The effect of activated carbon and membrane filtration in the removal of pharmaceutical products in hospital wastewaters

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ABSTRACT

The removal of 10 OMPs was studied in two MBRs treating a synthetic hospital wastewater and using two different membrane configurations: hollow fiber ultrafiltration and flat sheet microfiltration. In both reactor configurations, high COD removal and nitrification was achieved (>95%), while a reduction of total nitrogen concentration was observed after PAC addition due to the enhancement of denitrification occurring in anoxic zones of the biofilm formed. Besides, sludge properties, such as filterability, and settleability, as well as microbial diversity and the quality effluent enhanced after PAC addition. Naproxen, ibuprofen, sulfamethoxazole and hormones were readily removed by biotransformation, with no effect caused by the different membrane types or the addition of PAC. On the other hand, the efficiency of PAC was very clear for carbamazepine and diclofenac, and to less extent for erythromycin, roxithromycin and trimethoprim, with evidences of PAC saturation with time mainly in the positively charged compounds. Concerning membrane configuration, no significant differences were observed between both reactors, except for diclofenac and ROX. As size exclusion is not expected to be significant neither for UF nor MF membranes, the difference between both membranes might be attributed to sorption and/or further biotransformation in the cake layer.

Keywords: emerging micropollutants, activated carbon, MBR, adsorption, membrane

1. INTRODUCTION

In the last decades, several studies are focussed on the study of the fate of organic micropollutants (OMPs) in conventional biological wastewater treatment [1, 2] due to the increasing concern in modern societies about their toxicity, estrogenecity and bioaccumulation potential. In this sense, in 2012 the European Union proposed 15 additional substances to be included in the “list of priority substances” defined by the Water Framework Directive (proposal COM(2011)876), which includes three OMPs (estradiol, diclofenac and ethinylestradiol). The conventional biological processes are mainly oriented to the removal of organic matter and macronutrients (N, P). Although these processes are also able to degrade some OMPs, such as IBP, NPX or ERY [1, 3], a wide range of other OMPs are poorly biotransformed. Therefore, physico-chemical treatments (e.g. ozone, activated carbon, etc.) are necessary in order to increase the number of OMPs removed from the wastewater, which are applied mainly as post-treatment or also for the treatment of drinking water [4, 5, 6].

The use of membranes in biological reactors enhances the quality of the final effluent in terms of suspended solids and microorganisms concentrations. Residual levels of colloidal and soluble organic pollutants are removed in MBR with ultrafiltration (UF) and microfiltration (MF) membranes [7]. Although OMPs cannot be removed by size exclusion in UF and MF membranes, the use of MBRs allow to work at very high SRTs [8], which implies a longer contact time between the sludge and the OMPs which could enhance their removal.

The conventional combination of biological treatments and activated carbon is normally based on the use of granular activated carbon (GAC) columns as a post-treatment of the secondary effluent to retain the recalcitrant compounds [9]. However, the integration of the sorption and biological processes by means of a direct addition of PAC into the MBR implies some beneficial synergic effects [10], such as the reduction of membrane fouling, as well as the enhancement in the removal efficiencies of conventional pollutants due to the formation of a biofilm onto the activated carbon [11, 12], being the powdered activated carbon (PAC) retained by the membrane.

The aim of this study is to determine the effect of the use of PAC on the removal of 10 OMPs in two MBR configurations using different membranes (UF hollow fiber vs. MF flat sheet), as well as the influence of PAC in physic and microbiological characteristics of the biomasses and in the operation of both biological reactors.

