a hydrophilic cellulose acetate membrane with 100 kDa molecular weight cut-off) and mode of operation (crossflow) were investigated, to our knowledge, for the first time for this set of target contaminants, water matrix and research objectives.

2 Materials and Methods

2.1 PPCPs

The five PPCPs selected were purchased from Sigma-Aldrich (Germany) with 99 % purity or higher. The initial concentration of PPCPs in the experiments was 1 μ M of each compound. Table 1 summarizes the selected compounds, their main use and relevant physical-chemical properties, namely molecular weight (MW), charge, log K_{ow} and log D. The octanol/water partition coefficient (K_{ow}), usually expressed in log scale (log K_{ow}), was used to express the hydrophobicity of neutral compounds and follows the order: benzotriazole < DEET < methylindole < chlorophene. Nortriptyline contains an ionizable functional group and can ionize to become positively charged depending on pH. In this case, hydrophobicity should be assessed through $\log D_{(pH)} = \log K_{ow} - \log (1 + 10^{(pH - pK_a)})$ in the pH range studied, 7.0–7.5. The other

Table 1 Physical-chemical characteristics of the PPCPs studied

PPCP	Structure	Molecular formula	MW, g mol ⁻¹	V _{molar} , cm ³ a	Log K _{ow}	Charge at pH 7	Log D pH 7–7.5	Category
1-H-benzotriazole (BZ)		C ₆ H ₅ N ₃	119.1	88.3	1.44	n	1.42–1.39	Anticorrosive
DEET (DT)		C ₁₂ H ₁₇ NO	191.3	194.0	2.18	n	2.18	Insect repellent
3-methylindole (ML)		C ₉ H ₉ N	131.3	118.1	2.60	n	2.60	Fragrance
Chlorophene (CP)		C ₁₃ H ₁₁ ClO	218.7	179.2	4.18	n	4.18	Biocide
Nortriptyline HCl (NH)		C ₁₉ H ₂₁ NO · HCl	299.8	242.9	4.51	+	1.40–1.80	Antidepressant

(1) "n" neutral charge, "+" positive charge; (2) Calculated by ChemSketch.

n neutral charge, '+' positive charge

^a Calculated by ChemSketch

contaminants selected are neutral; thus, the values of $\log K_{ow}$ are equal to those of $\log D$.

2.2 Water Matrices

Two water matrices were studied aiming at evaluating the influence of EfOM nature and concentration in PAC/UF process, namely WW (wastewater) and DS (deionised water with salts) (Table 2).

WW is a real urban wastewater collected after secondary treatment and sand filtration which was further subjected to microfiltration through a 0.1 μm ceramic membrane (Kerasep), at LNEC's laboratory. The microfiltration allowed producing a large volume of disinfected wastewater, more stable and easier to be preserved (by refrigeration) and used in all experiments, to minimize the feed water quality variations and improve the results reproducibility. After the microfiltration step, the investigated PPCPs (1 μM each) were spiked into the resulting filtrate, which was then used in the adsorption experiments and in the UF and PAC/UF runs.

DS is a model electrolyte solution prepared in the laboratory to resemble an organic-free WW to serve as a control, i.e. deionised water was supplemented with CaCl_2 , NaHCO_3 and NaCl to achieve the WW ionic composition in terms of hardness, alkalinity, conductivity and pH. For studying the PPCP adsorption in the absence of EfOM, DS water was used spiked with the target PPCPs, 1 μM each.

2.3 Adsorbents

Two commercial PACs were selected for the present studies, namely PAC Norit SAE super (SAE) and PAC Norit SA Super (SA). These are fine-particle carbons (15 μm average particle diameters) designed for membrane retention and fast adsorption kinetics. Table 3 presents their textural characterisation and point of zero charge (pH_{pzc}), i.e. the pH at which they present as many positively as negatively charged surface groups. The textural characterisation was analysed by nitrogen adsorption isotherms in an external laboratory, and the pH_{pzc} was determined by mass titration following the methods proposed by Moreno-Castilla et al. (2000) and Noh and Schwarz (1989). The water pH was lower than the pH_{pzc} of both PACs in all experiments; hence, the PAC net surface charge was always positive. The two PACs presented

Table 2 Characterisation of the water matrices employed

	WW	DS
pH	7.4 ± 0.4	7.1 ± 0.2
DOC, mg CL ⁻¹	3.0 ± 0.6	–
Electrical conductivity, $\mu\text{S cm}^{-1}$	1432 ± 116	1523 ± 67
Alkalinity, mg CaCO ₃ L ⁻¹	117	117
Hardness, mg CaCO ₃ L ⁻¹	370	370
UV _{254 nm} , m ⁻¹	11.61 ± 0.27	–
A _{436 nm} , m ⁻¹	1.004 ± 0.035	–
SUVA, L m ⁻¹ mg ⁻¹ C	3.8 ± 0.4	–
EfOM composition, %		
Strongly hydrophobic	71.2	–
Moderately hydrophobic	14.0	–
Charged hydrophilic	10.5	–
Neutral hydrophilic	4.3	–

similar surface area, similar and high volume of mesopores, but SA had higher micropore volume (0.49 vs 0.40 cm³/g, i.e. 22 % higher).

