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Relating solute properties of contaminants of emerging concern and their rejection by forward osmosis membrane

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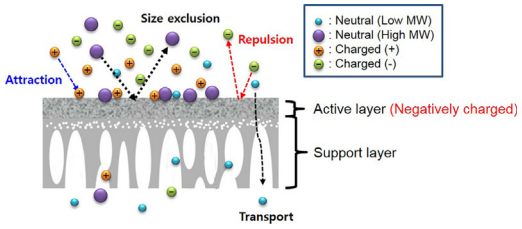
HIGHLIGHTS

- Molecular weight is the most significant factor in the rejection of neutral CECs.
- Rejection of negatively charged CECs is highest due to the electrostatic repulsion.
- Hydrophobicity of CECs is strongly correlated with the adsorption.

GRAPHICAL ABSTRACT



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ABSTRACT

To elucidate the transport of emerging contaminants (CECs) in forward osmosis (FO) membrane process according to their solute properties, the rejections of CECs with various molecular weight, octanol/water partition coefficient (log *K*ow), and dissociation constant (pK_a) were investigated. Among 12 selected CECs, negatively charged CECs exhibited the highest rejection efficiency than neutral or positively charged CECs due to the electrostatic repulsion between negatively charged CECs and membrane surfaces as well as diffusional hindrance by reversely transported salts from draw stream. The statistical analysis showed that the molecular weight was strongly correlated with the rejection of neutral CECs by size exclusion. Moreover, the correlation between adsorption and log *K*ow value of neutral CECs was observed due to the hydrophobic interaction. Positively charged CECs exhibited higher adsorption, but lower rejection than the negatively charged CECs due to the locally increased concentration by adsorption, and subsequent migration in FO membrane.

1. Introduction

Water scarcity is one of the major global issues; population growth, climate change, and pollution have accelerated water scarcity and restrict the availability of water relative to demand. Production of clean water from wastewater or seawater would provide many technical and economic benefits (Shannon et al., 2008). However, the occurrence of contaminants of emerging concern (CECs) in wastewater effluents and water bodies (levels of ng/L to μg/L) is a major obstacle for water reuse. CECs can persist in wastewater effluent because conventional wastewater treatment plants have not been specifically designed to remove CECs (Bolong et al., 2009). Therefore, many CECs have been analyzed in aquatic environments, threatening aquatic ecosystems and human health (Luo et al., 2014).

Several membrane processes that could provide a more efficient barrier against CECs have been explored (Abtahi et al., 2018; Arriaga et al., 2016; Rodriguez-Mozaz et al., 2015). Nanofiltration (NF) and reverse osmosis (RO) membranes have been mainly studied for CEC rejection (Doederer et al., 2014; Jin et al., 2010; Yüksel et al., 2013). The fundamental rejection mechanisms in NF/RO membrane processes are primarily governed by size exclusion, electrostatic repulsion, and hydrophobic interactions (adsorption) (Bellona et al., 2004). More specifically, CECs rejection depends on many factors, including solute

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properties (e.g., molecular weight (MW), solubility, hydrophobicity, and charge), membrane characteristics (e.g., permeability, surface potential, and hydrophobicity), aquatic chemistry (e.g., pH and temperature), and operating conditions (e.g., flux, transmembrane pressure, and recovery) (Madsen, 2014; Ruengruehan et al., 2016a). Although NF/RO membrane processes can be attractive options to control CECs in low-quality water, these high-pressure-driven membrane processes are limited by their high energy consumption and accelerated fouling propensity (Greenlee et al., 2009). Therefore, alternative membrane processes that can provide a high rejection with a low fouling potential and low energy consumption are required.

Forward osmosis (FO) is a novel membrane process with potential in advanced water and wastewater treatment (Cath et al., 2006). In the FO process, the absence of applied hydraulic pressure could reduce operational and energy costs, and provide a better fouling control than high-pressure-driven membrane processes due to physically reversible fouling layer (Lee et al., 2010; Mi and Elimelech, 2010). These advantages make the FO process a promising technology for advanced pretreatment when combined with other membrane-based technologies (e.g., RO, NF, membrane distillation, and electro dialysis) (Chekli et al., 2016). In hybrid FO systems, CECs in the feed side are first subjected to rejection by the FO membrane; then, a subsequent process is used to concentrate the draw solution and produce freshwater, thereby providing a dual barrier for CECs (Choi et al., 2017). Therefore, it is important to elucidate the rejection and transport of CECs during the FO process.

CECs transport and rejection by FO membranes have been reported in previous studies. Xie et al. (2012) compared rejection behaviors of three CECs in FO and RO membranes; an osmotic gradient (FO mode) provided higher rejections than a pressure gradient (RO mode). Jin et al. (2012) explored the rejection performance of a commercially available FO thin-film composite (TFC) membrane, and >94% of pharmaceuticals were rejected by the polyamide FO membrane. Madsen et al. (2015) reported that an aquaporin FO membrane provided rejections above 97% for selected trace organics.

