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Fate of pharmaceuticals and their transformation products in integrated membrane systems for wastewater reclamation

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ABSTRACT

The removal of pharmaceuticals (PhACs) present in urban wastewater by membrane bioreactors (MBRs) followed by reverse osmosis (RO) or nanofiltration (NF) membranes has been frequently addressed in the literature. However, data regarding the removal of their main human metabolites and transformation products (TPs) is still scarce. In this study, the presence of 13 PhACs and 20 of their metabolites and TPs was monitored during 2 consecutive years in the different treatment steps of urban raw wastewater (sewer, primary treatment, MBR and RO/NF). Rejection of the selected contaminants when using low pressure NF membranes (NF-90) or RO membranes (ESPA 2) after the MBR step was also investigated. The analgesic acetaminophen, which was found at the highest concentrations in the sewer and influent samples (18–74 $\mu g\,L^{-1}$) over the two experimental periods, was fully eliminated during MBR treatment. Those PhACs that were only partially removed after the MBR, were almost completely removed (> 99%) by the RO membrane working under different process conditions. At a similar average permeate fluxes ($18\,L\,m^{-2}\,h^{-1}$), the NF membrane showed high removal efficiencies (> 90%) for all of the PhACs and their metabolites, though lower than those achieved by the RO membrane. When the flux of the NF90 membrane was increased to $30\,L\,m^{-2}\,h^{-1}$ (while still operating at a feed pressure lower than the RO membrane at $18\,L\,m^{-2}\,h^{-1}$) the performance of the membrane increased, achieving 98% rejection of PhACs.

1. Introduction

As human health is increasingly depending on pharmaceutical products, the scientific community together with environmental and public health authorities have made a significant effort in understanding the fate of pharmaceutically active compounds (PhACs) both through engineered urban wastewater treatment processes as well as in the natural environment. This has been reflected in the high number of scientific publications devoted to this subject in the last two decades. On the contrary, modification of legal regulations up to now is basically inexistent. However, water scarcity and water reuse have become essential issues in water resource management worldwide, always considering the conservation of aquatic ecosystems as a final goal and main driver of the involvement of the scientific community.

So far, most of the research carried out regarding the fate of PhACs through MBR processes has mainly focused on the study of parent compounds, neglecting their metabolites. Only recently, the environmental presence of human metabolites and different transformation products (TPs) of these PhACs has been included within the scope of removal efficiency studies of different wastewater treatments technologies [1–3]. It should be considered that, once released onto the environment, these metabolites and TPs can be both innocuous [4], but also nocuous and even more toxic than the original substance against different aquatic organisms. Furthermore, the coexistence of the original drugs with these metabolites and TPs could lead to additive, antagonistic and/or synergetic effects which are hard to predict and that should be investigated. For instance, the assessment of the ecotoxicity of the photoproducts of the anti-inflammatory diclofenac (DCF) or naproxen has provided the evidence that acute and chronic toxicity can be greater for these photoproducts than for the parent compounds [1].

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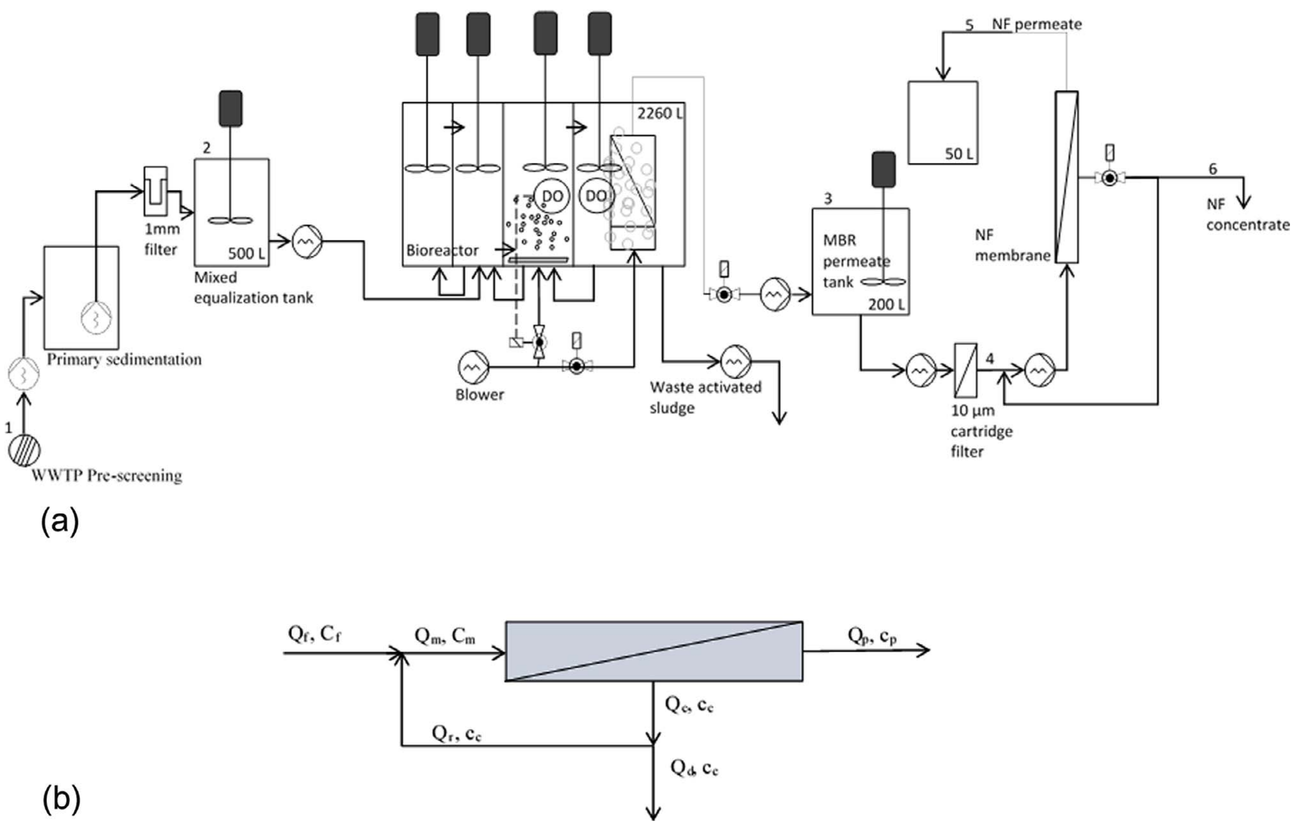

