

Removal of endocrine disrupting compounds and pharmaceuticals by nanofiltration and ultrafiltration membranes

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Abstract

With the recent emergence of endocrine disrupting compounds, pharmaceuticals, and personal care products (EDC/PPCPs) as an important potable drinking water and reclaimed wastewater quality issue, our study has investigated the removal of EDC/PPCPs of 27 compounds by nanofiltration (NF) and ultrafiltration (UF) membranes from various drinking water sources using a dead-end stirred-cell filtration system. Experiments were performed at environmentally relevant initial EDC/PPCP concentrations ranging typically from 2 to <150 ng/L. EDC/PPCP retention was quantified by liquid chromatography with mass spectroscopy-mass spectroscopy. We have observed a general separation trend due to hydrophobic adsorption as a function of octanol–water partition coefficient between the hydrophobic compounds and porous hydrophobic membrane during the membrane filtration. The results have showed that both hydrophobic adsorption and size exclusion mechanisms are dominant to retain EDC/PPCP for the NF membrane, while the UF membrane retained typically hydrophobic EDC/PPCPs due mainly to hydrophobic adsorption.

Keywords: Endocrine disrupting compounds; Hormones; Nanofiltration; Ultrafiltration; Water treatment

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1. Introduction

Reports of endocrine disrupting compounds (EDCs) and pharmaceuticals and personal care products (PPCPs) in wastewater effluents and surface waters used as drinking water supplies have raised substantial concern in the public and regulatory agencies. For years, EDC/PPCPs have been detected in wastewater effluents and raw drinking source waters around the world at concentrations of sub $\mu\text{g/L}$ [1–3]. Since potential risk to humans and wildlife even at those trace levels increases, removal of EDC/PPCPs will likely become important in water industry to protect the environment and eliminate refractory organics.

Nanofiltration (NF) and ultrafiltration (UF) processes have been used in wastewater reclamation and drinking water to remove micropollutants and natural organic matter (NOM). Numerous studies have shown the removal of conventional micropollutants such as pesticides and alkyl phthalates and NOM by the NF and UF membranes [4–6]. In addition, these previous studies investigated existing separation mechanisms (e.g., size/steric exclusion, hydrophobic adsorption, and electrostatic repulsion). The rejection of uncharged trace organics by NF membranes is influenced by steric hindrance, while the rejection of polar trace organics can be explained by electrostatic interactions with the charged membranes. Kiso et al. [4,5] tested strong hydrophobic compounds including aromatic pesticides, non-phenylic pesticides, and alkyl phthalates by NF membranes and concluded that compound rejection was correlated significantly with molecular width and size in addition to compound hydrophobicity. They observed that rejection of non-dissociated organic compounds were insensitive to feed water pH and removal increased linearly with the molecular weight and molecular width.

Numerous recent studies have examined the removal of emerging micropollutants (e.g., EDC/PPCPs) by reverse osmosis (RO), NF, and UF

membranes using a dead-end stirred-cell filtration system and a cross-flow filtration system [7–9]. All these experiments were conducted with a few target compounds spiked in synthetic model waters in the absence or in the presence of dissolved organic carbon (DOC) from secondary effluent. However, these studies are still limited to a few compounds and cover synthetic model waters. To our knowledge, however, very little information is available in nanofiltration and ultrafiltration, which has examined the effects of drinking source water NOM on adsorption of a wide range of emerging micropollutants onto the membrane surface and into the membrane pores.

This work evaluates initial interactions between 27 EDC/PPCPs and NF and UF membranes having different compounds and membrane properties (e.g., solute size/structure/polarity/hydrophobicity and membrane pore size/charge/hydrophobicity) in various waters using a dead-end stirred-cell filtration system. The interactions were related to physico-chemical properties of the membranes and the source waters.

2. Materials and methods

2.1. Water matrices

One model water was prepared from Suwannee River RO isolated NOM water (SRW) purchased from International Humic Substances Society (St. Paul, MN, USA), spiked into deionized water (DI) at pH 7.5 buffered by 1 mM sodium bicarbonate. Three surface waters that provide raw water to water treatment plants, Colorado River water (CRW) directly collected from Lake Mead, Nevada, Ohio River water (ORW) collected in Louisville, Kentucky, and Passaic Valley water (PVW) collected in Totowa, New Jersey, were also investigated. Background EDC/PPCP concentrations in the three ambient surface waters (CRW, ORW, and PVW) were generally less than 10 ng/L for any specific compound. The waters were prefiltered with a 0.7 μm glass fiber

filter (Whatman® International Ltd., Maidstone, England) to remove particulate matter prior to spiking target EDC/PPCPs.

