

Rejection of Emerging Organic Micropollutants in Nanofiltration–Reverse Osmosis Membrane Applications

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ABSTRACT: The rejection of emerging trace organics by a variety of commercial reverse osmosis (RO), nanofiltration (NF), and ultra-low-pressure RO (ULPRO) membranes was investigated using TFC-HR, NF-90, NF-200, TFC-SR2, and XLE spiral membrane elements (Koch Membrane Systems, Wilmington, Massachusetts) to simulate operational conditions for drinking-water treatment and wastewater reclamation. In general, the presence of effluent organic matter (EfOM) improved the rejection of ionic organics by *tight* NF and RO membranes, as compared to a type-II water matrix (adjusted by ionic strength and hardness), likely as a result of a decreased negatively charged membrane surface. Rejection of ionic pharmaceutical residues and pesticides exceeded 95% by NF-90, XLE, and TFC-HR membranes and was above 89% for the NF-200 membrane. Hydrophobic nonionic compounds, such as bromoform and chloroform, exhibited a high initial rejection, as a result of both hydrophobic–hydrophobic solute-membrane interactions and steric exclusion, but rejection decreased significantly after 10 hours of operation because of partitioning of solutes through the membranes. This resulted in a partial removal of disinfection byproducts by the RO membrane TFC-HR. In a type-II water matrix, the effect of increasing feed water recoveries on rejection of hydrophilic ionic and nonionic compounds was compound-dependent and not consistent for different membranes. The presence of EfOM, however, could neutralize the effect of hydrodynamic operating condition on rejection performance. The ULPRO and *tight* NF membranes were operated at lower feed pressure, as compared to the TFC-HR, and provided a product water quality similar to a conventional RO membrane, regarding trace organics of interest. *Water Environ. Res.*, 77, 40 (2005).

KEYWORDS: disinfection byproducts, emerging organic micropollutants, integrated membrane systems, nanofiltration, pesticides, pharmaceutical residues, reverse osmosis, water reuse, reclamation.

Introduction

An increasing number of municipalities are using surface water, under the effect of wastewater effluent or recycled wastewater, as a source to augment drinking water supplies. Membrane treatment of source water of impaired quality by an integrated membrane system (IMS), such as microfiltration (MF) pretreatment followed by reverse osmosis (RO), represents the industry standard for either subsurface injection projects leading to groundwater recharge or for surface-water-augmentation projects (Alexander et al., 2003; Drewes et al., 2003; National Research Council, 1998). Such an IMS is primarily driven by high removal efficiencies for regulated-organic contaminants, pathogens, and total nitrogen. However, the rejection of unregulated organic-trace pollutants, which are associated with potential adverse human-health effects, such as endocrine-disrupting compounds, pesticides, emerging disinfection byproducts, pharmaceutical residues, personal-care products, and organic compounds appearing on the U.S. Environmental Protection Agency's (U.S.

EPA's) candidate-contaminant list, is of increasing interest for membrane applications. While findings of previous studies have contributed to an improved empirical understanding of rejection mechanisms for trace organics during RO and nanofiltration (NF) treatment, a fundamental or mechanistic understanding of factors affecting the rejection of organic solutes in high-pressure membrane systems is still lacking.

The rejection of trace organic compounds by high-pressure membranes represents a complex interaction of steric hindrance, electrostatic repulsion, solution effects on the membrane, and solute and membrane properties. Some interactions, such as solute rejection by physical sieving, are fairly well-understood, while others, such as electrostatic exclusion, hydrophobic–hydrophobic interactions between solute and membrane, solution chemistry, and membrane fouling are considered important, but a detailed knowledge is still lacking. Bellona et al. (2004) conducted a comprehensive literature review on rejection mechanisms for organic solutes and identified the following physicochemical properties to primarily affect solute rejection: molecular weight (MW), molecular geometry (length and width), acid dissociation constant (pK_a), hydrophobicity–hydrophilicity (qualified through the octanol-water partitioning coefficient, $\log K_{ow}$), and diffusion coefficient (D_p). Key membrane properties affecting rejection that were identified include molecular weight cutoff (MWCO), pore size, surface charge (measured as zeta potential), hydrophobicity–hydrophilicity (measured as contact angle), and surface morphology (expressed as surface roughness). In addition, solution chemistry (such as feedwater pH, ionic strength, hardness, and the presence of organic matter), extent of membrane fouling, and hydrodynamic condition (i.e., feed pressure and feed water recovery) may considerably influence the rejection of trace-organic pollutants.

