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Fate of pharmaceuticals and cosmetic ingredients during the operation of a MBR treating sewage

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Abstract

Municipal wastewaters contain many organic compounds, among them active ingredients as pharmaceuticals and cosmetic products, which are used in large quantities throughout the world. Most of these compounds come either from domestic sewage or from hospital or industrial discharges and enter municipal sewage treatment plants (STPs). Modern STPs can effectively accomplish carbon and nitrogen removal, as well as microbial pollution control. However, these plants have not been specifically designed to remove these trace polluting compounds.

The dynamics of 12 micropollutants in a membrane bioreactor (MBR) have been studied when treating synthetic sewage. These selected substances correspond to different therapeutic groups such as antiepileptics (carbamazepine), tranquillisers (diazepam), analgesics (ibuprofen, naproxen, diclofenac), antibiotics (roxithromycin, erythromycin, sulfamethoxazole, trimethoprim) and three polycyclic musk fragrances (galaxolide, tonalide, celestolide). These micropollutants are spiked into the synthetic wastewater fed to the reactor at environmentally relevant concentrations ranging from 10 to 20 μg/L.

Taking into account previous researches, the MBR is operated at a sludge retention time (SRT) of 44–72 days, since a high value of this parameter is considered as crucial for the removal of these micropollutants. Under these conditions, different fates are observed depending on pharmaceutical and personal care products (PPCPs) characteristics. Hydrophobic organic substances, like musk fragrances, are partially sorbed onto the sludge. This explains the partial removal observed in the reactor, with an overall efficiency around 50%. Other substances, like the anti-inflammatories ibuprofen and naproxen, are not sorbed but they are eliminated almost completely (98% and 84% of removal, respectively). On the other hand, substances like carbamazepine or diclofenac show a recalcitrant character and their elimination from the effluent is very limited, below 9%.

Keywords: Pharmaceuticals; Synthetic musks; Micropollutants; Urban wastewater; Membrane bioreactors; Ultrafiltration; SRT

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1. Introduction

There is a rising concern about the occurrence and persistence of active substances such as the ingredients of pharmaceutical and personal care products (PPCPs) in the aquatic environment, due to their specific characteristics. High worldwide consumption of pharmaceuticals provides a continuous release of the present substances or their metabolites into the environment, mainly via human or animal excretions [1]. Most of them show a recalcitrant behaviour and are not easily removed from wastewaters in sewage treatment plants (STPs) [2,3]. Pharmaceutical compounds are designed to produce a biological activity on human beings or animals. As a result, there are possible side-effects on aquatic ecosystems still not cleared.

Although some studies have shown the toxic potential of several pharmaceutical ingredients, the knowledge in this field is still limited. For example, some synthetic polycyclic musks are considered as potential endocrine disruptors. Estrogenic effects and antiestrogenic activities have been observed even at very low concentrations. Besides, they are lipophilic and consequently may bioaccumulate in biota [4]. In this sense, recent research showed high concentrations of the fragrance galaxolide (up to 4100 ng/L) and other polycyclic musks in blood plasma of healthy adults [5]. In the case of antibiotics, its widespread use is closely linked with the rise of antibiotic resistance, and diseases that were considered eradicated, such as tuberculosis, are now making a comeback [6].

Recent improvements on chemical analytical methodologies have enabled to detect extremely low concentrations of xenobiotics. As a consequence, worldwide studies have been carried out over the last decade reporting concentrations of PPCPs up to several micrograms per litre in surface or groundwater, rivers, streams and sewage. STPs and hospital effluents were identified as important emission sources of PPCPs into the aquatic environment [1–3,7–9]. Micropollutants pass along the units of STPs with different fate, according to their structure and physico-chemical properties, thus several works have been carried out in order to characterise their overall removal efficiency. Regarding the biological degradation of pharmaceutical compounds, musk fragrances and estrogens, a classification scheme based on batch experiments with sewage sludge taken from a STP has been proposed recently. Among 35 different organic micropollutants, only 4 of them were removed in a significant extension [10]. Besides, experiments in lab-scale activated sludge plants were performed in order to find the main operation parameters which could affect PPCPs removal. No complete elimination rates were achieved in any case. Sludge retention time (SRT) and acclimation of the biomass were pointed as key issues to improve removal efficiencies when biological mechanisms are involved [11]. In conclusion, traditional and modern STPs equipped with activated sludge process have not been designed to remove micropollutants efficiently [9]. This is a matter of high concern, as PPCPs can reach water sources used for drinking water production [3]. Therefore, it is important to test new technologies for urban wastewater treatment.