2.2. Reagents and selected EDCs and PPCPs

All water treatment standards and chemicals were at least reagent grade and/or of the highest purity commercially available. For all membrane experiments, 27 EDC/PPCPs have been selected as target compounds. Table 1 summarizes the EDC/PPCP compounds that were studied by spiking the compounds into four source waters. In order to generate the target compounds, two

issues were considered. The first consideration was occurrence in source waters. The second consideration was the physico-chemical properties of a particular compound. All the target compounds were obtained from Sigma–Aldrich except atrazine and DEET, from Accustandard (New Haven, CT, USA); and iopromide from the United States Pharmacopeia (Rockville, MD, USA). Concentrated spiking solutions of the target compounds were prepared at high concentrations (100–250 mg/L) in methanol to minimize the volume of solvents introduced into experiments. Many compounds had low water solubility (e.g., steroids) and therefore could not be spiked

Table 1
Selected target EDC and PPCP compounds in order by Log K_{ow}

Analytes	Use	MW (g/mol)	pK _a	Log K_{ow}
Gemfibrozil	Anti-cholesterol	250.2	4.7	4.77
Triclosan	Antibiotic	289.6	8 (7.9)	4.76
Estradiol	Steroid	272.2	10.4	4.01
Ibuprofen	Pain reliever	206.1	4.5 (4.9)	3.97
Progesterone	Steroid	314.2	NA	3.87
Oxybenzone	Sunscreen	228.1	NA	3.79
Ethinylestradiol	Birth control	296.2	~10.5	3.67
Testosterone	Steroid	288.2	17.4	3.32
Naproxen	Analgesic	230.1	4.5 (4.2)	3.18
Estrone	Steroid	270.4	10.3 (10.5)	3.13
Erythromycin-H ₂ O	Antibiotic	733.9	(8.8)	3.06
Diazepam	Anti-anxiety	284.8	2.4, 1.5 (3.3)	2.82
Androstenedione	Steroid	286.2	NA	2.75
Atrazine	Herbicide	215.1	<2 (1.6)	2.61
Dilantin	Anti-convulsant	252.3	(8.3)	2.47
Carbamazepine	Analgesic	236.3	<2	2.45
Estriol	Steroid	288.4	10.4 & >15	2.45
DEET	Insect repellent	191.3	<2	2.18
TCEP	Fire retardant	285.5	NA	1.44
Trimethoprim	Antibiotic	290.1	6.3, 4.0, <2 (7.1)	0.91
Sulfamethoxazole	Antibiotic	253.1	2.1 & <2 (5.7)	0.89
Diclofenac	Arthritis	318.1	(4.2)	0.70
Meprobamate	Anti-anxiety	218.3	<2	0.70
Acetaminophen	Analgesic	151.2	9.7 (9.4)	0.46
Pentoxifylline	Blood viscosity control	278.1	6 & <2	0.29
Caffeine	Stimulant	194.2	6.1	-0.07
Iopromide	X-ray contrast media	790.9	<2 & >13	-2.1

as neat standards. A small volume of the spiking solutions (50–250 μL) was injected into a 30-L stainless steel tank containing a source water. The added methanol increased the DOC concentration by approximately 0.7 mg/L.

Depending upon the source water and compound class, initial EDC/PPCP concentrations ranged typically from 2 to <150 ng/L. Although the initial feed concentrations varied widely since it was very difficult to prepare the same initial concentration at the extremely low concentration levels (i.e., sub $\mu\text{g/L}$), the percentage retention of the compounds may not be influenced significantly by the feed concentrations. SRW (2–74 ng/L) had the lowest feed concentration for the compounds among the source waters. The concentrations of some of these compounds including acetaminophen, diclofenac, dilantin, gemfibrozil, iopromide, naproxen, oxybenzone, pentoxifylline, progesterone, sulfamethoxazole, TCEP, and triclosan are near the minimum reporting level (MRL = 1 ng/L), suggesting that in these cases the maximum percentage removal can be limited by the MRL of the compounds.