During previous studies, rejection of hydrophilic nonionic solutes correlated well with molecular-size parameters, such as molecular width and length, and less with molecular weight (Bellona et al., 2004; van der Bruggen et al., 1999), and steric hindrance has been identified as the driving mechanism for rejection. Negatively charged hydrophilic solutes can be further rejected by electrostatic repulsion through negatively charged membrane surfaces (Ozaki et al., 2002). The degree of electrostatic repulsion and rejection of negatively charged solutes is mainly dependent on the amount of membrane surface charge, but it also depends on the size of the compound and the pore size of a membrane (Bellona and Drewes, in press; Ozaki et al., 2002). Because membrane surface charge is dependent on the pH and ionic strength of the feedwater and the accumulation of organic

Table 1—Membrane properties and operational conditions.

Membrane	NF-200	NF-90	XLE	TFC-SR2	TFC-HR
Manufacturer	DOW/Filmtec (Midland, Michigan)	DOW/Filmtec	DOW/Filmtec	Koch (Wilmington, Massachusetts)	Koch
Classified as MWCO, Daltons (manufacturer)	NF 300	NF 200	ULPRO 100	NF 400	RO 100
Contact angle, °	30.3	63.2	66.3	55.3	35.0
Zeta potential, mV ⁺	-15.3	-21.6	-2.5	-11.0*	-8.5
Pure-water permeability, L/m ² day kPa (25°C)	1.20	2.49	2.16	4.35	0.84
Applied feed pressure (kPa)					
1.3 Jo/k	345	414	483	Not applicable	621
2.4 Jo/k	552	621	758	414	N/A

⁺ Zeta potential measured at pH 6 in 0.01-M NaCl solution.

* Zeta potential measured at pH 6 in a solution with 0.01-M NaCl, 0.5mM CaCl₂, and 1-mM NaHCO₃ (data adopted from Schäfer et al., 2003).

foulants on the membrane, the rejection of negatively charged solutes is subject to dynamic property changes during membrane operation (Bellona et al., 2004; Ozaki et al., 2002; Shim et al., 2002). For nonionic hydrophobic compounds, hydrophobic–hydrophobic interactions with the membrane and steric hindrance have been reported to be the driving mechanisms for rejection (Kimura et al., 2003). The rejection of hydrophobic nonionic compounds has also been found to be dependent on operational conditions and solution chemistry. A study by Chellam and Taylor (2001) reported that operational conditions, such as feed water recovery, had a significant effect on the rejection of total hardness, haloacetic acids, and total trihalomethane precursors by NF membranes. In a study conducted by Nghiem et al. (2002), the rejection of the natural hormone estrone was decreased after adding organic matter to the feedwater.

Recent studies investigating removal mechanisms of organic solutes by high-pressure membranes have contributed greatly to the current knowledge base. Little work, however, has been completed investigating the removal of emerging organic-trace pollutants by commercially available membranes under operating conditions commonly used in water reclamation and reuse applications. The objectives of this study were threefold, namely to (1) investigate the rejection efficiencies of selected emerging trace organics occurring at the parts-per-trillion concentration level by several commercially available NF, ultra-low-pressure reverse osmosis (ULPRO), and RO membranes on a laboratory-scale; (2) compare the effect of water-quality matrices on rejection performance; and (3) study the effect of hydrodynamic conditions on the rejection of selected trace-organic compounds.

Methodology

Chemicals and Materials. All chemicals used were of reagent grade or higher, purchased from J. T. Baker, Inc. (Phillipsburg, New Jersey), Sigma-Aldrich (St. Louis, Missouri), Sigma-Aldrich (Steinheim, Germany), Chem Service (Chester, Pennsylvania), Eastman Organic Chemicals (Rochester, New York), and Fisher Scientific, Inc. (Fairlawn, New Jersey). Reagent water (type I) was obtained from an ultrapure laboratory-water-purification system (Barnstead, Dubuque, Iowa). The average total organic carbon (TOC) concentration for the ultrapure water was 0.06 mg/L. Deionized water (type II) was obtained from a laboratory-water-purification system (U.S. Filters, Warrendale, Pennsylvania).