2.4 Adsorption Kinetics Experiments

Batch tests with efficient mixing were conducted in two jar test apparatus with six jars each. Prior to its addition to the solutions, PAC was soaked overnight in ultrapure water to allow for the complete wetting of the pores. Identical mixing (200 rpm), water volume (500 mL) and temperature conditions (19–21 °C) were applied to all batch reactors. The PAC concentration varied in the 3–15 mg L⁻¹ range. PAC concentration was kept as low as possible, lower than the usual values in industrial applications and in the range used in earlier studies (Campinas and Rosa 2006, 2010a, b), to allow observing differences in the uptake of the chemically different PPCPs studied, and therefore allow investigating the phenomena behind their adsorption. Samples were taken at predetermined time intervals over a 3-h period (3, 5, 10, 30, 60, 120 and 180 min of contact) and filtered through a 0.7 μm glass fibre filter (GF-F Whatman) for PAC particle retention. The filtered water samples were analysed for pH, electrical conductivity, EfOM and PPCPs ("Section 2.7"), and the results were presented as residual concentration (C/C_0) as a function of time. The percentage removals were computed as $(1-C/C_0) \times 100$.

Table 3 PAC characterisation

PAC	Particle diameter μm	S_{BET} $\text{m}^2 \text{g}^{-1}$	V_{total} $\text{cm}^3 \text{g}^{-1}$	V_{micro} $\text{cm}^3 \text{g}^{-1}$	V_{meso} $\text{cm}^3 \text{g}^{-1}$	pH_{pzc}
SAE	15	1093	0.79	0.40	0.39	9.9
SA	10–20	1156	0.89	0.49	0.40	11.3

S_{BET} surface area (Brunauer, Emmet and Teller isotherm), V_{total} total pore volume (N_2 adsorption at $p/p^0 = 0.995$), V_{micro} total micropore volume (t-plot method), V_{meso} mesopore volume ($V_{\text{total}} - V_{\text{micro}}$)

2.5 UF and PAC/UF Runs

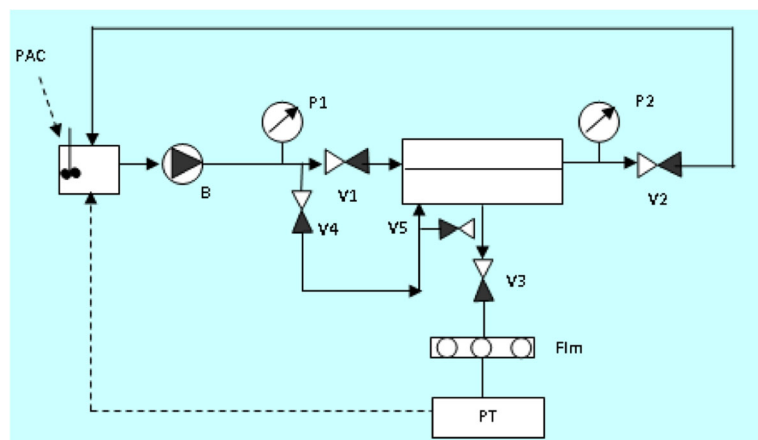
UF experiments used a hollow fibre cellulose acetate membrane from Aquasource (inside-out configuration) previously used in other PAC/UF studies (Campinas and Rosa 2010a, b). This UF hydrophilic membrane has a cut-off of 100 kDa. The module has 16 fibres, 1.1 m length and 0.93 mm internal diameter, with a total surface area of 0.05 m^2 . The manufacturer recommends a maximum pressure of 1.5 bar and a maximum backflushing pressure of 2.5 bar. The module was mounted in a bench-scale apparatus that includes a feed tank (FT), a positive displacement pump, two manometers (P1, P2), one flow meter (Flm), a permeate tank (PT) and the valves (V1–V5) and tubing in the backwashing and in the recirculating loops (Fig. 1). The module was operated under the inside-out configuration during the filtration cycles and membrane flushing, and under outside-in flow during backwashing.

All the UF experiments were conducted in a cross-flow filtration mode as earlier described (Campinas and Rosa 2010a, b). Time-depending fouling runs were

performed with the concentrate and the permeate being recycled back to the feed tank during 2 h at a constant transmembrane pressure of 0.9 bar. The positive displacement pump provided the necessary pressure and recirculation, and a variable-frequency drive allowed adjusting the cross-flow velocity in the hollow fibres. Permeate flow rate and temperature were periodically measured and, whenever necessary, transmembrane pressure was adjusted by manual control of the concentrate valve. At given time intervals (after 2, 15, 30, 60, 90, and 120 min of filtration), permeate samples were collected for analysis. At the end of each experiment, membranes were backwashed and flushed. Backwashing lasted 1 min with a 5 mg L^{-1} (as Cl_2) sodium hypochlorite solution to inhibit the biological activity on the UF system, and flushing was performed with deionised water during 5 min.

In PAC/UF experiments, PAC (10 mg L^{-1}) was directly added to the feed tank, which was continuously stirred. The total mass of PAC was always added at the beginning of the filtration cycle and was only discarded at the end of the run. A low PAC concentration was used for the reasons explained in the earlier section.

Fig. 1 Flow diagram of the UF system. FT stirred feed tank, B positive displacement pump, P manometers, Flm flow meter, PT permeate tank, V1, V4, V5 valves for backwashing, V2 concentrate valve, V3 permeate valve



Normalised flux as a function of time was used as the membrane fouling indicator. Normalised fluxes were calculated as the ratio of solution flux over the pure water flux before starting the run. All flux values were corrected to a constant temperature of 20 °C as described in Campinas and Rosa (2010a, b).

