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Nanofiltration for wastewater reuse: Counteractive effects of fouling and matrice on the rejection of pharmaceutical active compounds

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ABSTRACT

This study investigates the influence of fouling and solute–solute interactions on the rejection of four pharmaceutical active compounds (PhACs) by two commercial nanofiltration (NF) membranes for a water reuse purpose. Membrane bioreactor effluent was filtered and modification of membrane surface was fully characterized (roughness, MWCO, contact angle, zeta potential...). It was shown that polysaccharides and humic acid were the major compounds adsorbed on the membrane which causes the flux decline. Flux decline was more severe for NF-90 than NF-270 due to a higher roughness and hydrophobicity and smaller pore size. This fouling layer modified the membrane surface properties like hydrophobicity and charge. PhACs were then filtered in Milli-Q water, using virgin and pre-fouled membranes, or in real effluent, using virgin membranes, so as to identify basic phenomena involved in their retention. It appeared that changes in membrane surface affected transport and retention of salts and PhACs in comparison with unfouled membranes, especially for NF-270. The comparison between filtration of PhACs in Milli-Q water or real effluent evidenced the effect of solute–solute interactions on retention. For all tested PhACs, rejection by NF-270 was improved when filtering spiked MBR effluent in comparison with spiked Milli-Q. The influence of the matrice was less pronounced for the NF-90. Two counteractive mechanisms appeared to be involved in the rejection of pharmaceuticals by a loose-NF like NF-270: adsorption onto macromolecules in the surrounding matrice resulting in increased rejection and the presence of a fouling layer leading to decrease in rejection. Finally, NF-90 could be a possible alternative to the systematic reverse osmosis scheme and allowed great rejection capacities and cost saving.

1. Introduction

Extreme scarcity of freshwater resources for drinking water use in many areas of the world creates a severe situation that must be addressed. Establishing a method of supplying stable, sufficient, and safe drinking water to communities is imperative. Possibly the best solution to overcome this lack of water is the process of recycling wastewater for drinking water use. While it assists in mitigating the shortage of water, wastewater reuse leads to an important issue, i.e., the water quality being produced which impacts the social acceptability of any wastewater reuse practice. Indeed, water is nowadays most commonly treated to levels that are satisfactory for irrigation or groundwater recharge as unplanned indirect potable reuse of wastewater is a common practice all over the world [1]. Many countries have adopted regulations standards for reclaimed and reused wastewater based on bacterial and bulk parameters inspired by the OMS, Australian EPA or the Californian title 22 [2]. While regulations standards on reclaimed/reused wastewater ensure a reliable and safe quality, there is still a lack of regulatory standards in regards with emerging pollutants as pharmaceutical active compounds (PhACs), endocrine disruptors and others synthetic organics while they are also discharged from municipal wastewater treatment plants (WWTP) and have to be removed from water. For example, beta-blockers, anti-inflammatories, anti-epileptic and X-ray contrast media exhibited removal efficiencies below 20% in conventional WWTP [3]. Therefore, development and application of appropriate treatment technologies to meet the requirements of water quality are critical to the success of wastewater reuse.

Membrane filtration processes such as nanofiltration (NF) and reverse osmosis (RO) have been recognized as effective means of providing a safe and reliable source of supply water by reuse for both drinking water and non-drinking water purposes [4,5]. Nonetheless, NF option for wastewater reclamation is still mainly confined to laboratory research. To avoid systematic use of RO, thus minimize operating costs, NF treatment could be preferred if a complete removal of ions is not necessary as an effective removal

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of organic pollutants is expected [5–7]. However, rejection mechanisms by NF (steric effect, electrostatic repulsion, hydrophobic interactions, partitioning and diffusion) are highly dependent on membrane properties, physico-chemical properties of solutes and feed water characteristics (ions content, pH, organic matter, etc.) [8]. Natural organic matter (NOM) in natural matrices seems indeed to influence organic trace rejections by two main mechanisms: fouling (or matrice solute-membrane interactions) and matrice solute–solute interactions [9,10].

Membrane fouling by effluent organic matter (EfOM) results in a flux decrease and could increase or decrease solute rejection, depending on the type of solute (ionic, hydrophobic and hydrophilic neutral) in comparison with clean membranes by modification of the membrane surface characteristics and adsorption of trace organics in the fouling layer [11]. Bellona et al. found that non-ionic PhACs (acetaminophen, carbamazepine, bisphenol-A, etc.) rejections by NF were found to be negatively impacted by EfOM fouling and authors assigned this result to cake-enhanced polarization concentration (CECP) [12]. This phenomenon suggested by Elimelech and co-workers [13–15] is the hindrance of solute diffusion from the vicinity of the membrane surface back to the bulk solution due to the presence of a porous cake layer. This would be responsible of the increase of organic compounds concentration at the surface of the membrane and in permeate and thus of the alteration of membrane rejection. In the same trend, Agenson and Urase [16] suggested that the adsorption and diffusion of larger target compounds (highly rejected by virgin membranes) across fouled NF membranes (by activated sludge or leachate) would limit their transport away from the membrane resulting in decreased rejection. On the contrary, Zazouli et al. [17] found an increase rejection for large drugs whereas smallest substance with moderate polarity (i.e., acetaminophen) presented a lower rejection due to the polymeric fouling layer (alginate as model compound). Hajibabania et al. [11], observed that the hydrophilic non-ionic and ionic solute rejections are lower when membranes are fouled with humic acids and even more with alginates. No influence of type of foulants was observed on hydrophobic solutes retention. Same trends were found by Nghiem et al. [18]. Plakas et al. [19] reported that the deposition of humic substances on NF membranes resulted in a decrease in herbicide rejection for a certain degree of fouling after which rejection increased due to a deposit of a denser fouling layer which enhanced compound adsorption. Finally, Yangali-Quintanilla et al. [20] found that NOM fouling improves rejection of most of the targeted neutral compounds and presents no significant impact on ionic PhACs rejection. Moreover, it appears that in addition of the type of solutes and foulants, the MWCO or pore size of the membrane determine the beneficial or negative influence of the fouling on PhACs rejection through promoting the establishment of pore restriction or CECP [17,20,21]. The understanding of the fouling effect requires both a comprehensive characterization of the fouled membrane and of the physicochemical properties of the selected PhACs.

