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Nanofiltration of pharmaceutically active and endocrine disrupting compounds as a function of compound interactions with DOM fractions and cations in natural water

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ABSTRACT

Nanofiltration (NF) of seventeen pharmaceutically active (PhAC) and endocrine disrupting compounds (EDCs), representing a wide range of physicochemical properties, was investigated using both laboratory-prepared (Milli Q®) and natural waters. While previous studies have probed compound removal by membranes pre-fouled with model foulants, and the impact of natural water colloidal materials, this study examined the impact of compound interactions with key organic matter fraction(s), in the absence of colloidal and suspended particles. Lake Ontario water, a Great Lakes' source of drinking water, was pretreated using ultrafiltration to remove colloidal particles but retain organic matter. Additionally, the concentration of cations in the water matrix was varied. Experiments were conducted at a recovery (50%) comparable to a full-scale system. PhAC/EDC rejection from Milli Q® water increased as a function of molecular weight and molecular volume, but significantly decreased with increasing compound hydrophobicity. Dissolved organic matter (DOM) fractions were found to interact preferentially with neutral PhAC/EDCs, causing increased rejection, presumably due to enhanced size exclusion of compound-humic substance (HS) pseudo-complexes arising from dipole–dipole interactions. Increased cation concentration resulted in decreased removal of the neutral compounds; presumably due to reduced HS interaction sites. The rejection of specific ionic compounds was influenced by both size and charge effects of the compound-HS complexes.

1. Introduction

Trace concentrations (ng/L) of pharmaceutically active compounds (PhACs), endocrine disrupting compounds (EDCs), and other emerging organic contaminants have been detected in surface water bodies around the globe [1–4]. While conventional water treatment has limitations in removing PhACs and EDCs [5,6], membrane treatment, particularly nanofiltration (NF) and reverse osmosis (RO) have been demonstrated as effective barriers to these compounds [7–9]. Many studies [9–11] have shown that the rejection of trace organics is governed by compound physicochemical properties including molecular weight (MW), molecular geometry, charge, hydrophobicity/hydrophilicity, and membrane properties such as molecular weight cut-off (MWCO), surface charge, morphology, porosity, and hydrophobicity. Fewer studies have examined micropollutant rejection as a function of the interactions between compounds and membrane surfaces, especially those modified as a result of fouling. Increased micropollutant rejection has been attributed to enhanced electrostatic repulsion [12], membrane pore restriction [13], and an additional hindrance layer [14], whereas decreased rejection of some organics was hypothesized to be driven by restricted back diffusion [11] and enhanced concentration polarization due to foulant deposition [14].

Most researchers have attempted to delineate rejection mechanisms as influenced by solute–membrane (clean and/or fouled) interactions, while few have focused on the impact of solute interactions with source water components such as natural organic matter (NOM) and cations [15–17]. Following an investigation on NF retention of selected herbicides in the presence of model organic matter and/or calcium ions, Plakas et al. [17] suggested that pseudo-complexes were formed with humic and fulvic acids, resulting in higher rejection when compared to deionized water. In a similar study, an increase in observed estrone rejection was believed to be due to the formation of estrone–humic acid (HA) macromolecules, which were retained along with HA due to size exclusion and charge repulsion [16]. While investigating the impact of NOM and cations on EDC/PhAC removal by nanofiltration, Comerton et al. [15] demonstrated increased compound rejection in the presence of Suwannee River NOM, but they did not observe

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any significant influence of cations spiked into laboratory-prepared waters. Comerton et al. [15] also reported a significant decrease in rejection due to increased cation concentration in natural waters; however, the specific impact of organic matter, decoupled from that of colloidal particles coexisting in the waters, was not investigated.

The observations of past research are mainly based on model foulants. Investigations of the composition of representative water matrices are required in order to derive practical conclusions for drinking water production from surface waters. Sadmani et al. [18] investigated the explicit impact of natural water colloidal particles, independently from dissolved NOM, and confirmed that colloidal particles indigenous to a typical surface water matrix negatively impact nanofiltration of specific PhAC/EDCs. The influence of solute interaction with indigenous organic matter fractions (independently from colloidal particles) on NF rejection remains to be examined. Organic matter in natural waters is a heterogeneous mixture of humic and fulvic acids, proteins, and carbohydrates [19], and needs further investigation to determine which fractions interact with organic micropollutants and other natural water components, ultimately influencing compound rejection when using membranes.

This study investigated the rejection of seventeen PhACs and EDCs, representing a wide range of physicochemical properties, via nanofiltration from a laboratory-prepared water and representative surface waters. The primary objective was to determine the influence of compound interactions with major organic matter fraction(s) and cations occurring in natural waters on the rejection of PhAC/EDCs when using nanofiltration. Lake Ontario water was pretreated with ultrafiltration (UF) to remove colloidal particles while allowing NOM molecules to pass through, to examine the impact of dissolved organic matter (DOM). Additionally, the concentration of cations in the water matrix was varied to examine the impact of cations on the interactions and rejection mechanisms. Unlike many previous bench-scale studies, rejection experiments in this study were conducted at a high system recovery (50%), which is within the range (30–90%) that is practiced in full-scale systems.