2.6 Analytical Methods

Samples were analysed for pH at 20 °C and electrical conductivity at 25 °C (Consort C863 multiparameter meter). The EfOM concentration was analysed as dissolved organic carbon (DOC), measured as non-purgeable organic carbon by ultraviolet-persulfate oxidation method in a Teledyne TEKMAN TOC Fusion analyser. The EfOM nature was assessed through UV_{254nm} absorbance (Jasco V630 UV/Vis spectrophotometer and Horiba Scientific Aqualog spectrofluorometer) and specific UV_{254nm} absorbance (SUVA), computed by UV_{254nm}/DOC. Absorbance at 436 nm (A_{436nm}) was used as colour indicator. The EfOM of WW was further characterised in terms of strongly hydrophobic, moderately hydrophobic, charged hydrophilic and neutral hydrophilic fractions using Chow's et al. (2004) method. For this purpose, three glass columns were set up in series and each column was filled with a different resin, namely DAX-8, XAD-4 and IRA-958. Samples were collected before and after each column, and the DOC values were used to calculate the organic matter of each fraction.

The concentrations of the five PPCPs selected were assayed by liquid chromatography in a Waters Chromatograph (Alliance 2695) equipped with a 2998 Photodiode Array Detector and a Phenomenex Gemini C18 column (5 µm, 150 mm × 3 mm) following the analytical method described in Benitez et al. (2013a, b). The analysis was performed in gradient mode with acetonitrile and 25 mM formic acid, at a flow rate of 0.2 mL min⁻¹. The injection volume was 100 µL in all cases. Detection was made at 250 nm for benzotriazole, nortriptyline HCl and DEET, and at 280 nm for methylindole and chlorophene.

The DS and WW samples taken before and after UF and PAC/UF runs needed no filtration prior to analysis for they were obtained from a model solution (i.e. from DS) or from microfiltered wastewater (WW) before (the feeds) or after (the permeates) ultrafiltration. The samples taken from the batch adsorption runs were filtered

immediately after the contact time for eliminating the PAC particles (Section 2.6).

Duplicate and/or triplicate samples of the analytical determinations were made to minimize statistical variance of the results. When the standard deviations of the samples were 5 % higher than the mean, the measurement was rejected, and a new determination was made.

3 Results and Discussion

3.1 Adsorption of EfOM and PPCPs on PACs

This study addressed the adsorption kinetics of EfOM and of the five PPCPs and also the PPCP-EfOM competitive adsorption. The adsorption kinetics of EfOM was studied for SAE and SA PACs, using WW (not supplemented with the PPCPs) and two PAC doses (7 and 15 mg L⁻¹) (Fig. 2).

For both PACs, the higher dose showed a significant improvement of the water quality in terms of UV_{254nm}, DOC and colour (A_{436nm}). This improvement was particularly noticeable for UV_{254nm} and colour and for SA PAC. Comparing SAE and SA PACs, for 3–180 min contact time and 7 mg L⁻¹ PAC, one obtained 10–20 vs. 14–29 % UV_{254nm} decrease and 15–28 vs. 15–35 % colour (A_{436nm}) removal. The same comparison for 15 mg L⁻¹ of SAE and SA PACs indicated 13–37 vs. 21–51 % UV_{254nm} decrease and 15–48 vs. 31–72 % colour removal, respectively.

The overall removal of organic matter, expressed by DOC, did not differ between carbons, and this is consistent with their similar textural properties in terms of transport pores, expressed by their similar mesopore volume (Table 3).

Both PACs showed higher UV_{254nm} and A_{436nm} uptake than DOC, which indicates a preferential adsorption of hydrophobic EfOM and colour substances, particularly for SA. The main difference between both activated carbons is in the micropore volume, which may determine differences in the adsorption equilibrium of smaller adsorbates, such as the PPCPs targeted.

The adsorption kinetics of the selected mixture of PPCPs was studied for five doses of SAE and SA PACs, in the absence (using DS) and in the presence (using WW) of EfOM (Fig. 3).

In the absence of EfOM (DS results in Fig. 3), PPCP uptake followed PPCP hydrophobicity (expressed as log

