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Rejection of pharmaceuticals by forward osmosis membranes

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HIGHLIGHTS

- Rejection of pharmaceuticals by FO membranes was systematically investigated.
- Rejection efficiency was compared between CTA membranes and TFC membranes.
- TFC membranes exhibited superior performance compared to CTA membranes.
- Hydrophobic interaction governs rejection by CTA membranes in acidic condition.
- At pH 8, charge repulsion and size exclusion attribute to rejection.

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ABSTRACT

Rejection of four pharmaceutical compounds, carbamazepine, diclofenac, ibuprofen and naproxen, by forward osmosis (FO) membranes was investigated in this study. For the first time, the rejection efficiency of the pharmaceutical compounds was compared between commercial cellulose triacetate (CTA) based membranes and thin film composite (TFC) polyamide based membranes. The rejection behavior was related to membrane interfacial properties, physicochemical characteristics of the pharmaceutical molecules and feed solution pH. TFC polyamide membranes exhibited excellent overall performance, with high water flux, excellent pH stability and great rejection of all pharmaceuticals investigated (>94%). For commercial CTA based FO membranes, hydrophobic interaction between the compounds and membranes exhibited strong influence on their rejection under acidic conditions. The pharmaceuticals rejection was well correlated to their hydrophobicity ($\log D$). Under alkaline conditions, both electrostatic repulsion and size exclusion contributed to the removal of deprotonated molecules. The pharmaceuticals rejection by CTA-HW membrane at pH 8 followed the order: diclofenac (99%) > carbamazepine (95%) > ibuprofen (93%) ≈ naproxen (93%). These results can be important for FO membrane synthesis, modification and their application in water purification.

1. Introduction

In the last few years, increasing attention has been paid to the widespread occurrence of pharmaceutical compounds in aquatic environment at concentrations ranging from ng/L to μg/L levels [1]. In their original or partially metabolized forms, pharmaceuticals can enter the environment via the discharge of wastewater effluent, disposal of unused or expired products and landfill leachate [2,3]. Because pharmaceuticals are designed to be biologically active, unintended exposure to them may adversely affect non-target organisms and thus cause unexpected physiological consequences [2]. For example, diclofenac was found to cause renal lesions in the kidneys and alterations of the gills in rainbow trout [4]. Moreover, long-term risks of ingestion of mixed pharmaceuticals at trace levels are poorly understood [5]. In light of the potential risk to humans and wildlife, implementing advanced treatment technologies such as membrane processes is essential to remove pharmaceutical compounds from treated effluent before entering the aquatic environment as well as water reuse.

Removal of trace organic compounds by reverse osmosis (RO) and nanofiltration (NF) membranes has previously been studied [2,6–8]. The rejection mechanisms of organic compounds by RO/NF membranes include size exclusion, electrostatic repulsion and hydrophobic interactions between solute and membrane [9]. The rejection of organic compounds is reported to be governed by their physicochemical properties (molecular size, charge, hydrophobicity and polarity), membrane characteristics (material, surface charge and porosity) and feed solution chemistry (pH and ionic composition) [2,7–10]. Although RO/NF membrane processes can be powerful options to remove pharmaceutical compounds

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Table 1
Physico-chemical properties of selected pharmaceuticals.

Compound	Acronym	MW [g/mol]	pK_a	$\log K_{ow}$	$\log D$			Reference
					pH 3	pH 6	pH 8	
Carbamazepine	CMZ	236	n.a.	2.45	2.45	2.45	2.45	[28]
Diclofenac	DCF	296	4.08	4.51	4.48	2.58	0.59	[28]
Ibuprofen	IBU	206	4.47	3.97	3.96	2.43	0.44	[28]
Naproxen	NPX	230	4.2	3.18	3.15	1.37	−0.62	[29]

n.a., not applicable.

from water of impaired quality, these pressure-driven membrane processes are limited by membrane fouling and high energy consumption [11]. Therefore, alternative membrane processes with low fouling potential and energy consumption as well as high rejection is under development.

Forward osmosis (FO) is a membrane process in which water flows across a semi-permeable membrane from a feed solution of lower osmotic pressure to a draw solution of higher osmotic pressure [12]. It offers many advantages over pressure-driven membrane processes such as lower fouling potential, simplicity, and high recovery [13]. In recent years, FO is attracting increasing interests for its potential applications in wastewater reclamation [14–16], concentration of landfill leachate [12] and seawater desalination [17]. For these applications, fundamental understanding of the trace contaminants removal is very important. However, studies on the rejection of trace contaminants such as endocrine disrupting chemicals (EDCs) and pharmaceuticals by forward osmosis membrane processes are rather scarce [18–21]. Moreover, the intricate relationship between the physicochemical properties of trace contaminants, membrane characteristics, and FO membrane separation behavior is not well understood.

