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Assessing potential of nanofiltration and reverse osmosis for removal of toxic pharmaceuticals from water

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ABSTRACT

Concern about organic micropollutants, which are present in the environment at trace concentrations (ng L^{-1}–μg L^{-1}) is related to the adverse effects to organisms exposed to these substances. Pharmaceutically Active Compounds (PhCAs) may be present in natural waters and usually cannot be removed or degraded by conventional water treatment processes. For this reason, treatment techniques, such as Nanofiltration (NF) and Reverse Osmosis (RO) are recommended to improve their removal. In this context, the present study aims to evaluate the removal of five Non-steroidal anti-inflammatory drugs (NSAIDs), analgesics and anti-pyretic: acetaminophen, ibuprofen, dipyrone, diclofenac, and caffeine by NF and RO process. NF90 and BW30 membranes were characterized by scanning electron microscopic (SEM), contact angle and zeta potential. Retention of PhACs was evaluated considering pH feed solution and operating pressure. Results indicated that NF90 membrane was efficient to reach over 88% rejection for some selected PhACs. Best results were obtained at 20 bar and pH 5 with more than 90% of rejection. For nonionic compounds acetaminophen and caffeine, exclusion by size is the main mechanism for rejection by NF90 membrane, whereas for anionic compounds ibuprofen, dipyrone, and diclofenac, electrical exclusion predominated at pH 5 and 7. Rejection results with NF90 membrane show that hydrophobicity has an important role due to the adsorption on the membrane surface. Conversely, lower rejections for hydrophilic compounds were observed due to the adsorption/diffusion mechanisms, both in NF90 and RO at pH 5.

1. Introduction

Human health is increasingly dependent on pharmaceutical products. Also, water scarcity and water reuse have become essential issues in water resource management worldwide, always considering the conservation of natural water system as a final goal and primary driver of the scientific community. As a result, they along with environmental and public health authorities have been making a significant effort in order to understand the fate of pharmaceutically active compounds (PhACs) both in engineered urban wastewater treatment processes and in the natural environment. This has been reflected in the high number of scientific articles devoted to this subject in the last two decades. On the other hand, there are no modification of legal regulations yet [1].

Although usually at very low concentrations compared to other the organic compounds involved, there is a considerable group of emerging organic micropollutants that have been detected in raw wastewaters of various natures, in surface and groundwaters, in drinking water sources and in some cases in treated waters as well. This group includes pesticides, pharmaceutical products (PhACs), personal hygiene products and several other industrial pollutants [2]. The highest possibility of their occurrence is in industrial wastewater or sanitary sewage due to inefficient treatment or even direct discharge without prior treatment, which does not comply with legislation. Socioeconomic and other cultural factors related to the indiscriminate marketing, consumption, improper disposal and destination of medicines in the countries also contribute negatively for the spread of these compounds in waters and wastewaters [3].

Removal of some PhACs in conventional treatment stations is almost

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impossible due to several factors, including low volatility, different hydrophobicity, complex structures, recalcitrance, very low concentrations, influence of microorganisms and interaction with other solutes and separation media. These compounds remain dissolved in urban effluents or may connect to sludge which later is released into the surrounding aquatic environment and soil; in other words, a lot of water-soluble substances can be transported and distributed more easily in the water cycle, causing impact on the environment and human beings [4,5].

There is still little knowledge about the impact that can be created by this exposure and what are the long-term effects on human health and environment [6]. Nevertheless, some consequences are already known: a) antibiotics have been blamed for the development of bacterial resistance in the environment; b) endocrine disruptors affect the reproductive and endocrine system of aquatic organisms, inducing genotoxocity, acute and chronic toxicity, for example causing the feminization of male fish that live in contaminated rivers [7], and c) anti-inflammatory drug diclofenac induces chronic toxic effects on the fish kidneys after exposure at the dose of 0.001 mg L^{-1} [3].

Emerging micropollutants from anthropogenic origin are one of the primary pollutant sources. Particularly speaking of pharmaceuticals, they are persistent compounds that present high potential for bioaccumulation, low biodegradability and concentration in the range of ng L^{-1} to μg L^{-1} in aquatic environments. These facts indicate that conventional treatment technologies do not entirely remove them, which leads to their subsequent release into the aquatic environment through discharge and/or reuse applications. Therefore, there is a need to investigate alternative technologies for their removal in municipal wastewater treatment [2,8].

Due to this concern, different physicochemical processes have been proposed as a tertiary treatment for effluents from water treatment plants. Among them are membrane separation processes, which have proved ability to remove these pollutants, achieving high removal rates for pharmaceutical compounds. Membrane separation processes (MSP) have been increasingly used in the treatment of reused water, drinking water and water for industrial purpose and their use has increased exceptionally due to technological, economic and environmental needs [8].