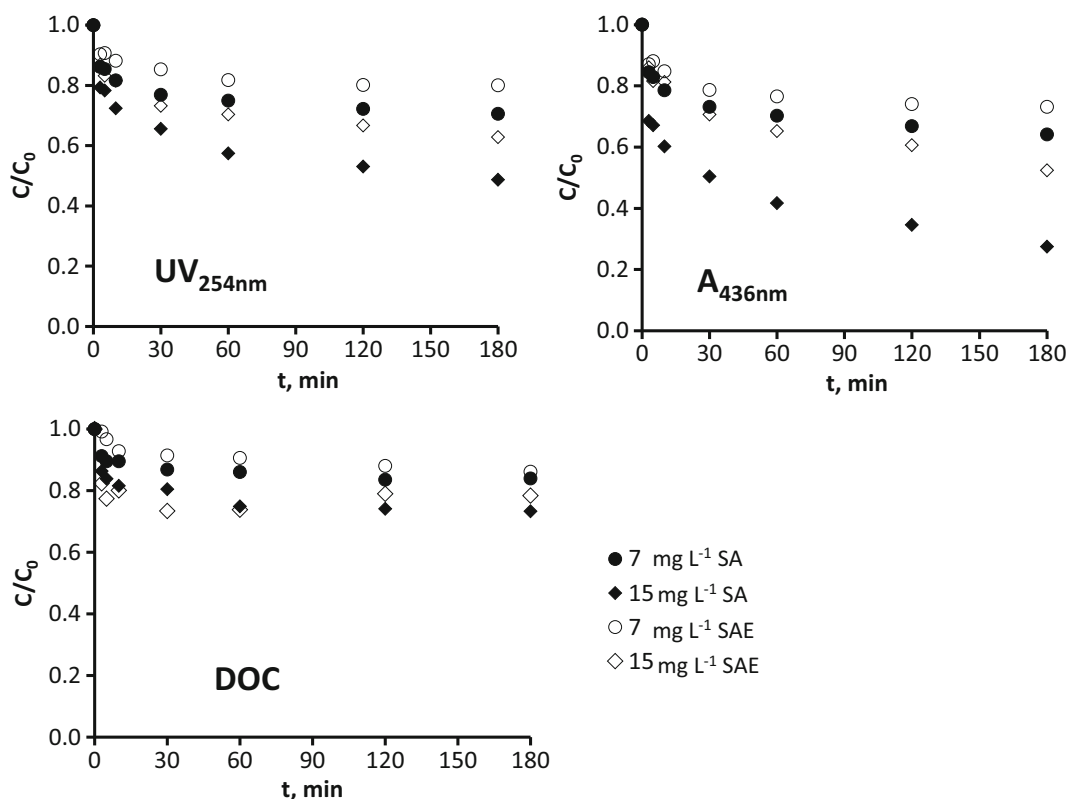


Fig. 2 Residual values of DOC, UV_{254nm} and A_{436nm} in adsorption experiments performed with WW water matrix and two doses of SA and SAE PACs

K_{ow} , Table 1), i.e. benzotriazole < DEET < methylindole < nortriptyline < chlorophene (Fig. 3), except for nortriptyline. Nortriptyline was less adsorbed than expected based on its log K_{ow} , but more than expected from log D (Table 1). The uptake lower than expected from log K_{ow} may be justified by nortriptyline-PAC electrostatic interactions. At neutral pH, nortriptyline-HCl carries the same positive charge as PAC surface, and therefore an overall electrostatic repulsion develops between nortriptyline and PAC, which attenuates hydrophobic interactions and hinders adsorption.

Three possible effects may explain the nortriptyline uptake higher than expected based on log D value. Firstly, the electrostatic repulsion may be partially cancelled due to the shielding effect from the water background ions, as found in earlier studies (Campinas and Rosa 2006). Secondly, the strong aromatic character of nortriptyline may explain its significant adsorption. In fact, nortriptyline presents the highest value of molar extinction coefficient at 254 nm amongst the selected

PPCPs (Benitez et al. 2013a, b). Other authors (Dickenson and Drewes 2010) also found that adsorption of solutes with low log D value was favoured by the presence of functional groups capable of forming hydrogen bonds or by aromaticity allowing the formation of pi-pi bonds. Finally, though the overall net charge of the activated carbon is positive at the water pH of the experiments, some acidic groups within the PAC pores (such as carboxylic groups) may be charged, and these negative charges may promote local attractive interactions with the positively charged nortriptyline.

The WW results depicted in Fig. 3 show that, in the presence of EfOM, the PPCP uptake followed the same order than in EfOM absence. This suggests that the higher uptake of positive PPCPs does not depend only on the often suggested PPCPs-organic matter interactions, but also on other effects, such as the local attractive interactions developed with PAC acidic groups. Further, the results show that the EfOM effect depended