2. MATERIAL AND METHODS

2.1. Experimental set-up

Two membrane biorreactors were started-up and operated at lab scale with two different membrane configurations: microfiltration (MF) flat sheet membrane (Kubota, pore size 0.45 μm) and ultrafiltration (UF) hollow fiber membrane (Zenon ZW-20, pore size 0.045 μm). The reactors were inoculated with 3 gVSS/L of biomass collected from the conventional activated sludge (CAS) reactor of a wastewater treatment plant (WWTP) in the NW of Spain. A hydraulic retention time (HRT) of 24 hours was maintained in both reactors. The flat sheet membrane was operated with a permeate period of 7.5 min and a relaxation time of 1.25 min, while the hollow fiber membrane permeated during 7 min followed by a backwashing of 0.5 min. Four periods can be distinguished: the initial period of 97 days in which the MBRs were operated without PAC (P1) and three additional periods (P2, P3, P4) of 35 days each, at the beginning of which one addition of 250 mg/L of PAC was performed, without purges during the whole operational period (i.e. 750 mg/L of PAC were added in total). A synthetic influent simulating a hospital wastewater was fed continuously to both reactors, which contained sodium acetate (400 mg COD/L), ammonium chloride (35 mg N-NH_4^+/L), monopotassium phosphate (5 mg P-$PO_4^{-3/}$L) and trace elements at a pH of 7.5. These influents were spiked with 10 OMPs belonging to different therapeutic groups at concentrations between 1-40 ppb including: three antiphlogistics (ibuprofen (IBP), naproxen (NPX) and diclofenac (DCF)), four antibiotics (trimethoprim (TMP), sulfamethoxazole (SMX), erythromycin (ERY) and roxithromycin (ROX)), two estrogens (estrone (E1) and ethynilestradiol (EE2)) and one antiepileptic (carbamazepine (CBZ)). The commercial powdered activated carbon (PAC) used was Norit® W35, whit a specific surface area of 875 m^2/g and a iodine number of 850, which was purchased from Cabot Corporation (USA).

2.2. Analytic methods

Influent, mixed liquor and effluent samples were taken twice a week to determine total suspended solids (TSS), volatile suspended solids (VSS), COD, ammonium, nitrite, nitrate, phosphate and turbidity, according to Standard Methods (APHA) [13]. Temperature, dissolved oxygen (DO) and pH were measured daily with a Hach HQ40d multi-parameter digital device. Soluble samples were obtained using 0.45 μm nitrocellulose membrane filters (HA, Millipore). The filterability was measured by the filter test (FT) described by Nurishi et al., [14].

Several sampling campaigns were carried out during seven months to determine MP concentrations in solid and liquid phase by LC/MS/MS. Samples were taken in the influent, mixed liquor and effluent. The method EPA 1964 was used for OMP determination.

3. RESULTS AND DISCUSSION

3.1. Reactors performance

Both reactors were operated along 200 days at ambient temperature (20-22ºC) under aerobic conditions. The overall COD removal and nitrification efficiencies were always above 95% in both reactors, with no significant influence of PAC addition. However, the addition of PAC led to a certain removal of nitrate (35%) which was attributed to nitrate sorption onto the activated carbon [15], as well as to the growth of a biofilm onto the activated carbon surface which creates anoxic zones that enable biological denitrification [16]. In the case of the turbidity, a better performance of the UF MBR was observed (0.55 and 0.32 NTU in the MF and UF permeate, respectively), being the effluent quality better in both reactors after PAC addition (0.4 and 0.25 NTU in the MF and UF permeate, respectively).

3.2. Biomass characterisation

The particle size was measured in both reactors in P1 and P3 and no significant influence of the presence of activated carbon was observed on the average particle size. However, the particle size in the UF MBR was lower than in the MF MBR (77 vs. 42 μm, respectively) which might be the result of the higher aeration intensity in the UF MBR [17].

The settleability, which was followed by the sludge volume index (SVI), was affected by both parameters: the activated carbon addition and the type of membrane. In the case of MF unit a good settleability was observed in all periods of operation (SVI=203 ml/gVSS in P1 and SVI=160 ml/gSSV in P4), while with the UF configuration worse results were determined (SVI=1000 ml/gVSS in P1 and SVI=850 ml/gSSV in P4). This fact is explained by the presence of filamentous bacteria and the lower medium particle size in the UF MBR. An enhancement in the settleability of the sludge in both reactors was observed after PAC addition.

Although a good filterability was observed along P1 in both reactors, as in the case of the settleability, the filterability was enhanced after PAC addition [11, 18] from 17 to 25.5 and 30 mL in the MF MBR and UF MBR, respectively. The fouling rate in the MBR correlates with the accumulation of biopolymer clusters (BPC) in the sludge [19]. Therefore, BPC allows the monitoring of the sludge fouling layer formation on the membrane surface. Although the average value of BPC before PAC addition was low, a diminution was observed after PAC addition from 31 to 14 mg/L in the UF MBR and from 24 to 15 mg/L in the MF MBR, which is in accordance to Ying et al., who reported that permeable PAC filter out microbial cells and colloids [20].