Although these studies have shown the great potential of CECs rejection by an FO membrane, the current understanding of the rejection mechanisms in the FO process is limited. Moreover, there is few study on the rejection of CECs by their physico-chemical properties in FO processes. Therefore, a complete understanding of the rejection mechanism of CECs by FO membrane is still a challenging issue.

To elucidate the relation between the solute properties of CECs and their rejections by the FO membrane, this study examined the rejection of 12 selected CECs with a wide range of physico-chemical properties in FO processes. The adsorption of the CECs onto the FO membrane was also quantified and correlated with physico-chemical properties of CECs.

2. Materials and methods

2.1. Membrane

A commercially available TFC FO membrane (Toray Chemical, Korea) was used in this study. The TFC FO membrane has an asymmetric structure that consists of a selective polyamide active layer formed by interfacial polymerization on top of a polysulfone porous substrate. Prior to use, the membrane coupons were soaked in deionized water and stored at 4 °C. More details on the membrane properties can be found elsewhere (Fagkaew et al., 2017; Ruengruehan et al., 2016a)

2.2. Model CECs

Twelve CECs that have been frequently detected in secondary treated effluent (Verlicchi et al., 2012; Xie et al., 2014) were selected in this investigation. They were categorized according to their physico-chemical properties (e.g., molecular weight; MW, charge, and hydrophobicity) as provided in Table 1. All CECs were purchased as analytical grades (Sigma Aldrich, USA), and stock solutions were prepared with the concentration of 1 g/L, and used within one month.

2.3. FO system and operational condition

A laboratory-scale FO system consisting of a cross-flow membrane cell with an effective membrane area of 20.15 cm^2 was used (Fig. S1). The flow rates of the feed and draw solutions were kept constant at 702 mL/min (corresponding to a cross-flow velocity of 15 cm/s) using a gear pump (Longer Precision Pump, China). The initial volumes of the feed and draw solutions were 2 L and 4 L, respectively, and the weight of feed solution were recorded using a computer to calculate the permeate water flux. In the feed, the CECs stock solutions were diluted to be 100 μg/L using an electrolyte solution (10 mM NaCl and 1 mM $NaHCO_3$) to simulate the ionic strength of typical secondary effluents, and the draw solution contained 0.5 M NaCl. The concentrations of the selected CECs in this study are higher than normally detected in real wastewater effluents (Yang et al., 2017). This is because the proposed concentration (100 μg/L) was low enough to simulate adsorption interactions between membranes and CECs in real conditions. The pH of feed and draw solutions were adjusted to 7 ± 0.2 using HCl (1 M) or NaOH (1 M), and the temperature of the feed and draw solutions was kept at 21 ± 0.5 °C using a temperature control unit (Jeio Tech, Korea). The experiment was terminated after 3 h operation when 200 mL of feed water were permeated through FO membrane (10% recovery). Samples (100 mL) were taken from the feed and draw solutions before and after the experiments to measure the rejection of CECs and mass balance of each CEC.

The CECs rejection is calculated from:

$$R\ (\%) = \left(1 - \frac{DF \times C_{ds(f)}}{C_{fs(i)}}\right) \times 100 \quad (1)$$

where $C_{ds(f)}$ is the final CECs concentration in the draw solution, $C_{fs(i)}$ is the initial CECs concentration in the feed solution, and DF is the dilution factor (DF) defined by the ratio of the final volume of the draw solution and the initial volume of the feed solution.

The mass of CECs adsorbed to the membrane was calculated as follows:

$$m_{membrane} = m_{fs(i)} - m_{ds(f)} - m_{fs(f)} \quad (2)$$

where $m_{membrane}$ is the mass of CECs adsorbed to the membrane, $m_{fs(i)}$ is the initial mass of CECs in the feed solution, $m_{ds(f)}$ is the final mass of CECs in the draw solution, and $m_{fs(f)}$ is the final mass of CECs in the feed solution.

Table 1
Physico-chemical properties of the selected contaminants of emerging concern (CECs).

Compounds (ID)	pK_a	MW (g/mol)	log K_{OW}[a]	Class
Metronidazole (MTR)	2.6	171	−0.10	Antibiotic
Phenazone (PHZ)	1.4	188	0.38	Anti-inflammatory
Sulfamethoxazole (SFZ)	5.2	253	0.68	Antibiotic
Diclofenac (DIC)	4.2	296	4.51	Anti-inflammatory
Bezafibrate (BZF)	3.3	362	4.25	Fibrate drug
Amitriptyline (ATT)	9.2	277	4.92	Antidepressants
Trimethoprim (TMP)	7.0	290	0.91	Antibiotic
Acetaminophen (ACT)	9.3	151	0.46	Analgesic
Caffeine (CFF)	14.0	194	−0.07	Stimulant
Carbamazepine (CBZ)	13.9	236	2.45	Anticonvulsant
Linuron (LNR)	12.1	249	3.20	Herbicide
Triclosan (TCS)	7.8	289	4.76	Biocides

[a] Logarithm of octanol/water partition coefficient.