Nanofiltration (NF) membranes have come a long way since their beginning in the late 1980s. NF is a MSP that uses pressure gradient as the driving force. With properties between those of ultrafiltration (UF) and reverse osmosis (RO) membranes, NF membranes have attracted interest due to their versatility as a separation process. Their pore size is typically in the order of 1 nm, which corresponds to a molecular weight cut-off (MWCO) in the range of 100–5000 Da. Therefore, this type of process may seem interesting for organic micropollutants removal. NF membranes also exhibit a moderate level of charge due to the dissociation of surface functional groups or the adsorption of charged solutes. For example, polymeric NF membranes contain ionizable groups such as carboxylic and sulfonic acid groups which result in charged surfaces in the presence of an aqueous feed solution. NF membranes operate with no phase change and typically at low pressures, reaching high rejections of multivalent inorganic salts and small organic molecules. This makes the separation process highly competitive regarding selectivity and cost-benefit when compared to traditional separations. Thus, NF has found wide range of application across of industrial sectors including water and wastewater treatment, pharmaceutical and biotechnological processes, and food engineering to name a few. As the use of NF technology becomes increasingly widespread, efforts will increase for more effective separation projects with the ultimate aim of reducing costs [6,9,10].

Although RO has a capacity of separation similar to that of NF, with high solute rejection rates and, in some cases, being a concurrent process, it has a higher operating cost than NF, usually, because of the need of high operating pressure (to overcome lower permeability) and a greater fixed investment. Membranes used in RO processes do not have pores or convective flow, and the separation occurs by the sorption-diffusion mechanism in which species permeate and are solubilized in the material that composes the membrane and, then, diffuses through their thickness moved by a gradient of chemical potential until the desorption step on the permeate side [9].

Some studies in literature report the employment of NF and RO membranes for the removal of different endocrine disruptors and PhACs in real matrices [11–16]. According of these studies, high removals of compounds can be obtained by the NF and RO membranes. Many studies investigate the removal of organic contaminants using NF and RO in real matrices spiked with PhACs (treated municipal wastewaters, treated water from drinking water plant, surface waters, among others), and this is the main limitation to study the contribution of each compound separately for the process performance, because of the influence from the other compounds and from organic matter existing in these matrices [10,12–14,17–21].

In the last decades, attention was given to the interactions between contaminants, membranes and components in the water that impact the rejection of solutes with different geometries and physicochemical properties [9]. Membranes can remove PhACs either by size exclusion, electrostatic repulsion, hydrophobic interaction or adsorption [10,12,14,19,22–24]. It is noteworthy that the interaction of the solute with water, as well as the nature of the polymer responsible for the separation, are also fundamental factors for the efficiency of the process, thus it is necessary to know the properties and characteristics of the polymers that constitute the polymer matrix so that the membrane separation process can be optimized [5]. In addition, membrane operating conditions, such as feed rate, flow, recovery, pressure and temperature, are fundamental for the operation and rejection values [25].

Size exclusion is always considered the most important mechanism of rejection. Often, the main rejections are expected from membranes that have molecular weight cut off (MWCO), for organic contaminants with a higher molecular mass than the MWCO. Molecular mass is not a correct prediction when the molecules are charged or have a high hydrophobicity [26].

Verliefde et al. [10] evaluated the rejection efficiency of twenty pharmaceutical compounds with different electrostatic charges of NF membranes. Removal of the pharmaceutical compounds was partially determined by exclusion by molecular weight, but the charge of the compounds also appeared to play an essential role in the rejection of neutral solutes. Ozaki and Li [24] studied the influence of molecular mass on the retention of organic and inorganic compounds on reverse osmosis membrane. The study concluded that polar compounds, either positively or negatively charged, are more effectively removed compared to less polar or neutral charged compounds because they interact with the membrane surface.

The understanding of these interactions is essential for the improvement and selection of suitable membranes, as well as for the development of tools that will allow the prediction of process efficiency for a wide spectrum of micropollutants [9]. However, these effects have not been properly discussed in the literature, mainly regarding the evaluation of membrane performance at different pH and zeta potential analyzes throughout the pH range.

To date, the intrinsic relationship between the physiochemical properties of PhCAs at trace levels, the solution pH and the membrane retention behavior remains poorly understood. Thus, this study aimed to evaluate the rejection performance by NF and RO membranes for the following PhCAs – dipyrone, paracetamol, diclofenac, ibuprofen and caffeine – and to elucidate their removal mechanisms in different pH conditions. These compounds represent different pharmaceutical groups with quite distinct physicochemical properties and are commonly detected in aquatic samples. Paracetamol (*N*-4-hydroxyphenylacetamide) is one of the most commonly used non-narcotic analgesic and antipyretic in the world. Diclofenac (2,4,6-dichlorophenyl-aminobenzeneacetic acid) has antirheumatic and anti-inflammatory use. Ibuprofen is a derivative of 3-phenoxybenzeneacetic