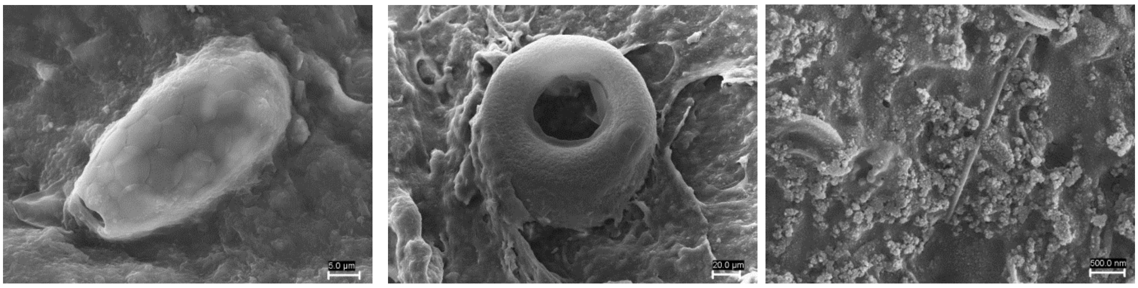

Figure 1. SEM photographs: Euglypha, Arcella and the PAC integrated in the sludge structure

Optical photographs and SEM images of the sludge surface were studied in order to determine the effect of PAC in the sludge structure. Although biomass particle size distribution remained constant after the addition of PAC [21], it was observed that a homogeneous matrix of the PAC and the biomass flocs was formed (Fig. 1, 2), increasing the strength of its structure, as well as allowing the formation of a biofilm [16]. Additionally, the presence of PAC increased the diversity of species present in the sludge which enhances the biotransformation potential of the biomass. For instance, protozoan as *Euglypha* o *Carchesium polypinum*, which are known to enhance the quality of the effluent, were observed, as well as amoebas, as *Arcella* o *Centropyxis* which is related to the improvement of the nitrification (Fig. 1, 2).

Figure 2. Optical photographs: Carchesium polypinum, Centropyxis and the PAC integrated in the sludge structure

3.3. Micropollutants fate

Antibiotics

Along period P1, the average removal efficiency of all the antibiotics was above 70% in the MF MBR, except in the case of TMP (Fig. 3, 4). SMX and ERY can be considered readily biodegradable compounds with a removal efficiency of 80% in both reactors, while 50% of the antibiotic TMP remained stable. No significant differences were observed in terms of removal between the two MBRs, except in the case of ROX (Fig. 3). In the case of this antibiotic, a removal close to 90% was obtained in the UF MBR, while the average removal in the MF MBR was below 70%. As size exclusion is not expected to be significant neither for UF nor MF membranes, the difference between both membranes might be attributed to sorption and/or further biotransformation in the cake layer, which is especially interesting in the case of UF membranes, which retain smaller particles [22].