Presently, membrane bioreactors (MBRs) constitute a promising technology in industrial and urban wastewater treatment. Membrane filtration retains suspended solids that are usually washed out in biological reactors coupled with secondary settlers. As a result, it is feasible to work with high biomass concentrations and to control SRT accurately, obtaining a high quality permeate-effluent [12]. High solids concentration inside the reactor might improve removal rates of lipophilic substances following a mechanism of sorption onto the sludge, and a longer SRT could favour the slowly growing bacteria, improving this way the biodiversity of microorganisms inside the MBR [6], and achieving a complete adaptation to the presence of PPCPs [13].

This work is focussed on the fate of 12 micropollutants as well as the assessment of their potential toxic effects exerted on activated sludge in a submerged MBR. This system was operated with synthetic sewage at long SRT and high biomass concentrations. MBR efficiency in terms of ammonia and COD removal were also tested, as well as membrane performance by measuring transmembrane pressure (TMP).

2. Materials and methods

2.1. Membrane bioreactor

The MBR–used in this work (Fig. 1) is a pilot-scale unit with a liquid capacity of 220 L and equipped with a Zenon ZW-10 submerged hollow fibre membrane module. Its main characteristics are an average pore size of 0.04 μm and a nominal surface area of 0.9 m^2. This unit comprises an extended aeration device with air diffusers located on the bottom header, where air is supplied by a blower in order to ensure the required level of oxygen for biological oxidation and to facilitate membrane scouring. Besides, a 22 L tank is available to receive permeate, which is finally discharged by gravity. The membrane module is connected to a micro gear pump capable of reversing speed, serving both as permeate and backwash pump. The filtration cycle, i.e., permeate production time and backwash duration is controlled with a timing device. The chosen cycle was adjusted to 15 min of permeate production followed by 45 s of backwashing.

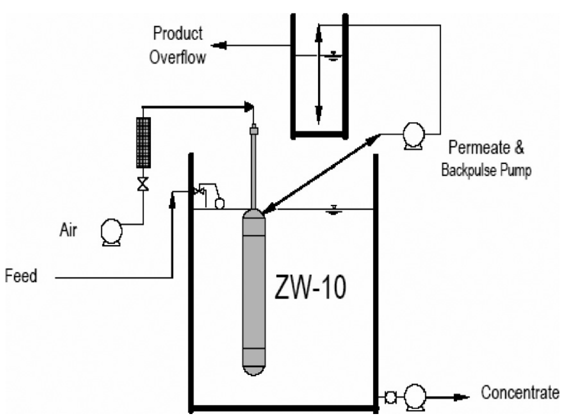

Fig. 1. Flow sheet of the MBR.

MBR was inoculated with 2.5 g VSS/L of biomass obtained from a full-scale conventional activated sludge (CAS) which treats industrial wastewater from fish-meal and fish-oil production. Temperature and pH are monitored but not adjusted to selected values in order to maintain the same operating conditions as in full-scale plants, varying in the range of 18–24°C and 7.5–8.5, respectively. Devices for the measurement of dissolved oxygen, established at 2–3 ppm, and a Bourdon-Type manometer to monitor the TMP are available.

The influent, which simulates domestic sewage, is stored in a stainless steel tank prior to the feeding to the pilot plant. The average composition is shown in Table 1. A solution of several trace metals which serve as nutrients for biomass is also added. PPCPs were spiked into the influent in order to ensure environmentally relevant concentrations inside the MBR, as the following concentrations (ppb): carbamazepine (20), diazepam (20), galaxolide (20), tonalide (20), celestolide (20), ibuprofen (10), naproxen (10), diclofenac (10), sulfamethoxazole (10), erithromycin (10), trimethoprim (10) and roxithromycin (10).

Table 1
Average composition of the synthetic feed

Compound	Concentration (mg/L)
$AcNa \cdot 3H_2O$	490
NH_4Cl	150
Na_2HPO_4	25
KH_2PO_4	12
$NaHCO_3$	200

2.2. Analytical methods

Samples were taken regularly from the feeding and permeate. These samples were analysed for conventional physical–chemical parameters (soluble COD, solid content, nitrogen) following standard methods [14].

The soluble content of the fragrances, anti-inflammatories, carbamazepine and diazepam was determined after solid-phase extraction (SPE) of 300 mL samples using 60 mg OASIS HLB cartridges (Waters, Milford, MA, USA). Meclofenamic acid and dihydrocarbamazepine were added to the samples as surrogate standards. All compounds were quantitatively eluted from the cartridge using 3 mL of ethyl acetate. This extract was then divided into two fractions: one of them was used for the direct determination of the soluble content of carbamazepine, diazepam and fragrances; the second one was employed for the determination of the anti-inflammatory species. In this case compounds were silylated previously to their gas chromatographic separation according to a previously published method [15]. In both cases, GC/MS was used to determine the concentration of the investigated compounds in the SPE extract. Antibiotics were determined by LC-MS after an enrichment step using an SPE method of 500 mL samples with addition of surrogate standards. Steps of conditioning and loading were carried out automatically. After loading, the cartridges were dried with nitrogen gas during 20 min. To elute the cartridges, MeOH at pH = 2 was used.