The second mechanism of organic matter (OM) action on organic compounds rejection is via compounds binding. The formation of compound-OM complexes involves higher rejection due to a higher size and negative charge compared to the compound alone [10,22,23]. It was observed that the presence of OM (natural OM or model organic compounds) enhanced removal of estrogens [24], PhACs [9] and pesticides [25] via solute–solute interactions. The adsorption of PhACs onto organic macromolecules depends of the solutes and type of macromolecules which could be very different [11]. Besides, calcium content seems to play a key role in both fouling and PhACs retention in NF application. The competition between divalent cations and PhACs to form complexes with OM would result in lower PhACs rejections in presence of divalent cations [10,23]. Many studies reported that in presence of calcium, the carboxylic groups of humic substances and polysaccharids are neutralized which promote a denser fouling [26,27]. However, above a critical calcium concentration, complexation can also occur in the solution (bulk complexation), leading to the formation of aggregates and a lower organic fouling [28].

Conflicting results about effects of fouling and secondary effluent matrice itself on micropollutant rejection suggest a need for more research about interactions between commercial membranes and most encountered organic micropollutants. Moreover, many studies are performed using synthetic water with model macromolecules as well as virgin membranes and little is known about rejection of nanofiltration membranes under fouled conditions representative of full-scale operation. Thus, rejection measurement in specific effluent to be treated needs to be performed in order to provide an accurate estimate of how the membrane will perform at full-scale. Furthermore, the research focused on characterization of either EfOM in secondary effluents or membrane foulants in order to investigate effects of EfOM characteristics on membrane properties is relatively rare.

In this way, the aim of this paper is to investigate the effect of fouling and effluent matrice by analyzing rejection of PhACs during nanofiltration of a real wastewater effluent so as to promote NF in place of RO as an effective barrier against PhACs for a reuse application. The present study focuses on four selected pharmaceuticals, namely, acetaminophen (ACT), atenolol (ATL), carbamazepine (CBZ) and diatrizoic acid (DTZ) which represent four important drug categories found in WWTP effluent. ACT, unlike others, is reduced during conventional biologic waste water treatment (activated sludge), however, μg/L order concentration still remains in urban effluent due to a large consumption. CBZ, ATL and DTZ are practically not degraded in WWTP and are also detected at micrograms order [3]. The secondary effluent composition and fouled membrane surfaces were rigorously characterized using conventional and advanced characterization analyses according to physicochemical properties, in terms of molecular weight distribution (high performance size exclusion chromatography (HPSEC)) and spectral characteristics (3-D fluorescence excitation-emission matrixes (3D EEM)). Rejection was measured on virgin and pre-fouled (secondary effluent) membranes with milli-Q water and on dynamically fouled membranes with secondary effluent matrice. The fully characterization of the feed water and fouled membrane surface should permit to understand interactions between (i) the fouled membrane surface and PhACs (ii) the matrice and PhACs.

2. Materials and methods

2.1. Organic solutes and pharmaceutical compounds selection

The organic compounds employed in the study could be divided into four groups, membrane characterization compounds, (slightly) hydrophobic and hydrophilic non-ionic organic contaminants and ionic organic contaminants (Table 1). Due to their hydrophilic ($\log K_{OW} \ll 2$) and neutral nature, the characterization compounds are not expected to interact with the membrane polymer and their removal is expected to be primarily due to steric interactions which allow the characterization of the sieving properties of a membrane by MWCO and pore radius (r_P) determination. The four selected PhACs (ACT, CBZ, ATL and DTZ) present differences in terms of molecular weight (from 151.2 g mol^{-1} for ACT to 631.9 g mol^{-1} for DTZ), hydrophobicity (from 0.10 ± 0.28 for ATL to 2.67 ± 0.38 for CBZ) and shape that are anticipated to influence membrane rejection. This wide range of properties should help in better understanding basic mechanism of rejection. All the pharmaceuticals compounds were purchased at Sigma–Aldrich. Stokes radii r_S of all organic compounds were determined using the Stokes–Einstein equation: