Rejection of pharmaceutically active and endocrine disrupting compounds by nanofiltration as a function of source water humic substances

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ABSTRACT

The impact of source water humic substances (HS) on the rejection of selected pharmaceutically active compounds (PhACs) and endocrine disrupting compounds (EDCs) via nanofiltration was investigated using two source waters with significantly different HS concentrations (Lake Ontario and Otonabee River, Ontario, Canada). To remove the effects of colloidal particles, raw waters were pre-treated with ultrafiltration, which removed most (up to 93%) of the colloidal and suspended particles but allowed passage of indigenous HSs. The effect of cation concentrations was examined by spiking beyond ambient levels in UF-pretreated Otonabee River water. There were no significant differences in rejection of the ionic PhAC/EDCs from the raw and UF-pretreated water matrices examined. Rejection of neutral compounds in colloid-free natural waters increased in the presence of HSs. The negative impact of cations on rejection was more prominent in the HS-dominated River water when compared to the Lake water. Increased compound rejection was not linearly related to higher concentrations of humic substances in the source waters. The rejection of neutral compounds increased due to the presence of humic substances up to a certain concentration, above which additional HS had no additional effect on PhAC/EDCs removal via nanofiltration.

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1. Introduction

The occurrence, fate, and ecotoxicology of emerging organic micropollutants including pharmaceutically active compounds (PhACs) and endocrine disrupting compounds (EDCs) are of interest in terms of potential health risks associated with long-term human exposure. In addition, their transformation products following various oxidative treatments, as well as public perception serve as challenges to the drinking water industry. Limitations associated with conventional water treatment in dealing with emerging micropollutants have brought about the exploration of membrane technologies as viable options [1,2]. In part due to operational benefits, nanofiltration (NF) has emerged as a preferred technology for surface water treatment while imposing an effective barrier to pharmaceutically active and endocrine disrupting compounds [3–5].

Previous studies have examined PhAC/EDC rejections as influenced by solute interactions with both clean membranes and membranes that were pre-fouled using organic and inorganic model foulants [6–9]. Few studies, however, have investigated the impact of natural water matrices on membrane rejection of PhACs and EDCs [10,11]. Additionally, solute interactions with water matrix components should be examined in view of practical implications of surface water treatment using nanofiltration. Any increasing trend in solute rejection arising from these interactions may support the application of comparatively looser NF membranes, aimed at lower operating cost while providing a barrier to emerging contaminants. Recently, Sadmani et al. [12] investigated the explicit impact of naturally occurring dissolved organic matter (DOM) (separated from indigenous colloidal particles) and determined that the humic substance (HS) fraction of DOM in one natural water increased NF rejection of specific PhAC/EDCs.

This study extends the work of Sadmani et al. [12] to investigate the rejection of PhACs and EDCs via a loose NF membrane (molecular weight cut-off, MWCO = 350 Da) as a function of humic substances from different source waters. To preclude the impact of colloidal particles, raw waters were pre-treated using ultrafiltration that removed most (up to 93%) of the colloidal and suspended

particles while allowing the organic fractions to pass through. The impact of dominant cations on rejection was also verified.

2. Materials and methods

2.1. Selected PhAC/EDCs and nanofiltration membrane

Selected pharmaceutically active and endocrine disrupting compounds, previously reported to be present in the US and Canadian surface waters [13–16], were examined (Table 1). As a result of their wide range of physicochemical properties (molecular weight and geometry, hydrophobicity, polarity, and charge) these compounds are representative of various classes of organic micropollutants.

A polyamide nanofiltration (NF) membrane (NE70, NE 4040-70, Saehan-CSM Membranes, Woongjin Chemical America Inc., CA, USA) was used throughout the study (Table 2). Due to the large molecular weight cut-off (MWCO = 350 Da) of the membrane, filtration could be conducted at a lower pressure while facilitating investigation of rejection mechanisms, disregarding steric exclusion due to reduction in membrane effective MWCO [19].

2.2. Water matrices

Lake Ontario and the Otonabee River are both drinking water sources in Ontario, Canada, yet contain significantly different concentrations of humic substances (HS) (Table 3). Raw Lake and River waters were pre-treated using an ultrafiltration (UF) membrane (MWCO = 100 kDa, TriSep UE50, TriSep Corporation, Goleta, CA, USA) to remove colloidal and suspended particles while allowing indigenous dissolved organic matter fractions to pass through. Two laboratory-prepared waters (buffered with 1 mM sodium bicarbonate, pH ∼ 8) were spiked with cations Ca^{2+}, Mg^{2+}, and Na^+ (as $CaSO_4$, $MgSO_4$, and NaCl, respectively) at approximately the same ambient concentration present in the surface waters. These served as "controls" viz., Milli Q®-1 and Milli Q®-2, respectively. To confirm the impact of cations on PhAC/EDC rejection in HS-dominated, colloid-free water, an additional matrix with the cation concentration approximately doubled was investigated.

2.3. Experimental protocol and NF filtration set-up

Both ultrafiltration pre-treatment and PhAC/EDC rejection experiments using NF membrane were conducted using a bench-scale flat-sheet membrane apparatus (Fig. 1). The experimental set-up consisted of three stainless steel cross-flow membrane cells (Sepa CF II, Sterlitech Corp., Kent, WA, USA), a Hydracell constant flow diaphragm pump (M03SASGSSSPA, Wanner Engineering Inc., Minneapolis, MN, USA), a stainless steel valveless piston pump (RK-07104-50, Cole-Parmer, Montreal, QC, Canada), pressure gauges, flow meters, chiller/heater, stainless steel storage and equalization tanks, and stainless steel tubing.

To remove colloidal and suspended particles, raw Lake Ontario or Otonabee River water was pre-treated using coupons of UF membrane placed into the cross-flow filtration cells. Ultrafiltration was conducted at a constant flux and the pre-treated water was then placed back into a feed tank, to subsequently be used for NF rejection experiments that followed.

Prior to each PhAC/EDC rejection experiment, a new NE70 membrane coupon was cleaned and compacted by filtering Milli-Q® water for 24 h. A mixture of PhACs and EDCs was spiked directly into the feedwater (controls, raw, or UF-pretreated water) at a target dosage of approximately 1 μg/L. Using a temperature controlled (20 ± 1 °C) equalization tank (S1), the feedwater was circulated through the membrane cells for approximately 24 h to reach equilibrium with respect to potential adsorption by the membrane [20], followed by an additional 24 h to evaluate membrane rejection (Fig. 1). The rejections were determined based on individual compound concentration in one feed (S1) and three permeate samples (S3a, S3b, and S3c) measured at the end of each experimental run. Filtration was carried out in a recycle mode at a high system recovery ($r(\%)$ = permeate flow (Q_p)/influent flow (Q_{in})) of 50%, within the range practiced in full-scale systems (30–90%) [21].

2.4. Analytical methods

Total organic carbon (TOC) and dissolved organic carbon (DOC) (method detection limit, MDL = 0.1 mg/L) were analyzed using an Aurora 1030 TOC analyzer fitted with a Model 1088 autosampler (O-I Corporation, College Station, TX), following the wet-oxidation method as outlined in Standard Method 5310 D [22]. UVA at

Table 1
Investigated PhAC/EDCs and their physicochemical properties.

Compound	Size parameters					Hydrophobicity, polarity, and charge		
	Molecular weight (g/mol)	Molecular length[a] (Å)	Molecular width[a] (Å)	Molecular depth[a] (Å)	Molecular volume[a] (Å³)	Log D[b] @ pH 8	pKₐ[b]	Dipole moment[a] (Debye)
Acetaminophen	151	9.1	4.4	1.8	498.5	0.23	10.2	3.66
Bisphenol A (BPA)	228	9.5	5.9	4.6	719.4	3.86	10.3	1.26
Carbamazepine	236	9.3	5.4	5.0	673.6	2.23	14.3	4.10
Clofibric acid	214	9.9	4.5	3.6	617.9	−0.98	4.0	3.36
Diclofenac	296	9.6	7.2	4.7	748.0	0.73	4.3	4.88
Diethylstilbestrol	268	10.3	10.0	3.1	814.0	4.42	9.7	1.22
Estriol	288	12.1	5.9	3.9	827.0	2.45	10.0	2.87
Estrone	270	11.6	5.5	4.3	797.7	3.46	10.3	3.93
Gemfibrozil	250	12.2	6.8	5.3	843.5	1.33	4.9	2.69
Ketoprofen	254	9.6	7.0	5.0	757.9	−1.01	4.3	2.89
Naproxen	230	11.4	5.4	4.9	697.6	−0.54	4.3	2.74
Pentoxifylline	278	11.0	7.2	6.4	821.9	0.48	N/A[c]	3.07
Sulfachloropyridazine	285	9.7	5.6	4.6	699.1	−1.14	6.1	3.07
Sulfamethizole	270	9.9	7.1	4.8	700.7	−2.11	5.3	6.37
Sulfamethoxazole	253	12.4	5.0	3.8	687.4	−1.43	5.7	5.51
17β-Estradiol	272	12.1	6.2	4.2	809.0	3.35	10.3	1.8

Log D, octanol–water partition coefficient (ionized and neutral species); pKₐ, acid dissociation constant.
[a] Determined using HyperChem 8.0 Student edition.
[b] Determined using ACD/I-Lab's physicochemical and ADMET prediction software (Advanced Chemistry Development Inc., Toronto, ON).
[c] N/A, not applicable (does not dissociate).