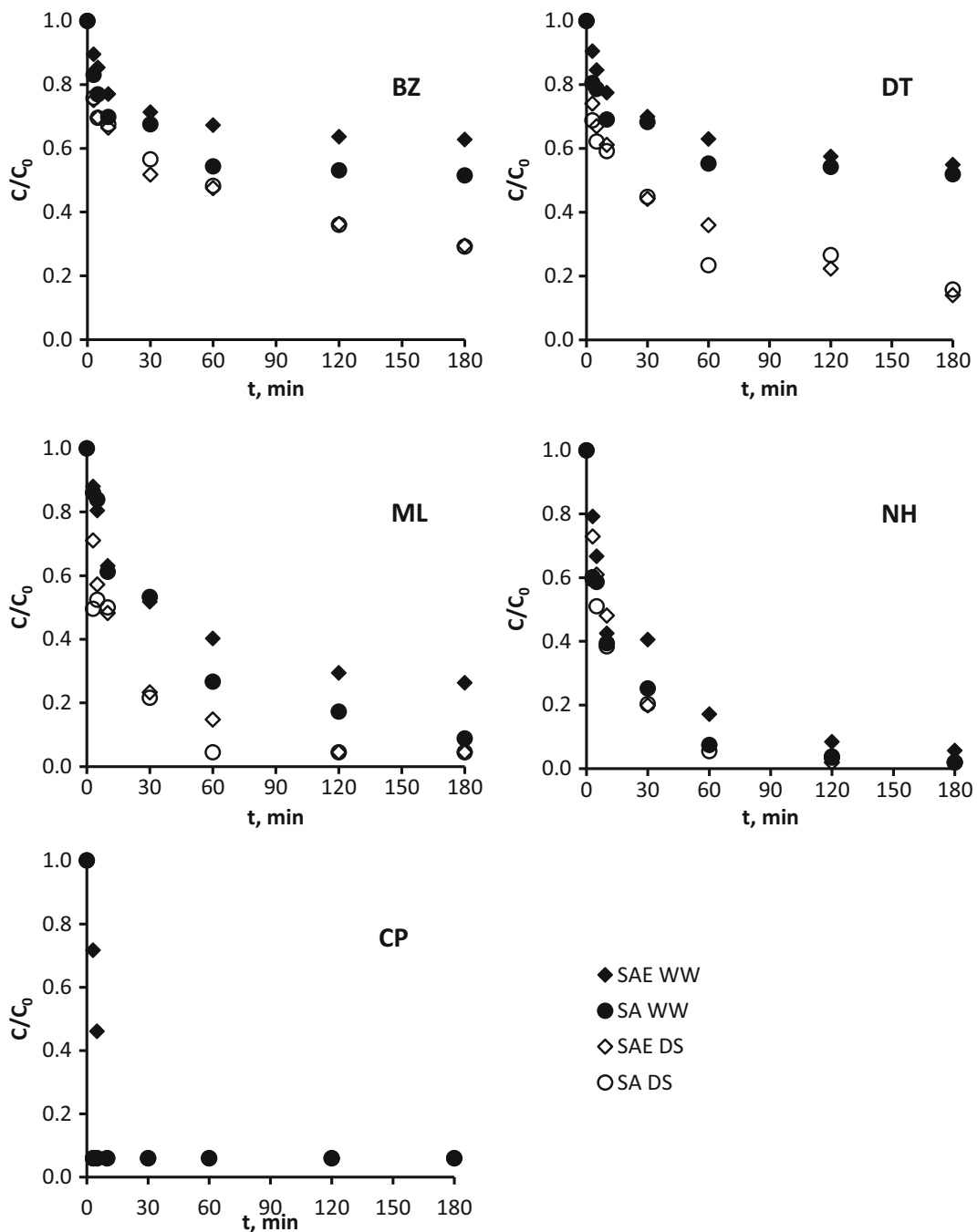


Fig. 3 Residual concentration of PPCPs in adsorption experiments performed with 10 mg L^{-1} SA and SAE PACs and DS and WW water matrices

on the compound. The more hydrophobic contaminant, chlorophene, did not show EfOM competition; the strongly hydrophobic and positively charged nortriptyline exhibited a slight EfOM effect only with SAE PAC, whereas the less hydrophobic compounds, benzotriazole, DEET and methylindole, were indeed affected.

In addition, for benzotriazole and methylindole, the EfOM negative impact was more pronounced for SAE PAC than for SA, whose major difference relies on the higher secondary micropore volume of the latter. Therefore, the EfOM competitive effect was more noticeable for the PPCPs less

amenable to adsorption. For these PPCPs, PACs with higher volume of secondary micropores or small mesopores might be a strategy for attenuating EfOM competition.

Solute hydrophobicity, charge and size are the physicochemical candidate descriptors for adsorption. Hydrophobic interactions depend on the hydrophobicity of both the solute and the activated carbon surface, which can be related to the quantity of oxygen-containing functional groups and basic sites. Solute hydrophobicity is often represented by the octanol-water partition coefficient. Figure 4 relates the residual PPCP concentrations after 3 h contact time (the last contact time in adsorption kinetics, to infer the adsorption capacity) with $\log K_{ow}$. This figure highlights the importance of $\log K_{ow}$ on PPCP adsorption, showing a turning point at 2.2–2.6 $\log K_{ow}$. The same trend was observed for both PACs, in the presence and absence of EfOM and for PAC/UF process (further discussed in “Section 3.2”). In general, compounds with low K_{ow} values (e.g. below 10, i.e. $\log K_{ow} < 1$) may be considered relatively hydrophilic (Dalrymple 2005; Rosa et al. 2009) while those with high K_{ow} values are hydrophobic (e.g., above 10^2 , $\log K_{ow} > 2$; Rosa et al. 2009) or very hydrophobic (K_{ow} above 10^4 , $\log K_{ow} > 4$; Dalrymple 2005). Between these limits, there is a turning point, which explains the 2.2–2.6 $\log K_{ow}$ range herein observed.

No trend was found between PPCP adsorption and PPCP molar volume (Figure S1). Further, benzotriazole and DEET (neutral compounds with 1.4–2.2 $\log K_{ow}$) showed very similar behaviour in WW water matrix both in terms of adsorption kinetics (Fig. 3) and adsorption capacity (inferred from Fig. 4). The same analysis applied to nortriptyline and chlorophene allowed concluding that these PPCPs, with 4.2–4.5 $\log K_{ow}$, showed similar

adsorption capacity in the presence of WW EfOM, though the positively charged nortriptyline showed slower kinetics than the neutral chlorophene. Therefore, for the assayed PACs (with high meso- and microporosity and overall positive charge) and PPCPs (100–250 cm^3 molar volume, 1.4–4.5 $\log K_{ow}$), the adsorption capacity seems to be mainly related to PPCP hydrophobicity whereas the adsorption kinetics seems to further depend on other property, such as charge.

Figure 5 shows the residual concentrations of benzotriazole, the poorly adsorbed PPCP, and chlorophene, the better adsorbed, with different PAC doses in WW matrix. The results obtained for the remaining PPCPs are depicted in Fig. S2. For the more easily adsorbed PPCPs, such as chlorophene or nortriptyline, equilibrium was reached after very short contact time and at very low residuals (<0.1) regardless of the PAC dose employed in the 10–15 mg L^{-1} range. Doses below 7 mg L^{-1} required higher equilibrium time. SA PAC reached the same residual concentration for all PAC doses tested, while for SAE the PAC dose of 3 mg L^{-1} limited the residual to approx. 0.4. On the other hand, the uptake of the less adsorbed contaminants, i.e. benzotriazole, DEET and methylindole, increased with PAC dose in the full range of 3–15 mg L^{-1} . For instance, with SA PAC, C/C_0 for benzotriazole varied from 0.85 to 0.4.