Membranes selected for this study were characterized as thin-film-composite (TFC) polyamide membranes and included RO (TFC-HR, Koch Membrane Systems, Wilmington, Massachusetts), ULPRO (XLE, Dow/Filmtec, Midland, Michigan), and NF membranes (NF-90 and NF-200, Dow/Filmtec and TFC-SR2, Koch Membrane Systems). The selected membranes represented a wide range of nominal molecular weight cutoff (MWCO) values as reported by the manufacturers. The RO and ULPRO membranes, TFC-HR and XLE, had the lowest MWCO of 100 Daltons. The *tight* NF membrane, NF-90, had a MWCO of 200 Daltons followed by the *loose* NF membrane, NF-200, with 300 Daltons and the *fairly loose* membrane, TFC-SR2, with 400 Daltons. Each membrane was tested in a spiral-wound element (6.25 × 100 cm) configuration. The membranes used in the experiments, their properties, and operational conditions of the experiments are summarized in Table 1. All membranes are negatively charged at pH 6. The active layer of NF-200 and TFC-HR is hydrophilic, while the NF-90, XLE, and TFC-SR2 layers are hydrophobic based on contact-angle measurements. In this study, the pure-water permeability (at 25°C) of the five selected membranes varied from 0.84 to 4.35 L/(m²·day·kPa).

Surrogate Compounds. Compounds selected for this study represent a wide range of physicochemical properties, such as hydrophilic ionic (ibuprofen, diclofenac, ketoprofen, naproxen, gemfibrozil, and mecoprop), hydrophilic nonionic (primidone), and hydrophobic nonionic (bromoform and chloroform). The properties of the surrogate compounds are listed in Table 2. The acid dissociation constants (pK_a) of the ionizable compounds ranged from 3.1 to 4.9, indicating that they were negatively charged in the pH range of the membrane experiments (pH 6 to 8). The molecular weight of the compounds ranged from approximately 200 to 300 g/mol. The software package Hyperchem 7.0 (Hypercube, Gainesville, Florida) was used for molecular-structure modeling. Once a molecule was optimized by energy minimization, molecular geometry at an unhydrated state was measured by performing single-point calculations. Within this geometry, molecular length was defined as the maximum length of a molecule, and the cross-sectional diameter represented the molecular width.

Sample Collection and Storage. Synthetic feedwaters were used to simulate feedwater compositions of treated domestic wastewater. For hydrophilic ionic and nonionic surrogate compounds, feed solutions of 300 ng/L nominal concentrations were prepared by

Table 2—Physical–chemical properties of target compounds.

Characteristics (CAS-No.) Origin	Formula	Molecular weight (g/mol)	Molecular width (Å)	Molecular length (Å)	Water solubility* (mg/L)	Log K _{ow} * ¹	pKa*
Ibuprofen (15687-27-1) analgesic	C ₁₃ H ₁₈ O ₂	206.28	5.04	10.56	21	3.97	4.91
Diclofenac (15307-86-5) analgesic	C ₁₄ H ₁₁ Cl ₂ NO ₂	296.16	7.20	9.37	2.37	4.51	4.15
Ketoprofen (22071-15-4) analgesic	C ₁₆ H ₁₄ O ₃	254.28	6.90	9.28	51	3.12	4.45
Naproxen (22204-53-1) analgesic	C ₁₄ H ₁₄ O ₃	230.26	5.32	11.23	159	3.18	4.15
Gemfibrozil (25812-30-0) blood lipid regulator	C ₁₅ H ₂₂ O ₃	250.34	6.46	13.27	19	4.39	4.77
Mecoprop (93-65-2) pesticide	C ₁₀ H ₁₁ ClO ₃	214.65	4.67	9.39	620	3.13	3.1
Primidone (125-33-7) antiepileptic	C ₁₂ H ₁₄ N ₂ O ₂	218.25	6.23	7.26	500	0.84	12.26
Bromoform (75-25-2) DBP ²	CHBr ₃	252.73	2.27	3.12	3100	2.42	N/A
Chloroform (67-66-3) DBP ²	CHCl ₃	119.38	2.53	2.87	7950	1.97	N/A

Reference source: * ChemFinder.com, experimental data from SRC PhysProp database.

¹ Log K_{ow} is the octanol-water partitioning coefficient of a compound at a nondissociated state.

² DBP = Disinfection byproduct.

spiking a cocktail of the surrogate compounds from a stock solution (concentration 1.5 mg/L) to 50 L of type-II water stored in a 200-L stainless steel drum. The feedwater was adjusted to pH 6, using 3-N sodium hydroxide (NaOH) solution, a conductivity of 750 µS/cm, using sodium chloride (NaCl), and total hardness of 120 mg/L as calcium carbonate (CaCO₃), using calcium sulfate. To evaluate the effect of effluent organic matter (EfOM) on rejection of trace organics, the above type-II-water matrix was additionally spiked with preisolated EfOM concentrate to obtain a nominal TOC concentration of 5 mg/L. Experiments were conducted over a period of 2 hours to maintain steady-state conditions before collecting samples from the feed and permeate. For hydrophobic nonionic surrogate compounds, feed solutions were prepared by establishing nominal concentrations of 100 µg/L bromoform and chloroform, using a stock solution (concentration 2.0 g/L) in 190 L of type-II water stored in a 200-L stainless-steel drum. The feedwater was adjusted to pH 8, using 3-N NaOH solution, and a conductivity of 600 µS/cm, using NaCl. Before starting the experiments, the feed solutions were recirculated overnight by the membrane unit bypass system to assure proper mixing and dissolution of bromoform and chloroform and to presaturate the tubing. Samples were taken from permeate, feed, and concentrate streams at 0, 1, 3, 6, 12, 24, 48, and 72 hours. All water samples were stored at 4°C, extracted within a hold time of less than three days, and analyzed within two to three weeks.

To guarantee that membrane rejection tests were comparable, all EfOM water matrices were prepared from the same isolated EfOM concentrate. The EfOM isolate was generated from secondary treated effluent collected at the wastewater treatment plant in Boulder, Colorado, and filtered through a MF unit (nominal cutoff of 0.04 µm). After MF treatment, the secondary effluent was adjusted to pH 6 with sulfuric acid (H₂SO₄) and then concentrated using a two-stage, laboratory-scale membrane unit equipped with XLE ULPRO membranes (Dow/Filmtec). During these experiments, the recoveries were approximately 85% for MF and 60% for RO treatment. A concentration factor of 3 to 4 was achieved by discarding the permeate during the RO membrane operation, while recycling the concentrate back into the feed container. After the secondary effluent was concentrated, a laboratory-scale electrodialysis (ED) unit was used to partially remove mono- and divalent cations and anions. The ED was operated until the conductivity of the sample reached a value

of approximately 1500 µS/cm. The samples were then acidified to pH 4 by H₂SO₄ and stored in a refrigerated storage area (4°C). The EfOM isolate exhibited a TOC concentration of 28 mg/L and a UV absorbance of 49 m⁻¹, which remained stable during storage. Size-exclusion chromatograms of the water samples from each concentration step showed that a small portion of high-molecular-weight compounds, namely organic colloids, were removed by MF treatment, but humics and low-molecular-weight acids remained in the MF permeate (data not shown). In the RO concentrate sample after ED desalination, only a small portion of low-molecular-weight compounds was not recovered. In general, the EfOM concentrate was comprised of a broad range of different organic matter fractions commonly present in secondary-treated effluent.

Laboratory Studies. One-stage-membrane experiments were carried out with one spiral-wound-membrane element in a 6.25 × 100-cm pressure vessel. The feed flowrate for the one-stage-membrane experiments was 7.3 L/min and was generated by a Procon vane pump head (Murfreesboro, Tennessee). The feed pressure for the five membranes varied between 345 and 758 kPa (Table 1). A schematic of the one-stage-membrane unit is presented in Figure 1. Flowrates of feed, concentrate, and permeate were monitored by rotor flowmeters. Feed and concentrate pressure was monitored with pressure gauges. Feed pressure and permeate flux were controlled by adjusting a needle valve, located on the concentrate line, to establish certain recoveries representing predetermined hydrodynamic ratios *J_o/k*.

Membrane elements were flushed with approximately 100 L of type-II water before conducting rejection experiments with target compounds. After each membrane experiment, the membrane elements were flushed with a 0.01-N NaOH solution for 10 minutes to remove any adsorbed organics and subsequently flushed with at least 100 L of type-II water. All experiments were conducted at ambient temperature (25°C).

Analytical Methods. The analysis of hydrophilic ionic and nonionic target compounds (ibuprofen, diclofenac, ketoprofen, naproxen, gemfibrozil, mecoprop, and primidone) followed a protocol published by Reddersen and Heberer (2003). For this analysis, 1 L of each sample was collected and acidified to pH 2, using residue free hydrochloric acid. Two internal standards, 100 ng of 10,11-dihydrocarbamazepine and 100 ng of 2-(m-chlorophenoxy) propionic acid (100 µL of a 1 ng/µL solution in methanol), were spiked

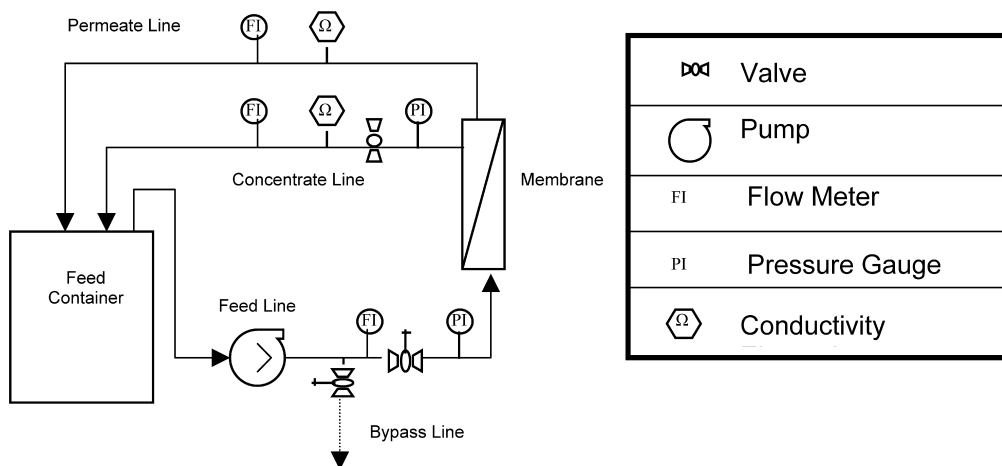


Figure 1—Flow schematic of the one-stage, laboratory-scale membrane unit.

into each sample for recovery corrections. Methanol (10 mL) was then added as a modifier for solid-phase extraction (SPE). The SPE was carried out by using 1 g of RP-C-18 material (Bakerbond Polar Plus, Mallinckrodt-Baker, Phillipsburg, New Jersey), filled in a 6-mL polyethylene cartridge. The cartridges were conditioned by applying 5 mL of acetone, 10 mL of methanol, and 10 mL of type-I water (adjusted to pH 2.0). After conditioning, a vacuum was applied to a PreSep 12-port manifold (Fisher Scientific, Inc., Pittsburgh, Pennsylvania), and the water samples were passed through the cartridges at a flowrate of 3 to 5 mL/min. The C-18 cartridges were then dried overnight, with a gentle stream of medical grade nitrogen. The analytes were eluted from the cartridges three times, with 1 mL of methanol directly into sampler vials (elution was stopped at an elution volume of approximately 1.5 mL). Afterwards, the eluate was dried again and the eluate dissolved in 100 μ L of a pentafluorobenzyl bromide solution (2% in toluene). Triethylamine (4 μ L) was added as a catalyst into the sample vial, which was then placed in a drying cabinet for one hour at 100°C. The residue was dissolved again in toluene (100 μ L), transferred into 200 μ L glass inserts, and analyzed by a HP 6890 gas chromatograph and a HP 5973 quadrupole mass spectrometer from Agilent Technologies (Waldbronn, Germany). The method detection limit of the surrogate compounds was 2 ng/L.

Bromoform and chloroform were quantified according to U.S. EPA method 551.1 for trihalomethanes (U.S. EPA, 1995). A 25- μ L surrogate standard (30 000 μ g/L 1,2,3-trichloropropane in acetone) was added in a 30-mL sample. After addition of 8.0 g of NaCl and 3.0 mL of methyl t-butyl ether, the samples were mixed for approximately 30 seconds, until most of the salts were dissolved. Next, the samples stood for approximately 15 minutes for separation. Then, 2 mL of the top organic layer was transferred to a gas-chromatography vial and analyzed by a HP 6890 series gas chromatograph with a microelectron-capture detector, a HP 7683 autoinjector, and autosampler tray module and a DB-1 capillary column coated with dimethylpolysiloxane (30 m \times 0.25 mm \times 1 μ m) from Agilent Technologies (Wilmington, Delaware). Nitrogen was used as the carrier gas at 30 cm/sec. The injection temperature was 200°C, and the oven temperature was programmed from 50°C (1 min) to 180°C at 10°C/min. A split mode (50:1) was used for injecting the 2- μ L sample, using the autoinjector module. The

method-detection limits of bromoform and chloroform were 0.320 and 0.560 μ g/L, respectively.

Conductivity was determined using an electrical conductivity meter (Cole-Parmer, Vernon Hills, Illinois). The pH was determined using an Accumet AP63 portable pH meter with combination of a glass electrode (Fisher Scientific). The UV absorbance, at a wavelength of 254 nm, was analyzed using a Nicolet 8740 UV/VIS spectrophotometer (Nicolet Instruments of Discovery, Madison, Wisconsin), with a 1-cm quartz cell for feedwater and a 5-cm quartz cell for permeate. The TOC was quantified using a Sievers 800 TOC analyzer with autosampler (Ionics Instruments, Boulder, Colorado).

The surface-charge values (zeta potential) of the flat-sheet membranes were determined from electrophoretic-mobility measurements, using a commercially available electrophoretic-measurement apparatus (ELS-8000, Photal, Otsuka Electronics, Japan), with a plate sample cell. Polystyrene latex particles (diameter 520 nm, Otsuka Electronics, Japan), coated with hydroxy propyl cellulose and with a molecular weight of 300 000 Daltons (Scientific Polymer Products, Japan), were used as mobility-monitoring particles. These were dispersed with a 0.01-M NaCl solution to prevent the interactions with, or adsorption onto, the quartz-cell surface during measurement (Shim et al., 2002).

The wetting and adhesion properties of membranes are characterized by contact-angle measurement, using a NRL contact angle Goniometer-Model 100-00 (Raméhart, Inc, Surface Science Instrument, Landing, New Jersey). Membranes were soaked and well-rinsed with type-I water, then dried for 24 hours at 25°C. A 5.0- μ L, type-I water droplet was applied on the specimen surface, and the contact angle was measured immediately after the droplet deposited on the membrane.

The pure-water permeability of membranes was measured with type-I water, using a bench-scale, cross-flow, flat-sheet membrane unit (Sepa CF II, GE Osmonics, Minnetonka, Minnesota). It was calculated from the linear correlation of permeate flux and applied feedwater pressure at 25°C.

Hydrodynamic Ratio Jo/k . The ratio Jo/k is used in this study to maintain similar hydrodynamic operating conditions for the different types of membranes investigated. The hydrodynamic parameter, Jo/k , represents the convection transport of a solute to the membrane boundary layer (permeate flux, Jo) and back-diffusive

transport away from the boundary layer into the bulk solution (mass transfer coefficient, k) (Cho et al., 2000). When the Jo/k ratio is larger than unity, the convection dominates solute transport; a Jo/k ratio less than unity indicates that back-diffusion dominates the mass transport.

$$J_0 = \frac{Q_p}{A_h} \text{ (cm/s)} \quad (1)$$

$$U = \frac{Q_t}{A_v} \text{ (cm/s)} \quad (2)$$

$$k = 1.62 \left(\frac{UD^2}{2bL} \right)^{0.33} \text{ (cm/s)} \quad (3)$$

Where

- Q_p = permeate flow rate (cm³/s);
- A_h = membrane surface area (cm²);
- U = average velocity of feed (cm/s);
- Q_t is the feed flowrate (cm³/s);
- A_v = cross-sectional area (cm²);
- b = channel height (cm);
- L = channel length (cm); and
- D = diffusion coefficient of solute in water (cm²/s).

Solute diffusion coefficient D is estimated from the Hayduk and Laudie method (Lyman et al., 1982), described as follows:

$$D = 13.26 \times 10^{-5} / (\eta_w^{1.14} \times V_B^{0.589}) \quad (4)$$

Where

- η_w = viscosity of water at 25 °C; and
- V_B = LeBas molar volume.

Because of the different LeBas molar volumes of each surrogate compound, the Jo/k ratios reported herein are representing average values. Three average Jo/k ratios were assessed for hydrophilic nonionic and ionic compounds in this study: 1.3 (1.18 to 1.35), 1.9 (1.81 to 2.07), and 2.4 (2.27 to 2.59), while the rejection of hydrophobic nonionic solutes was evaluated at a Jo/k ratio of 1.1 (1.06 to 1.09). These ratios correspond to recoveries generally exhibited by an individual spiral-wound-membrane element in water and wastewater treatment applications ($Jo/k = 1.1$ equals a recovery of 11.0%, 1.3 equals 12.7%, 1.9 equals 19.6%, and 2.4 equals 24.5%, respectively).

Results and Discussion

Effect of Hydrodynamic Operating Condition and Water Matrices on the Rejection of Hydrophilic Ionic and Nonionic Organic Solutes. In this study, the mass transfer coefficient (k) was kept constant during the experiments to evaluate the effect of pressure-driven convection on the rejection of trace-organic pollutants. Within the assessed range of Jo/k ratios from 1.3 to 2.4, all negatively charged compounds exhibited a rejection exceeding 89%, resulting in permeate concentrations below 25 ng/L for the NF-200 and below 10 ng/L for the NF-90 and XLE membranes, respectively (Figure 2). However, changing the hydrodynamic-operating conditions had slightly different effects on the efficiency of solute rejection, depending on the used membranes and water matrix. When Jo/k ratios increased from 1.3 to 2.4, the permeate concentrations of NF-200 membrane in a type-II water matrix decreased by 5 to 15 ng/L, indicating an improved rejection (Figure 2a). The XLE membrane displayed a similar rejection trend. When Jo/k ratios increased from 1.3 to 1.9, the permeate concentrations declined from 10 ng/L to 5 ng/L or nondetect, depending on specific compounds (Figure 2e).

The NF-90 membrane exhibited a rather inconsistent behavior, with generally low permeate concentrations not exceeding 10 ng/L (Figure 2c). While some compounds for the NF-90 remained at concentrations equal or below 5 ng/L, while the Jo/k ratios increased from 1.3 to 2.4, other compounds showed a slight increase of permeate concentration, at a Jo/k ratio of 2.4. In the presence of EfOM and Jo/k ratios of 1.3 and 2.4, the permeate concentrations of the NF-200 for ibuprofen, mecoprop, and gemfibrozil were approximately the same, whereas those of diclofenac and ketoprofen increased from nondetect to 10 and 5 ng/L, respectively (Figure 2b). For EfOM experiments, the variation of permeate concentrations ranging from nondetect to 4 ng/L, using the NF-90 membrane, was even smaller than variations observed during NF-200 experiments (Figure 2d). Because the method-detection limit of ionic surrogate compounds was 2 ng/L, these variations are not considered significant.

Primidone, representing a hydrophilic nonionic compound, exhibited permeate concentrations of less than 30 ng/L for NF-90, XLE, and NF-200 membranes in a type-II water matrix and concentrations below 22 ng/L in an EfOM water matrix (Figure 2f). This rejection is similar to the degree of rejection achieved for ionic solutes. In type-II water matrix, a higher Jo/k ratio led to a lower rejection for NF-90, and XLE membranes with permeate concentrations increased from nondetect to 30 and 10 to 15 ng/L, respectively. Permeate concentrations of primidone remained constant, at 15 ng/L, for the NF-200 membrane, with increasing Jo/k ratio. However, these trends were not obvious in the presence of EfOM. When Jo/k ratios increased from 1.3 to 2.4, the permeate concentrations of primidone remained constant, at 13 ng/L, for the NF-90 membrane, and increased slightly, from 19 to 22 ng/L, for the NF-200 membrane. An increase of 3 ng/L is well beyond the analytical precision of the analytical method and cannot be considered significant. Thus, it can be concluded that, in the presence of EfOM, hydrodynamic-operating conditions did not significantly affect the rejection of both hydrophilic ionic and nonionic compounds by high-pressure membranes.

It is noteworthy that the presence of EfOM also resulted in an improved rejection of ionic solutes. For the same Jo/k ratio, experiments in EfOM matrix exhibited permeate concentrations decreasing by 5 to 15 ng/L (except naproxen) for the NF-200 membrane (Figure 2b), to below 4 ng/L or nondetect for the NF-90 membrane (Figure 2d), and to below 5 ng/L or nondetect for the XLE membrane (Figure 2e). For NF-200, NF-90, XLE, and TFC-HR (see Figure 3a), rejection of negatively charged compounds increased on average from $93.5 \pm 2.3\%$, $97.1 \pm 1.4\%$, $93.5 \pm 1.0\%$, and $95.8 \pm 2.8\%$, in a type-II water matrix, to $97.7 \pm 1.0\%$, $99.3 \pm 0.3\%$, $97.2 \pm 0.6\%$, and $98.6 \pm 0.5\%$, in the presence of EfOM, respectively.

In contrast to *tight* NF and RO membranes, the *looser* NF membrane, TFC-SR2, showed a rather poor rejection of ionic solutes, despite a negatively charged membrane surface, and the presence of EfOM resulted in a decreased rejection (Figure 3b). The rejection for almost all the ionic solutes declined from $41.2 \pm 15.6\%$, in a type-II water matrix, to $32.6 \pm 23.1\%$, in an EfOM water matrix. Only the rejection of diclofenac increased by 11.5% in the presence of EfOM. For the TFC-SR2, diclofenac and gemfibrozil, with relatively large $\log K_{ow}$ and high pK_a values, exhibited rejection significantly higher (exceeding 55%) than the other compounds studied, which might be because of hydrophobic-hydrophobic interactions between the solute and the membrane surface.