To date, the synthesis of high performance FO membrane is still in the early stage. The only commercial FO membranes are made from cellulose triacetate (CTA) which has a relatively narrow range of pH tolerance as well as relatively low pure water permeability and solute rejection [22–24]. This limits their application in water purification. Meanwhile, significant progresses have been achieved in developing high performance TFC FO membranes that exhibit higher water permeability and better selectivity compared to commercial CTA based FO membranes [25–27]. As there are considerable differences between CTA and TFC polyamide membranes, it is worthwhile to compare the rejection efficiency of trace contaminants between the two types of FO membranes. However, to the best knowledge of the authors, the removal of trace contaminants by TFC polyamide FO membranes has not been reported.

This study aims to investigate the initial removal of four pharmaceutical compounds from aqueous solution by two commercial CTA membranes and two hand-cast TFC polyamide membranes. Rejection behavior was related to the physicochemical properties of the compounds and membranes. In addition, the effect of feed solution pH on the pharmaceuticals rejection was examined for one CTA membrane and one TFC membrane in order to evaluate the influence of membrane materials on the FO performance. On the basis of these results, the fundamental mechanisms governing pharmaceuticals rejection by FO membranes were elucidated and discussed.

2. Materials and methods

2.1. Chemicals and solution chemistry

Four pharmaceuticals, namely, carbamazepine, diclofenac, ibuprofen and naproxen, were examined in this study. They were selected on the basis of their environmental relevance [28,29]. All pharmaceuticals were purchased from Sigma–Aldrich (Saint Louis, MO) and were reported to be of 98% purity or higher. Table 1 summarizes their physicochemical properties including molecular weight (MW), dissociation constant (pK_a), partitioning coefficient ($\log K_{ow}$) and apparent partitioning coefficient ($\log D$), which takes into account the speciation of the compound at various pH levels [28].

In all FO experiments, the feed solution contained 10 mM NaCl and 250 μg/L of each pharmaceutical compound. The concentrations of the pharmaceutical compounds used in this study are higher than their environmentally relevant concentrations [20]. This is because the effective concentration of solutes permeating through the membrane can be significantly diluted by draw solution and thus the pharmaceutical compounds in the draw solution are difficult to be detected. For experiments with variable pH, the pH of feed solution was adjusted by adding 0.1 M HCl or NaOH solution. Unless otherwise specified, the draw solution was composed of 2 M NaCl.

2.2. FO membranes

Two commercial FO membranes were provided by Hydration Technologies, Inc. (Albany, OR). Both membranes were made of CTA supported by embedded polyester screen mesh. They are designated as CTA-HW (membrane coupon cut from a Hydrowell® FO module) and CTA-W (flat membrane coupon with a woven support), respectively, according to our previous study [27]. In addition, two hand-cast TFC FO membranes (TFC-1 and TFC-2 [27]) were evaluated. These membranes had a cross-linked aromatic polyamide active layer on a polysulfone support layer. The TFC polyamide membranes were prepared via two steps: (1) a phase inversion step to form the membrane substrate, and (2) an interfacial polymerization step to form the active rejection layer. Details about their preparation conditions have been fully described by Wei et al. [27]. During all FO experiments, the membrane was oriented with its active layer facing the feed solution.

The pure water permeability coefficient (A), NaCl permeability coefficient (B_s), and glucose rejection of the FO membranes were evaluated in a pressurized crossflow filtration test unit (i.e. under RO testing mode). The effective membrane area was 42 cm^2, and crossflow velocity was fixed at 23.2 cm/s. Feed water temperature was maintained at 24 ± 0.5 °C. The A value was determined by measuring the water flux over a range of applied pressures (60–200 psi). Using a feed solution containing 10 mM NaCl and 50 mg/L glucose, rejection of NaCl and glucose was determined based on feed and permeate measurements of conductivity (Ultrameter II, Myron L Company, CA) and total organic carbon (TOC-VCSH, Shimadzu, Japan), respectively. Glucose rejection was used as an indicator for the molecular weight cut-off (MWCO) of the FO membranes. B_s value was determined based on classical solution-diffusion theory [30]:

$$R = \frac{1}{1 + (B/(A(\Delta P - \Delta\pi)))} \quad (1)$$