Overall, SA PAC showed a better performance than SAE and taking into account the usual contact times in pressurised PAC/UF systems (below 1 h), 10 mg L^{-1} SA was selected for PAC/UF runs, as a compromise between PPCP removal and operating costs. Previous studies (Campinas et al. 2013; Margot et al. 2013; Löwenberg et al. 2014) indicated 10–20 mg L^{-1} PAC as typical concentration ranges to remove microcontaminants and organic matter from municipal secondary effluents by the PAC/UF process. Direct

Fig. 4 PPCP residual concentrations at the end of PAC and PAC/UF runs versus $\log K_{ow}$ (3 h PAC batch tests and 2 h PAC/UF cycles with 10 mg L^{-1} SA and SAE PACs and DS and WW water matrices; the trend lines are only to guide the eyes)

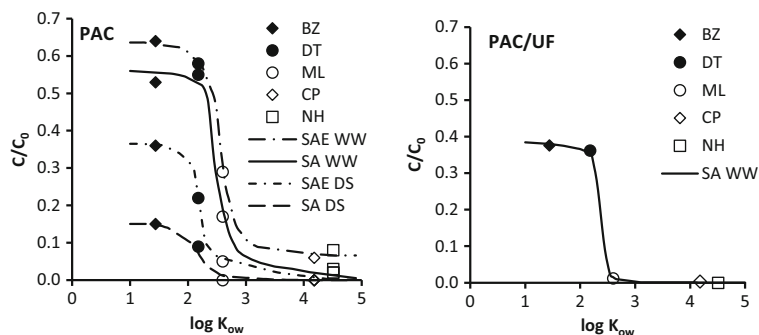
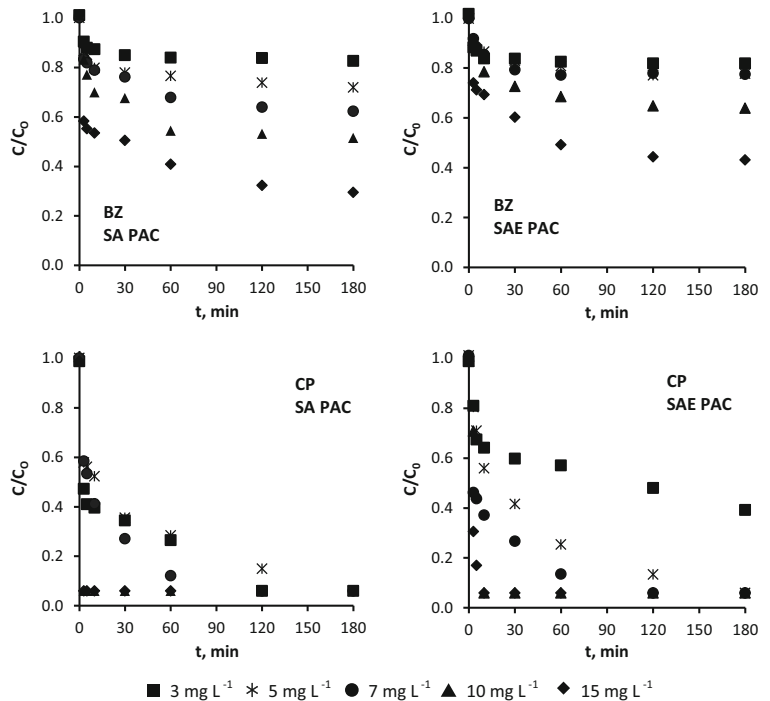


Fig. 5 Residual concentrations of benzotriazole and chlorophene in PAC adsorption experiments performed with WW water matrix



comparisons with the current study are however difficult given the different operating conditions (e.g. contact time) and water characteristics, including the PPCP content (in type and concentration). In any case, PAC/UF system is very flexible and PAC type and dose can be easily adjusted to the feed water and the contaminants targeted, including the DOC content.

3.2 PAC/UF Runs

A major limitation of UF application in water reclamation/reuse is the permeate flux reduction due to membrane fouling. Despite the vast number of membrane fouling studies reported in the literature, there is still disagreement on the main foulants and fouling-

control strategies. PAC may be an option, however, it is not yet clear whether PAC attenuates, aggravates or does not affect membrane fouling as different results have been reported (Campinas and Rosa 2010a, b; Nguyen and Roddick 2013; Jirankova et al. 2007; Gai and Kim 2008; Kweon et al. 2009). PAC overall effect seems to depend on PAC–membrane interactions and PAC cake-layer characteristics, which are influenced by the water matrix, membrane characteristics and activated carbons used. Figure 6 shows the UF normalised flux during the 2-h filtration cycles with DS and WW, with and without PAC addition. This figure shows no significant differences in the permeate flux (standard deviation <5 %) regardless of the different water matrices used. Furthermore, PAC addition had no effect on

Fig. 6 Normalised flux in UF and PAC/UF runs performed with DS and WW water matrices