2.3. Glassware and sample preservation

All glassware, supplies, and the stainless steel containers were solvent rinsed three times each using acetone, hexane, and methanol obtained from Burdick & Jackson (Muskegon, MI, USA) or Sigma–Aldrich (St. Louis, MO, USA). All samples were collected in 1 L silanized, amber glass bottles (Eagle-Picher, Miami, OK, USA) containing the test water. Without silanized glassware some EDC/PPCP adsorption was observed [10], and use of silanized glassware has been recommended elsewhere [11]. Samples were immediately preserved by adjusting to pH 2 with concentrated sulfuric acid (except SRW), stored at 4°C, and shipped to the laboratory within 48 h of collection for extraction. Samples were extracted within 14 days of collection.

2.4. Analyses

Liquid chromatography with tandem mass spectrometric detection (LC/MS/MS) was used to determine the relatively large polar and small volatile compounds (see Table 1). These methods have been published previously [10]. Briefly, the method involves the automated extraction of a 1 L water sample. The extract is used directly. Stable isotopically labeled surrogates and internal standards (hydrocodone-d6, $^{13}\text{C}_3$ -caffeine, $^{13}\text{C}_1$ -erythromycin, $^{13}\text{C}_3$ -atrazine, and diazepam-d5) were used to increase accuracy of the analytical data. Surrogate standards were added to the initial water sample and were followed through the entire extraction and analytical steps. Compounds were analyzed using an Applied Biosystems API 4000 triple quadrupole with an Agilent 1100 liquid chromatograph. Details with respect to retention times and basic information on the LC/MS/MS procedure are provided separately [10]. As part of quality assurance (QA)/quality control (QC), several spike and recovery experiments were performed on different days and by different analysts. More details with respect to QA/QC are provided separately [10].

2.5. Membranes and membrane testing unit

Commercially available NF and UF membranes were tested using a commercial bench-scale stainless steel dead-end stirred-cell filtration unit (SEPA[®] ST, Osmonics, Minnetonka, MN, USA) to evaluate flat-sheet membrane specimens for compound retention. The NF (ESNA, Hydranautics, USA) and UF (GM, Desal-Osmonics, USA) membranes are thin film composites with aromatic polyamide (ESNA) or sulfonated polyethersulfone coated with an ultrathin polyimide (GM), respectively. The effective membrane surface area is 16.9 cm^2 . All of the experiments were performed at room temperature (20°C) with a constant initial pure water flux of 1.3 m/day and pressures of 724–779 kPa for NF and 445–504 kPa for UF.

The NF and UF membranes have molecular weight cut-offs (MWCOs) of 600 (± 200) Da and 8000 (± 1000) Da.

A fresh membrane was used for each experiment. The membrane was soaked in ultrapure water for a minimum of 24 h prior to use. During this period, the ultrapure water was replaced every 4–8 h with another new volume of ultrapure water for membrane stabilization. The DOC of the final rinse water was checked to assure that it was at a negligible level. Additionally, the membranes were precompact for 5–7 h at the same pressures with ultrapure water until a constant flux was obtained. Only then was water in the stirred cell replaced by the test solution. An initial volume of 300 mL of a given sample was passed through the membrane until 200 mL of permeate was obtained, and the corresponding retentate was also collected. The experiments were repeated until a total volume of 1000 mL of permeate was obtained. 500 mL of retentate was diluted to 1 L with DI water. Reported concentrations in retentate account for the DI water dilution. A mass balance was calculated using Eq. (1) by measuring the concentration of each compound concentration in the feed, permeate, and retentate, while percentage adsorption was calculated using Eq. (2). Observed retention, R , of each EDC/PPCP was calculated using Eq. (3). Adsorbed mass was defined as the amount of solute adsorbed per unit area onto the membrane surface and into the membrane pores within the stirred-cell was calculated using Eq. (4).

Mass balance (% recovery)

$$= \frac{V_r C_r + V_p C_p}{V_f C_f} \times 100(\%) \quad (1)$$

Adsorption (%)

$$= 100\% - \text{mass balance (\% recovery)} \quad (2)$$

$$R (\%) = \frac{C_f - C_p}{C_f} \times 100(\%) \quad (3)$$

$$M_{\text{ads}} = [(C_f V_f) - \{(C_p V_p) + (C_r V_r)\}] / A \quad (4)$$

where V_r is the retentate volume (L), C_r is the retentate concentration (ng/L), V_p is the permeate volume (L), C_p is the permeate concentration (ng/L), V_f is the feed volume (L), C_f is the feed concentration (ng/L), M_{ads} is the amount of solute adsorbed per unit membrane area (ng/cm²), and A is the effective membrane area (cm²).