Samples were collected along different days during a week in order to get an integrated sample. For this purpose, glassware was always used for sampling in order to avoid sorption. Samples were mixed, stored in aluminium containers and kept at 4°C prior to the analysis.

3. Results and discussion

3.1. Operational parameters

The MBR was started with the inoculation of nitrifying sludge and the feeding of domestic synthetic wastewater. During a start-up period of 2 months, the hydraulic retention time (HRT) was maintained at 1 day, and stable conditions were obtained. The reactor showed excellent performance in terms of soluble COD and ammonia removal (mainly due to nitrification), with elimination rates up to 95% and 99%, respectively. In a second step, the HRT was lowered to 12 h maintaining the same efficiencies (Fig. 2a).

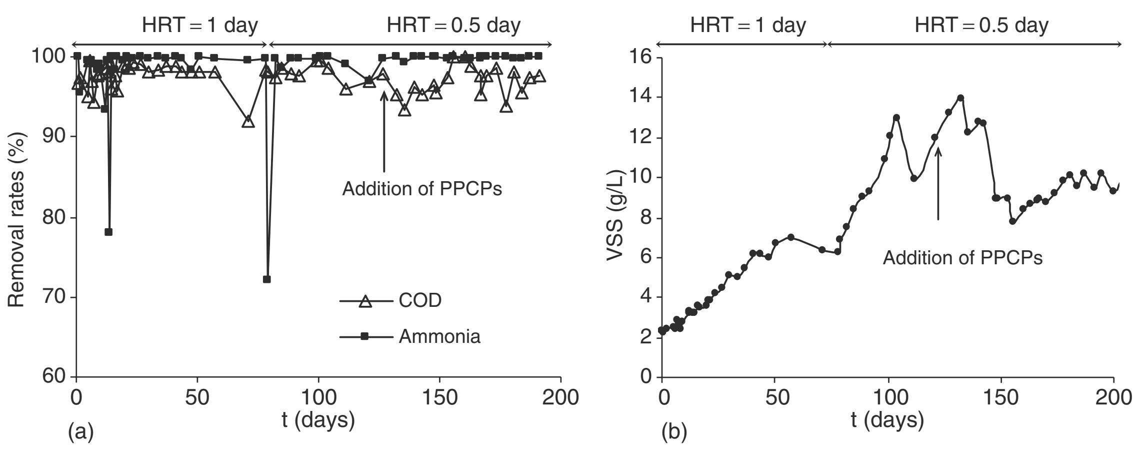

Fig. 2. Influence of HRT and PPCPs addition on (a) ammonia and COD removal and (b) biomass growth.

Fig. 2b also shows the growing of biomass content from 2.5 to 12 g VSS/L in 4 months. Limitations in the oxygen transfer efficiency were observed. The system was purged regularly in order to keep a biomass concentration of 10 g SSV/L, which is compatible with the maintenance of 2 mg/L of dissolved oxygen. The SRT under these conditions amounted to 72 days.

TMP was also monitored (Fig. 3) during the whole operation. A significant increase was observed when the applied HRT was reduced, but remained in optimum values for membrane maintenance. No chemical or mechanical cleaning was required during these experiments.

3.2. PPCPs removal

After the start-up period, PPCPs were spiked into the synthetic feeding. No inhibitory effects were observed in biomass growth, COD degradation and nitrification, as can be deducted from Fig. 2. The reactor was maintained under these conditions for two additional months, in order to allow the biomass to acclimate to the presence of PPCPs. When a SRT of 72 days was achieved, samples of feeding and permeate were collected and analysed.

Fig. 4 shows the measured concentration of PPCPs in the feeding and permeate. Strong

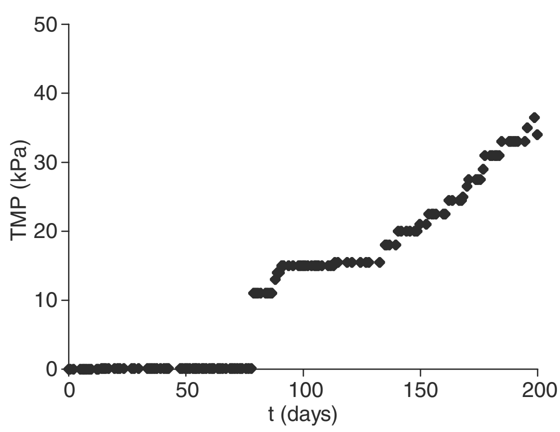

Fig. 3. Evolution of TMP during the operation period.

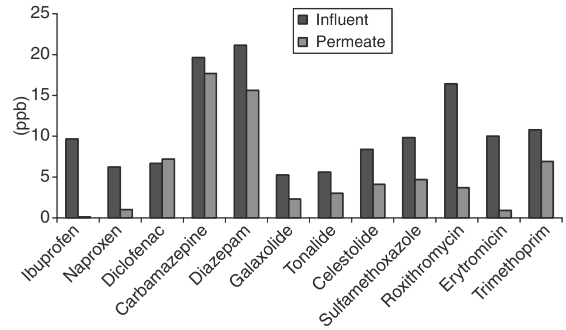

Fig. 4. Concentrations of selected PPCPs in the MBR influent and permeate.

variations among the different compounds and therapeutic groups are detected, ranging from diclofenac, whose concentration was maintained in the same level in the permeate and feeding, up to ibuprofen, that was almost undetected in the outflow. These eliminations observed are expected to be mainly due to mechanisms of sorption and biological degradation on the sludge. Besides, lipophilic compounds might also be sorbed on the surface of the membrane. Size-exclusion cannot be considered since the molecular weight cut-off of the considered substances is too low for an ultrafiltration membrane.

The acidic pharmaceuticals naproxen and especially ibuprofen were almost completely removed, with elimination rates up to 84% and 98%, respectively. These results are similar or slightly higher than other previously reported in STPs equipped with conventional systems [7,8]. For example, Suárez et al. [11] reported elimination rates of 68% and 82%, respectively, working with a lab-scale activated sludge plant. Kimura et al. [16] found better results for naproxen when working with MBR technology and no clear differences in the case of ibuprofen.

In the case of the tranquilliser diazepam and the antiepileptic carbamazepine, elimination data are also in good agreement with results found in previous studies. For both substances, poor removal rates were measured (9% for carbamazepine and 26% for diazepam). Joss et al. [10] studied PPCPs biodegradation in batch experiments with sludge taken from MBR and CAS systems. Results obtained for these substances were less than 20% of biological removal for both compounds. Again, removal rates measured in this MBR system were slightly higher. Thus, it can be concluded that they are not easily degraded by biological treatment in a MBR, even working at a high SRT. Similarly, diclofenac was not removed at any significant extent. Kimura et al. [16] also reported low elimination rates for diclofenac comparing MBR with other systems, suggesting that the presence of chlorine on its structure might enhance its persistence.

The results obtained for the removal of fragrances were around 46%–56%. These values are not very high taking into account the outstanding lipophilic character of these substances and thus their affinity to be sorbed onto the sludge. Carballa et al. [9] found removal rates around 40% for musk fragrances during the primary treatment of an urban STP, where no biodegradation mechanisms are expected. Taking into account the removal achieved in the biological reactor, the average removal efficiencies obtained in the whole treatment were in the range of 80%–85%. On the other hand, the works carried out by Clara et al. [13] with a MBR pilot plant and several STPs treating real sewage indicate surprisingly a high percentage of biodegradation operating with 27 days of SRT. The difference between these results and those presented in this work might be attributed to a better acclimation achieved under these conditions, since our MBR has been operated with PPCPs only during 2 months. Moreover, the sludges used as inoculum were not previously acclimated. Further analysis will be carried out in order to check this possibility.

In the case of antibiotics, macrolides roxithromycin and erythromycin were removed at a high extent (77% and 91%, respectively), and sulfamethoxazole was half-removed (52%). On the other hand, trimethoprim showed low elimination rates (36%). Göbel et al. [6] compared the performance of different wastewater treatment technologies, including a MBR operated at different SRT. Results from both works are similar for erythromycin and sulfamethoxazole when working with sludge age ranging from 60 to 80 days, but substantial differences were found in the case of trimethoprim, where removal rates up to 85% were measured. Again, more acclimation time might be needed for this substance.

4. Conclusions

In this work, a MBR was operated in order to evaluate its performance in terms of PPCPs removal treating synthetic sewage. Removal rates observed for COD and ammonia were always above 95%. Changes in operational parameters such as HRT did not affect the quality of the permeate, and the spike of PPCPs into the feeding had no effect on the performance of this system. SRTs in the range of 44–72 days were maintained, with VSS of 10 g/L. The ultrafiltration membrane showed excellent performance, although TMP was increased progressively, due to membrane fouling.

Ibuprofen, naproxen and erythromycin were almost completely removed from the influent, with elimination rates slightly better than other works previously reported, possibly due to the high SRT achieved. A partial removal was observed with sulfamethoxazole and musk fragrances. On the other hand, carbamazepine, diazepam, diclofenac and trimethoprim remained at high concentrations in the permeate.

According to the short period that this system has been treating PPCPs in the influent (2 months) and the source of the inoculum used (without any previous contact with these micropollutants), it is expected that acclimation phenomena might occur and lead to better results in the coming months.

Acknowledgements

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