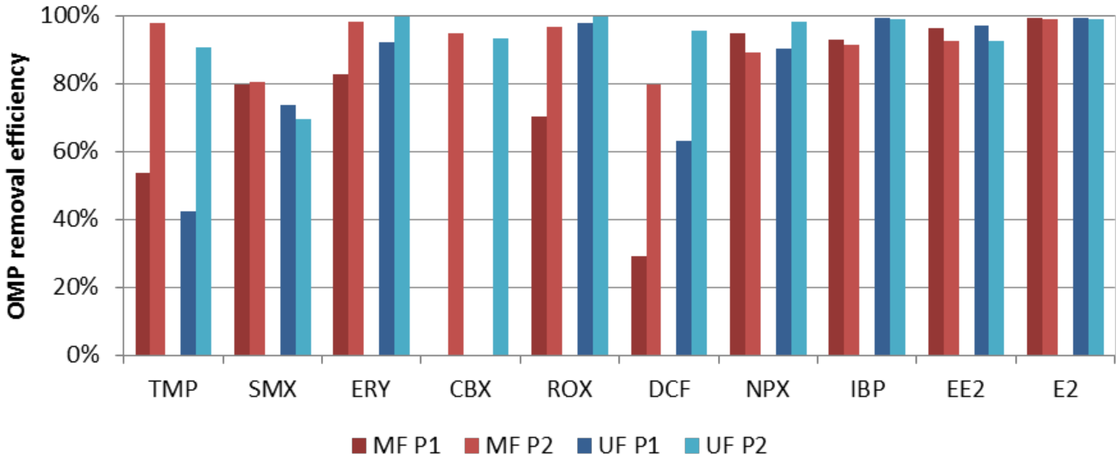

Figure 3. OMPs removal in the MF and UF MBR before PAC addition and 7 days after the first PAC addition

After PAC addition, an enhancement on the ROX, TMP and ERY removal was observed, while SMX removal remained stable in the MF MBR (Fig. 4, 5). In the case of ROX the effect of PAC was not significant in the UF MBR as its removal efficiency due to biotransformation was already above 95 % during P1. The affinity with the PAC is related to the hydrophobicity of the molecule [23, 24], being SMX, with a logD (pH=7) <0.1, the less hydrophobic antibiotic. In the case of TMP a progressive saturation of the PAC was observed which caused a decrease in the removal efficiency with time in the MF MBR, although the operation strategy of performing new PAC additions every 35 d allowed maintaining the efficiencies above 75% during the whole operation period. In the UF MBR the removal of TMP remained stable (around 90%) after PAC addition being no saturation of the PAC observed, which might be related with the higher microbial diversity and the retention of the cake layer and the membrane, as in the case of ROX.

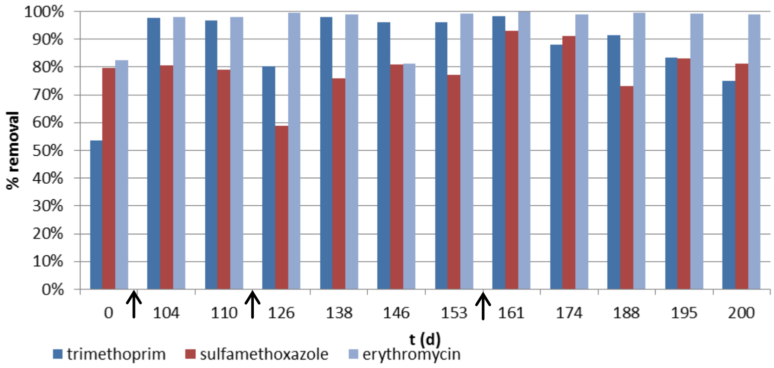

Figure 4. TMP, SMX and ERY removal in the MF MBR (time 0 is a summarize of the removal before PAC addition)

Antiinflammatories

Two behaviours were observed in the case of the antiinflamatories. On one hand, IBP and NPX were readily removed in both reactors (Fig. 5), as previously reported in MBRs and CAS units by Radjenović et al., [25]. No effect of PAC on IBP and NPX removals was observed (Fig. 5) since these compounds are hydrophilic, as SMX [24]. On the other hand, DCF removal efficiency was 60% and 30% in the UF MBR and MF MBR, respectively, before PAC addition (Fig. 3). Its removal increased in both reactors after PAC addition to efficiencies above 80% in both reactors, although the effect of the type of membrane was still visible during the periods P2, P3 and P4. In order to maintain the high efficiencies for DCF, it is essential to periodically replace the PAC due to its progressive saturation observed in both reactors.

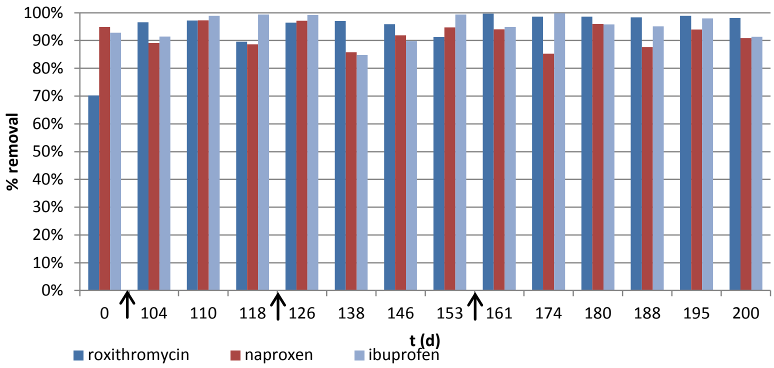

Figure 5. IBP, NPX and ROX removal in the MF MBR (time 0 is a summarize of the removal before PAC addition)