3. Results and discussion

3.1. Retention of compounds

For the dead-end stirred-cell experiments, average percentage retention by the NF membrane (approximately 30–90% except naproxen of <10% retention) was greater than that by the UF membrane that typically had less than 30% retention except a few compounds (triclosan, oxybenzone, estrone, progesterone, erythromycin) having $\text{Log}K_{\text{ow}}$ of >3 (see Fig. 1). The retention varied depending on source water. Since in this study, we used four different feed waters having different water chemistry conditions, it is difficult to compare retention trends for each compound.

Fig. 2 compares the retention of EDC/PPCPs as a function of $\text{Log}K_{\text{ow}}$ for the NF and UF membranes with various source waters. We observed visually that the retention increases with increasing the $\text{Log}K_{\text{ow}}$ value. This indicates that retention for the hydrophobic membranes is influenced by hydrophobic interaction (adsorption). As mentioned previously, the source waters have various water quality conditions. Thus, compound retentions are compared along with key parameters such as DOC, SUVA, conductivity, and pH. Compounds retention follows the order, ORW (relatively low SUVA and low conductivity) > CRW (relatively low SUVA and high conductivity) > PVW (relatively low pH and high conductivity) \cong SRW (relatively high DOC and high SUVA) for the NF membrane. However, a different retention trend was observed for

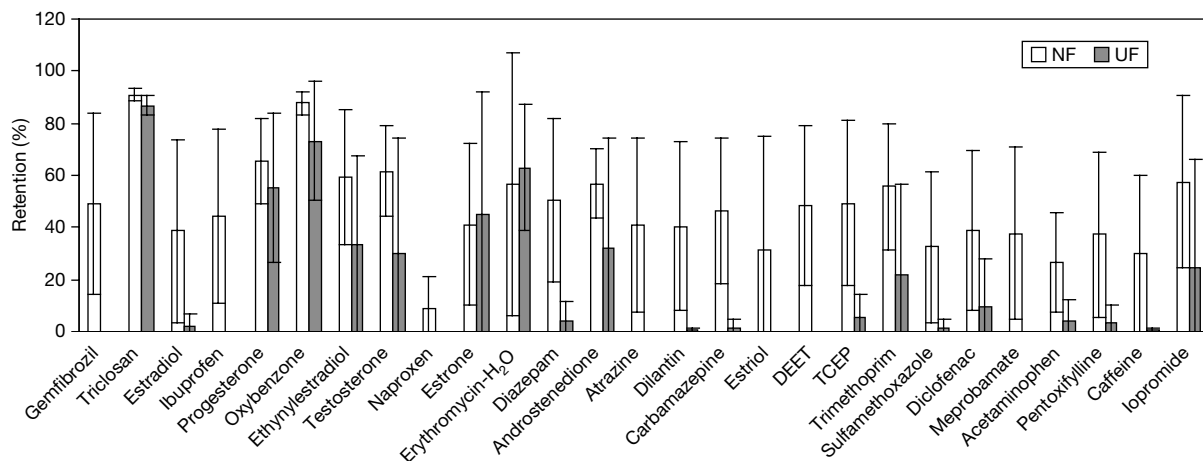


Fig. 1. Average percentage retention across four waters spiked with EDC/PPCPs (SRW, CRW, ORW, and PVW) by the NF and UF membranes.

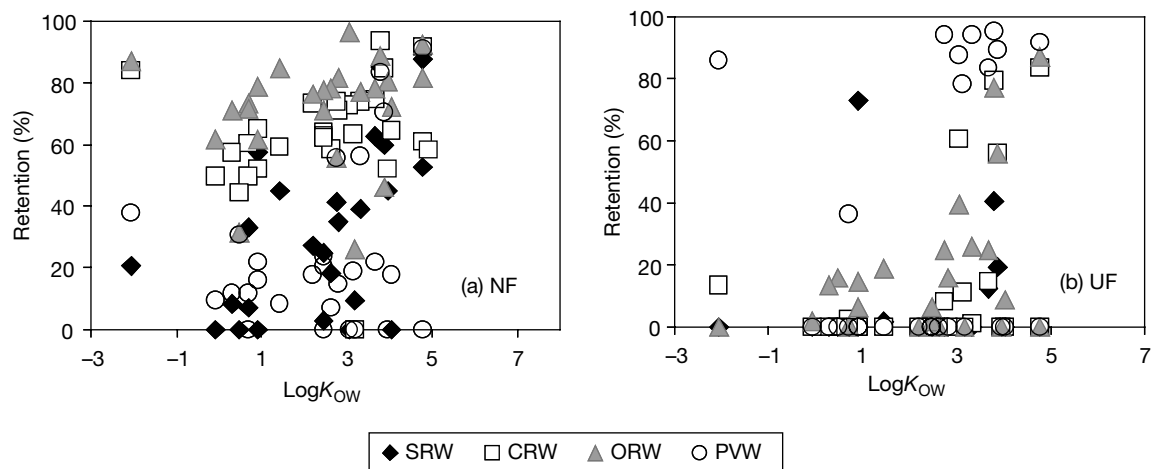


Fig. 2. Retention of EDC/PPCPs as a function of $\text{Log}K_{ow}$ for the NF and UF membranes in various source waters: (a) NF membrane and (b) UF membrane.

the UF membrane ($\text{PVW} > \text{ORW} \cong \text{CRW} > \text{SRW}$). There is no clear explanation for the highest PVW retention.

3.2. Compound adsorption onto membranes

It is useful to consider compound adsorption in order to understand retention mechanisms for hydrophobic compounds during NF and UF. To

quantify adsorption of EDC/PPCPs on the membranes, mass balances were calculated based on the concentration of each compound in feed, permeate, and retentate. The average adsorbed mass values for the compounds are shown for the four source waters (Fig. 3). We had very similar adsorbed mass values for the NF and UF membranes ($< 2.5 \text{ ng/cm}^2$). Eight of and fourteen of 27 compounds showed 100% recovery based

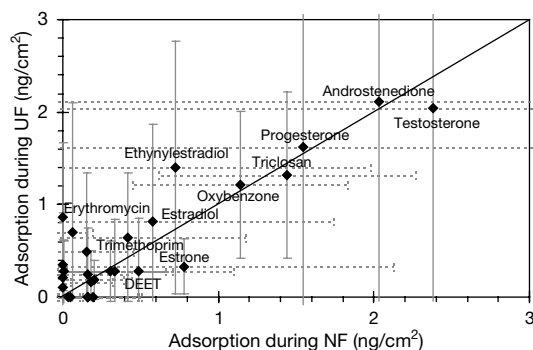


Fig. 3. Comparison of EDC/PPCP adsorption onto the NF and UF membranes.

on the mass balance for NF and UF membrane tests, respectively. Among the compounds showing less than 100% recovery, the compounds (androstenedione, oxybenzone, progesterone, testosterone, triclosan) having $\text{Log } K_{ow}$ of >2.8 exhibited typically less than 40% recovery except gemfibrozil and ibuprofen. However, the other compounds ($\text{Log } K_{ow} < 2.8$) showed higher recovery ($>75\%$). For the compounds, a general trend appears to exist with higher mass recovery at lower $\text{Log } K_{ow}$. Although experimental and analytical accuracy could vary the mass recovery, these results indicate that observed retention for the relatively hydrophobic compounds based on their $\text{Log } K_{ow}$ was significantly governed by adsorption.

4. Conclusions

In this work, NF and UF dead-end stirred-cell measurements were performed to determine removal of endocrine disrupting compounds, pharmaceuticals and personal care products (EDC/PPCPs) from one model water and three surface waters. More polar, less volatile, and less hydrophobic compounds had relatively low retention, which indicates that retention by NF and UF is clearly governed by hydrophobic adsorption. However, once steady-state operation

is achieved, size exclusion can be dominant for EDC/PPCPs retention. This result is also supported by the average adsorbed mass of EDC/PPCPs calculated using Eq. (4) (0 to $<2.5 \text{ ng/cm}^2$ for the compounds) onto the NF and UF membranes in the source waters. The NF membrane retained EDC/PPCPs greater than the UF membrane, implying that retention is affected by membrane pore size. In addition, the retention of EDC/PPCPs appears to be affected by source water chemistry conditions.

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