Fig. 1. (a) Scheme of the MBR-RO/NF pilot plant showing the sampling points: (1) sewer, (2) influent tank, (3) MBR permeate tank, (4) RO/NF feed, (5) RO/NF permeate and (6) RO/NF concentrate and (b) detailed scheme of the membrane system showing the inlet flow (Q) and concentration (C) of the system feed (f), membrane feed (m), permeate (p), concentrate (c), recirculation (r) and drain (d).

Effective concentration values (EC_{50}) obtained after 15 min assays for the antibiotic sulfapyridine (SPY) and its acetylated metabolite, N^4-acetylsulfapyridine (acSPY), demonstrated that the marine bacteria *Vibrio fischeri* was more sensitive to the presence of the metabolite than to the original drug, and according the EU legislation (Directive 93/67/EEC), the former could be categorized as toxic [2].

On the other hand, it has been demonstrated that conventional activated sludge (CAS) treatment processes in waste water treatment plants (WWTPs) do not adequately remove many of the most commonly used PhACs such as DCF, the anticonvulsant carbamazepine (CBZ) or the antibiotic sulfamethoxazole (SMX) [5,6]. Different studies have demonstrated that membrane bioreactors (MBRs) are capable of removing moderately biodegradable and hydrophobic trace organic pollutants more efficiently than CAS treatments processes [7]. During the last years, MBR technology has become an accepted alternative to CAS processes for municipal wastewater treatment, not only regarding PhACs removal but also the overall water quality [8]. Furthermore, the combination of MBR technology followed by the reverse osmosis (RO) process or nanofiltration (NF) is typically used when high quality product water is required for planned potable reuse or when a reduction in salinity is required for irrigation reuse applications [9]. Different works have demonstrated that both membrane processes alone yield high rejection rates for PhACs usually > 80% [10,11]. Various studies have shown that the combination of the MBR process with RO or NF results in higher removal rates for a wide range of PhACs, present in the wastewater (feed stream) to be treated; these are concentrated into a stream of water known as the concentrate stream (also known as the reject or brine stream) [12], leaving a permeate stream (also known as the product stream) with very low concentrations of the contaminants of interest. A recent work by Dolar et al. [13], which was carried in the same WWTP as this work, showed that removal rates for 22 PhACs by a Ropur TR70-4021-HF-RO membrane were above 99%.

A number of factors affect the removal of PhACs by the MBR-RO/NF process [14] which are not always properly considered when reporting removal efficiencies of the membrane processes involved. These include the membrane type (affecting molecular weight cut-off, surface morphology, hydrophobicity and charge), membrane fouling, membrane process parameters (membrane recovery and average permeate flux) and feed water quality including temperature, pH and concentration, particularly due to urban activity and weather related events (such as rain periods). Furthermore, a number of studies have also shown that NF and ultralow pressure RO membranes are not perfect barriers for various micropollutants including endocrine disruptors and some PhACs such as SMX or CBZ [15,16]. Both membranes had a negative surface charge in the pH range used in the study [17,18], whereas the hydrophobic nature of a membrane is typically characterised by its contact angle. Alturki et al. [7] measured the contact angle of both the NF90 and ESPA2 membranes for virgin membranes (1 h use) and after 25 h of use. Although both virgin membranes could be classified as hydrophilic (contact angle of 42.5° for NF90 and 60.63° for ESPA2), the measurements consistently showed that following filtration of MBR effluent, there was an increase in the membrane surface hydrophobicity after 25 h of use (contact angle of 77.6° for NF90 and 85.9° for ESPA2). In our case, since the membranes were in operation for a significantly longer period of time, the membranes are expected to be moderately hydrophobic.

It should also be considered that significant savings could be made in terms of energy reduction and chemicals and concentrate disposal costs when using NF in the place of RO membranes [19]. NF membranes are found in similar spiral wound configurations to RO membranes, making the switch during routine membrane replacement a feasible option to make.

Taking all this information into consideration, the objective of the present study is to evaluate and compare MBR-RO and MBR-NF in terms