Antiepileptic

Carbamazepine is a recalcitrant compound in biological treatments [26], so the use of physico-chemical processes is necessary for its removal. In the case of the two technologies studied, no removal of CBZ was observed before PAC addition (P1), while removals above 90% were achieved in the beginning of P2 (Fig. 6) because it is a hydrophobic compound with a log D 1.89 at pH= 7 [24]. However as in the case of DCF, CBZ removal diminished with time, meaning that a periodical addition of PAC is necessary to maintain the efficiency of the process. With the strategy carried out in this work (addition of 250 mg/L PAC every 35 days), it was possible to obtain removals above 40% in both reactors during the whole operation. Higher removal efficiencies of CBZ were achieved in the UF MBR compared to the MF MBR, being the effect of saturation more significant in the MF MBR.

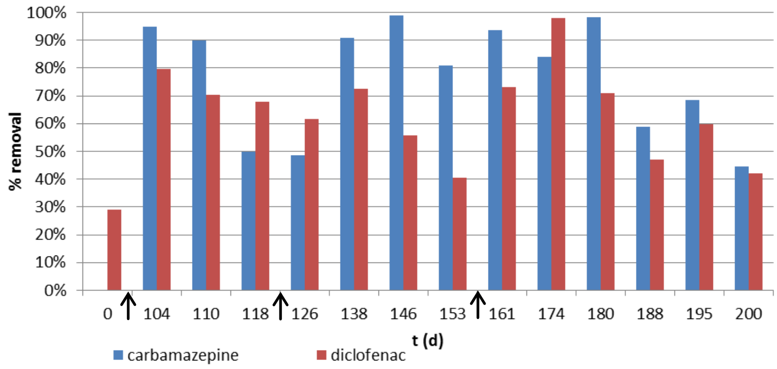

Figure 6. CBZ and DCF removal in the MF MBR (time 0 is a summarize of the removal before PAC addition)

The saturation of the PAC was observed first for DCF compared to CBZ or TMP. This fate is related with the rate of saturation, which is a function of the charge of the compound [9], being the breakthrough observed firstly for the negatively charged compounds, such as DCF or IBP, followed by the neutral charge compounds, such as CBZ, and finally for the positively charged compounds, such as TMP.

The sorption capacity of PAC is correlated with the Freundlich isotherm kinetic constant (k_f) and depends on the type of carbon. A batch test was carried out in order to obtain this parameter for CBZ and IBP and compare the affinity for PSC of both compounds. The trend in the batch test was the same than in the continuous operation of both MBRs, being the k_f in the case of CBZ (1400 $(mg/g)(L/\mu g)^{1/n}$) was much higher than for IBP (142 $(mg/g)(L/\mu g)^{1/n}$).

Hormones

In spite of the high hydrophobicity of the hormones, no effect related to the use of activated carbon was observed in terms of E2 and EE2 removal (Fig. 7) since these substances are readily biodegradable under aerobic conditions [3]. The same behaviour was observed for the two compounds in both reactors, with removal efficiencies remaining stable throughout all the periods of operation.

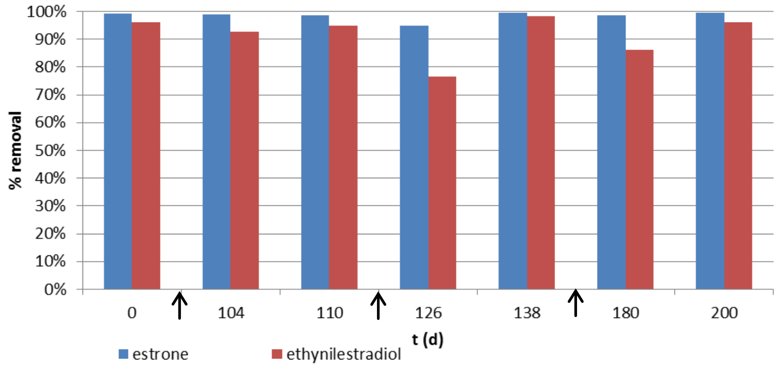

Figure 7. E1 and EE2 removal in the MF MBR (time 0 is a summarize of the removal before PAC addition)

3.4. Micropollutants fate in solid phase

In order to follow the saturation of the PAC and its influence on OMPs removal, the amount of micropollutants sorbed on the solid phase was followed in P1 and P2 (before and after the first PAC addition). OMPs concentration in the solid phase was constant in P1, as was observed by Fernandez-Fontaina et al. in flocculent biomass [27]. However after PAC addition (P2), a continuous increase in the solid phase was observed due to the accumulation of OMPs onto the PAC (Fig. 8). The amount of OMPs in the solid phase were observed to increase until the saturation of the PAC is reached, that is, until the equilibrium between the solid and liquid phases is achieved.

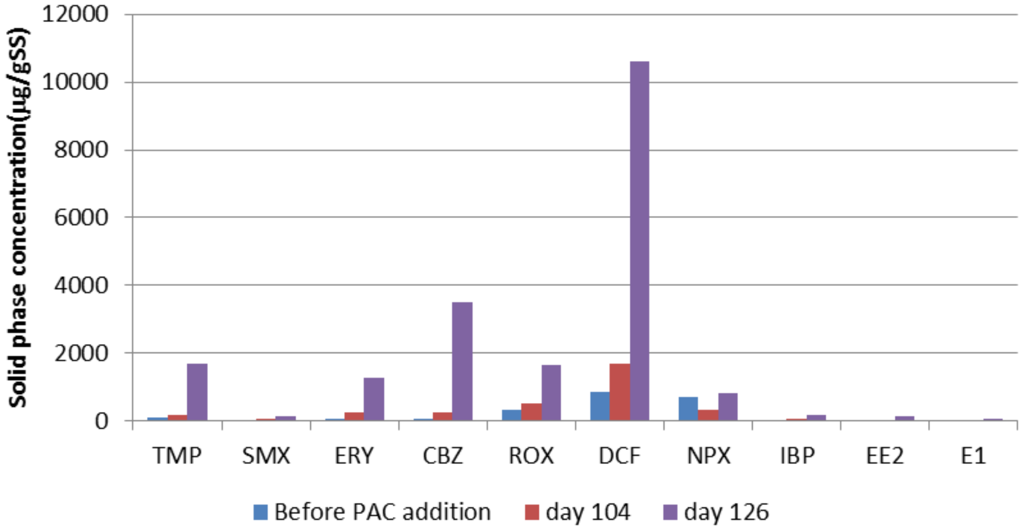

Figure 8. OMPs concentration is solid phase

The maximum concentration achieved in the solid phase of each OMPs has been correlated with the influence of PAC in their removal efficiencies. Therefore, the highest concentration in the solid phase was obtained in the case of the compounds with high affinity to the PAC, such as DCF and CBZ, while the concentration of SMX or IBP in the solid phase was negligible.

CONCLUSIONS

- Organic matter degradation and nitrification above 95% were achieved in both MBRs operating at aerobic conditions, independently of the PAC addition. However, a decrease in nitrate concentration was observed upon the operation with PAC, which could be related to denitrification occurring in the biofilm formed onto PAC particles or direct sorption of nitrate onto the PAC.
- The addition of PAC exerted a positive influence on the effluent quality in terms of turbidity, as well as on the membrane fouling.
- The best results in terms of turbidity, settleability and particle size were obtained in the UF MBR.
- The properties of the sludge, such as filterability, settleability and microbial diversity, were enhanced after PAC addition.
- NPX, IBP and hormones were already almost completely removed by biotransformation, while to guarantee good efficiencies for the retention of TMP, CBZ and DZP the addition of PAC was essential.
- ERY and ROX were removed partially by biotrasnformation and by sorption onto the PAC.
- The removal by PAC was related to the hydrophobicity of the compound, while the saturation of PAC was observed first in the negatively charged compounds, such as DCF.
- Only in the case of DCF and ROX an influence of the type of membrane on their removal was observed.

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