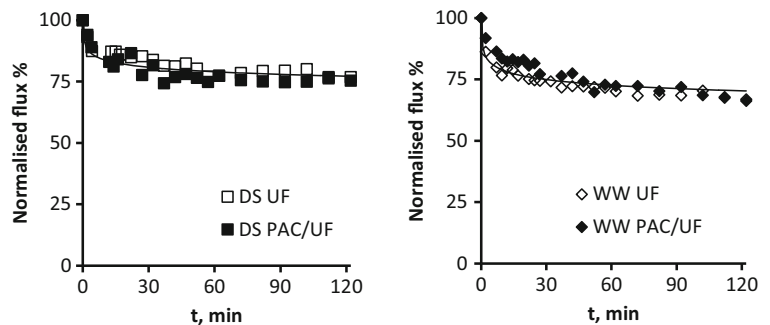
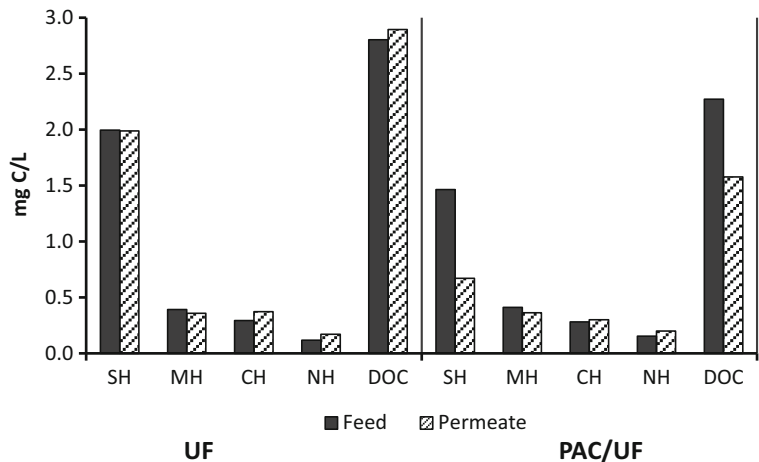


Fig. 7 Characterisation of EfOM fractions in UF and PAC/UF experiments with WW at the end of a 2-h filtration cycle. *SH* strongly hydrophobic, *MH* moderately hydrophobic, *CH* charged hydrophilic, *NH* neutral hydrophilic



the permeate flux during PAC/UF runs with or without EfOM. The same result was earlier found for the same membrane, installation and operating conditions though with a different PAC used for drinking water treatment (Campinas and Rosa 2010a). As proposed therein, PAC particles are large enough to avoid membrane fouling through pore blocking; in addition, PAC forms a ‘loose’ porous layer that allows the passage of water without increasing the resistance.

In order to assess UF and PAC/UF performance for EfOM removal, WW feed and permeate were analysed for strongly hydrophobic, moderately hydrophobic, charged hydrophilic and neutral hydrophilic organic fractions (Fig. 7).

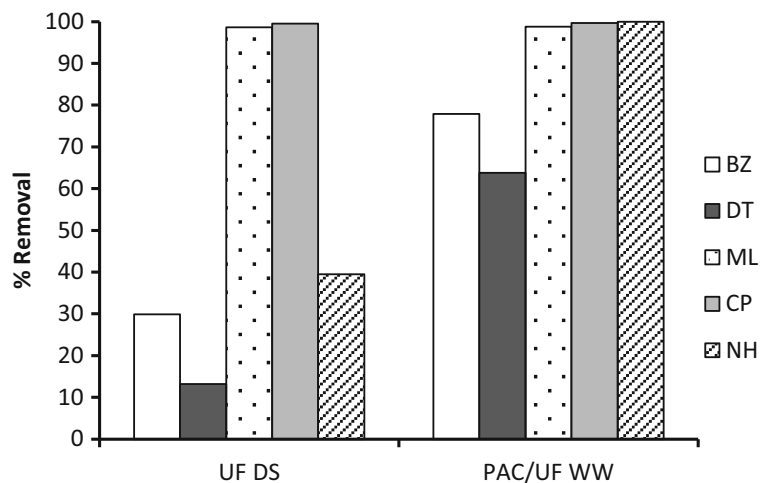
From the results shown in Fig. 7, it can be concluded that the UF membrane did not reject any EfOM fraction,

while PAC/UF highly rejected strongly hydrophobic EfOM. Therefore, the overall reduction of DOC (from 2.3 to 1.6 mg C L⁻¹) was mainly due to the PAC adsorption of hydrophobic EfOM. As the strongly hydrophobic fraction decreases significantly, a significant reduction of the disinfection by-products formation potential is expected. This reduction constitutes an advantage in water reuse projects since the reclaimed water is often chlorinated to prevent water quality degradation and biofilm growth in the distribution system.

Figure 8 displays the PPCP removal by UF and PAC/UF under the studied conditions.

The removals observed from organic-free water (DS) using standalone UF (i.e. without PAC addition) varied between 13 and >95 %; DEET and benzotriazole were removed by 13 and 30 %, respectively; nortriptyline by 40 % and chlorophene and methylindole were almost

Fig. 8 Percentage removal of each PPCP from DS and WW water matrices at the end of 2-h UF and PAC/UF cycles, the latter with 10 mg L⁻¹ SA



totally removed (rejection higher than 95 %). In this case, removals were not due to size exclusion or steric hindrance since the membrane molecular weight cut-off (100 kDa) is three orders of magnitude above the molecular weight of the PPCPs targeted (120–300 Da). In turn, adsorption may play the key role for PPCP removal, depending on the membrane and solute characteristics, particularly their hydrophobicity (Comerton et al. 2007; Snyder et al. 2007; Yoon et al. 2007). Most probably the contaminants were removed by adsorption on the UF membrane and UF system. This explanation is supported by the particularly relevant removals of the strongly hydrophobic PPCPs, more prone to adsorption, and agrees with the data published for other emerging contaminants. Comerton et al. (2007) have found a strong correlation ($r > 0.80$) between $\log K_{ow}$ and the adsorption onto a polysulfone UF membrane for 22 endocrine disrupting compounds and pharmaceutically active compounds with different properties (namely, solubility, hydrophobicity/hydrophilicity and polarity). Secondes et al. (2014) also found higher adsorption onto a polysulfone UF membrane of hydrophobic compounds, such as diclofenac and carbamazepine ($\log K_{ow} = 2.45$ and 4.29 , respectively) in comparison with amoxicillin ($\log K_{ow} = 0.61$). Moreover, Campinas and Rosa (2010b) found no adsorption of microcystins (less hydrophobic than benzotriazole) in the PAC/UF apparatus used in the present study.