2. Materials and methods

2.1. Selected compounds and properties

The 17 PhACs and EDCs examined were selected to represent various classes of micropollutants that have often been detected in the US and Canadian surface waters [1,2,20,21]. To facilitate the examination of NF rejection mechanisms, they also represent a wide range of physicochemical properties including molecular weight and geometry, hydrophobicity/hydrophilicity, polarity, and charge (Table 1).

2.2. Selected membranes

An ultrafiltration membrane (TriSep UE50, TriSep Corporation, Goleta, CA, USA), offering high specific flux rates (42 L/m^2 h bar) and a tight MWCO (100 kDa), was used to remove colloidal particles from raw Lake Ontario water. Colloidal particles, ubiquitous in natural waters, have characteristic size range of nanometer to sub-micrometer [22] or may include even larger particles [23], and hence, are likely to be efficiently removed by ultrafiltration (pore size = 2–100 nm) [24]. A polyamide nanofiltration (NF) membrane (NE70, NE 4040-70, Saehan-CSM Membranes, Woongjin Chemical America, Inc., CA, USA) was selected for this study. The MWCO of NE70 (350 Da) [25,26] is greater than the MW of the selected PhACs and EDCs (<300 Da). Tighter membranes (MWCO < 300 Da) would have predominantly exhibited steric interactions with the selected compounds. The NE70 membrane was chosen to allow the investigation of altered size and/or charge effects due to compound interactions with organic matter fractions in the bulk water matrices, in addition to interactions with the membrane matrix.

2.3. Water matrices

Lake Ontario water, which represents a Great Lakes source of drinking water for millions of consumers, was selected to serve as a background matrix to examine PhAC/EDC rejection. Trace concentrations (ng/L) of PhACs and EDCs have been detected in municipal wastewater plant effluents discharging to Lake Ontario [19] as well as in locations close to ($\leqslant$500 m) the points of effluent discharge [27]. Lake Ontario water was collected at the intake of Ajax Water Supply Plant (Ajax, Ontario, Canada). None of the PhACs and EDCs examined in this study were detected in the water collected (data not shown). In total, three water matrices were used for PhAC/EDC rejection experiments in this study: (1) Milli Q® water (18.2 MΩ cm @ 25 °C, Millipore (Canada) Ltd.) as a "control" (buffered with 1 mM sodium bicarbonate, pH = 8.1), spiked with cations Ca^{2+}, Mg^{2+}, and Na^+ (as $CaSO_4$, $MgSO_4$, and NaCl, respectively) at approximately the same concentration as Lake Ontario water [15], (2) UF-pretreated Lake Ontario water, and (3) UF-pretreated water with cation concentrations approximately doubled.

2.4. Filtration experimental set-up

Both ultrafiltration pre-treatment and PhAC/EDC rejection experiments using NF membrane were carried out in a bench-scale membrane filtration set-up (Fig. 1). Flat-sheet membrane coupons (19 cm × 14 cm) with 155 cm^2 effective membrane area were placed into stainless steel cross-flow filtration cells (Sepa CF II, Steriltech Corp., Kent, WA, USA). Feedwater contained in a storage tank was transferred to a temperature-controlled (20 ± 1 °C) stainless steel equalization tank (S1) via a stainless steel valveless piston pump (RK-07104-50, Cole-Parmer, Montreal, QC, Canada) with a variable speed drive (RK-07104-31, Cole-Parmer). Thereafter, the water was delivered to the membrane cells using a Hydracell constant flow diaphragm pump (M03SASGSSSPA, Wanner Engineering, Inc., Minneapolis, MN, USA), with a three-phase variable speed motor (FC000404, V.J. Pamensky Canada Inc., Toronto, ON, Canada) and a variable frequency drive (ID15J101-ER, Baldor Electric Co., Fort Smith, AR, USA). The influent flow rate (Q_{in}) and transmembrane pressure were controlled by varying the piston pump speed and controlling a needle valve in the main retentate stream, respectively. The filtration units were run in triplicate to facilitate analyses of statistical significance of experimental results.

2.5. Experimental protocol

To remove colloidal particles, Lake Ontario water was pre-treated with an ultrafiltration membrane (UE50) at a constant flux using the same membrane filtration setup shown in Fig. 1. Prior to PhAC/EDC rejection experiments, a new NE70 membrane coupon was inserted into each filtration unit, cleaned and compacted by filtering Milli-Q® water for 24 h. A mixture of PhACs and EDCs was spiked into the feedwater (Milli Q® (control), UF-pretreated Lake Ontario water, or UF-pretreated water with cation concentrations doubled) at a target dosage of 1 μg/L. The feed solution was circulated for approximately 24 h to reach equilibrium with respect to adsorption [28], followed by an additional 24 h to evaluate membrane rejection. Unlike many bench-scale experiments that have been conducted at ~0 to 25% recoveries [4,9,29] (r (%) = permeate flow/influent flow), rejection experiments in this study were carried out at a high system recovery (~50%), which is within the