When the combined PAC/UF process was used with WW substantially higher removals were found for benzotriazole and DEET, around 60 % (vs 30 and 13 %, respectively, using UF) and for nortriptyline (completely removed by PAC/UF vs 40 % removal by UF, Fig. 8).

Figure 9 highlights the advantages of PAC/UF over PAC. PAC/UF allowed reaching 20 % extra removal (or 30 % below 30 min) of both benzotriazole and DEET, and total removal of nortriptyline throughout the 2-h filtration cycle. For comparison, PAC yielded 60 % removal after 10 min contact time and around 90 % after 60 min.

One may then conclude that, in the PPCP concentration range tested (1 μM each PPCP), the addition of 10 mg L^{-1} of SA PAC to UF considerably improved the elimination of the less hydrophobic compounds targeted, i.e. nortriptyline, benzotriazole and DEET, which were also the most affected by EfOM competition.

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4 Conclusions

The results of PAC adsorption and PAC/UF hybrid process for the five PPCPs selected (four neutral compounds: 1-H-benzotriazole, DEET, chlorophene, 3-methylindole; one positively charged: nortriptyline HCl), two carbons and two water matrices (differing on EfOM nature and concentration) allowed the following conclusions to be drawn:

- the uptake of the neutral PPCPs in the adsorption kinetics runs followed PPCP hydrophobicity expressed by $\log K_{ow}$, either in the absence or in the presence of EfOM;
- the uptake of the positively charged nortriptyline HCl was lower than expected from $\log K_{ow}$, and it exceeded what was expected based on its $\log D$. This behaviour was explained by nortriptyline high aromaticity, which promotes adsorption through the formation of pi-pi bonds, the partial shielding of the electrostatic interactions by the water background ions and the local attractive interactions developed with PAC acidic groups;
- whereas the adsorption kinetics depended on PPCP hydrophobicity and charge, the adsorption capacity (i.e. the uptake 'at equilibrium', inferred from C/C_0 at the end of PAC batch tests and PAC/UF cycles) was in agreement with PPCP hydrophobicity for all microcontaminants and conditions studied. At 'equilibrium', PPCP residuals vs. $\log K_{ow}$ exhibited a sigmoid curve with a turning point around 2.2–2.6;

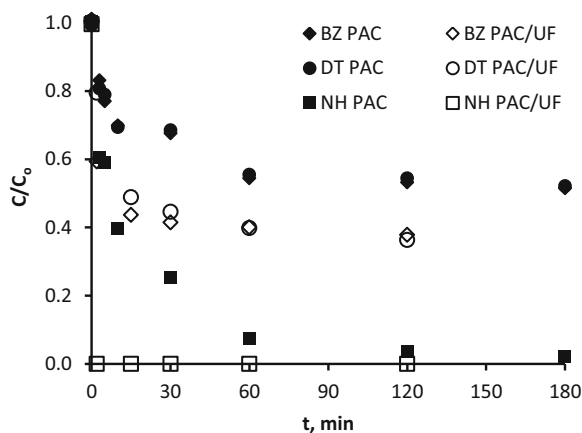


Fig. 9 Residual concentrations of benzotriazole, DEET and nortriptyline in PAC and PAC/UF experiments with WW water matrix and 10 mg L^{-1} SA

- iv. EfOM competitive effect was more noticeable for the PPCPs less amenable to adsorption, i.e. the less hydrophobic compounds, benzotriazole, DEET and methylindole;
- v. the PAC with higher secondary micropore volume presented greater uptake of hydrophobic EfOM and improved adsorption of the less adsorbable PPCPs, and attenuated EfOM competition;
- vi. PAC addition did not affect the permeate flux during PAC/UF runs (2-h filtration cycles) regardless of the water matrix employed;
- vii. Even in the low PAC concentration range studied (lower than the usual values in industrial applications), PAC/UF process significantly improved the removal of PPCPs over standalone PAC and UF, and it also significantly removed the strongly hydrophobic DOC, major precursor of disinfection by-products.

PAC/UF therefore constitutes a promising option for controlling the studied PPCPs in urban wastewater effluents and water reuse projects. In real applications, meso- and highly microporous PACs should be used, and the dose should be adjusted to meet the desired removals of the less adsorbable compounds ($\log K_{ow} < 2.6$).

As a final remark of this study, since PPCPs show highly diversified physicochemical properties, to overcome the practical difficulties of assessing the removal of each compound that may be present, it is important to develop methodologies for selecting representative contaminants that can be used in treatment trials and for regular control in water/wastewater treatment plants and in receiving bodies. Providing insights into the effect of the compounds properties in their removal, studies like this help establishing the list of 'indicators', i.e. the compounds which could represent the removal of a specific group of contaminants. Further, they help identifying key physicochemical descriptors for predicting the adsorption removal efficiency of the emerging contaminants actually detected in the water.

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