The improved removal of negatively charged compounds by *tight* NF and RO membranes in an EfOM water matrix was most likely attributed to membrane-surface modification. The EfOM concentrate

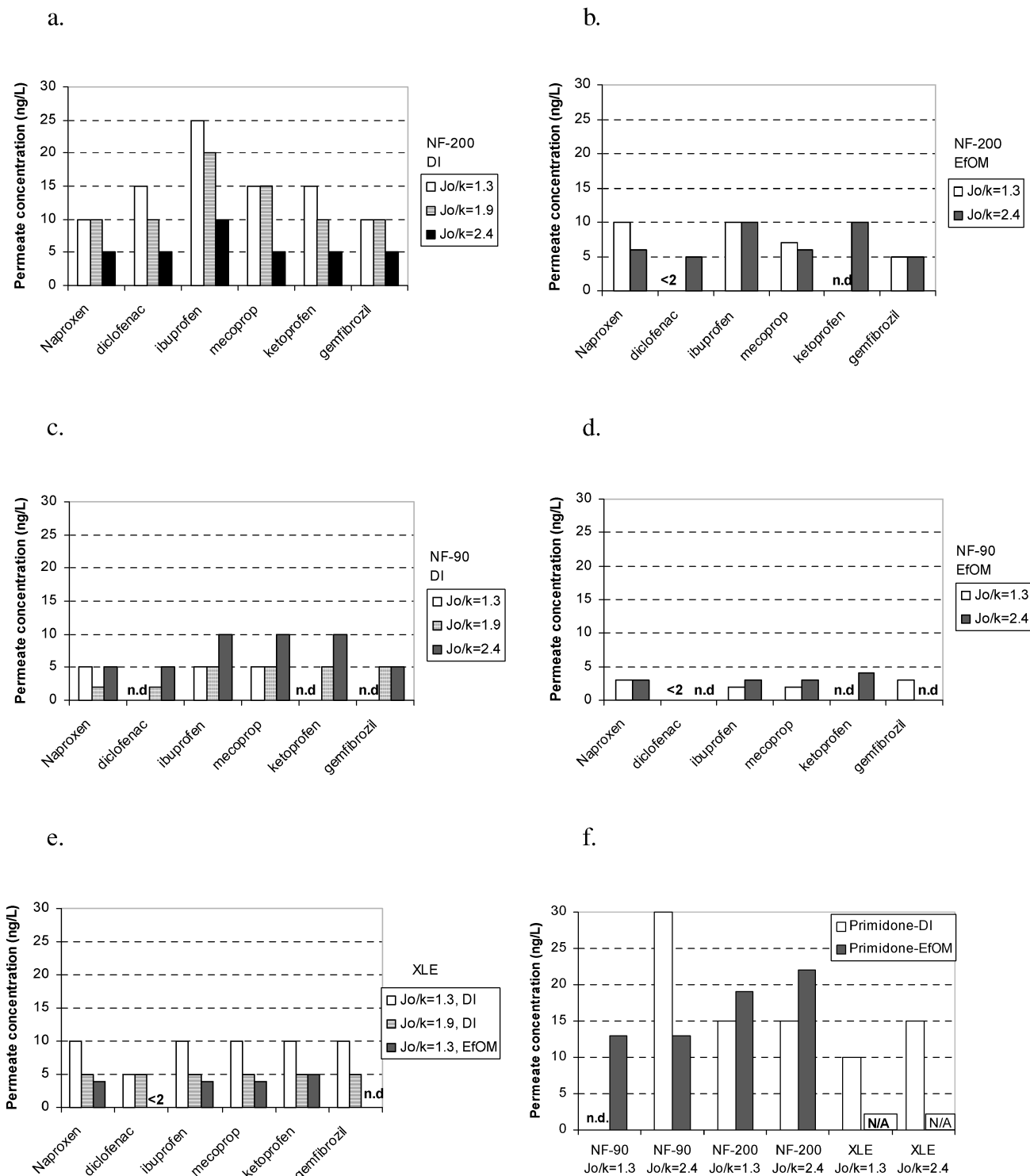


Figure 2—Permeate concentration of NF-200, NF-90, and XLE at varying Jo/k ratios in type-II water (deionized) and EfOM water matrix (nominal surrogate feed concentration 300 ng/L, pH 6.0, conductivity 750 μ S/cm, hardness 120 mg/L as $CaCO_3$, and TOC 5 mg/L for EfOM matrix).

used in the experiments represented a heterogeneous mixture of organic substances generally present in secondary treated effluent, including small colloids, natural organic matter, and soluble microbial products derived from biological wastewater treatment (Drewes and Fox, 2000). Adsorption of EfOM to a membranes

surface can cause pore clogging and a change in membrane-surface charge, resulting in an improved rejection by favoring steric and electrostatic exclusion. Thanuttamavong et al. (2002) reported that the surface charge of six virgin NF membranes exhibited almost the same level, after a fouling layer established shortly after the NF

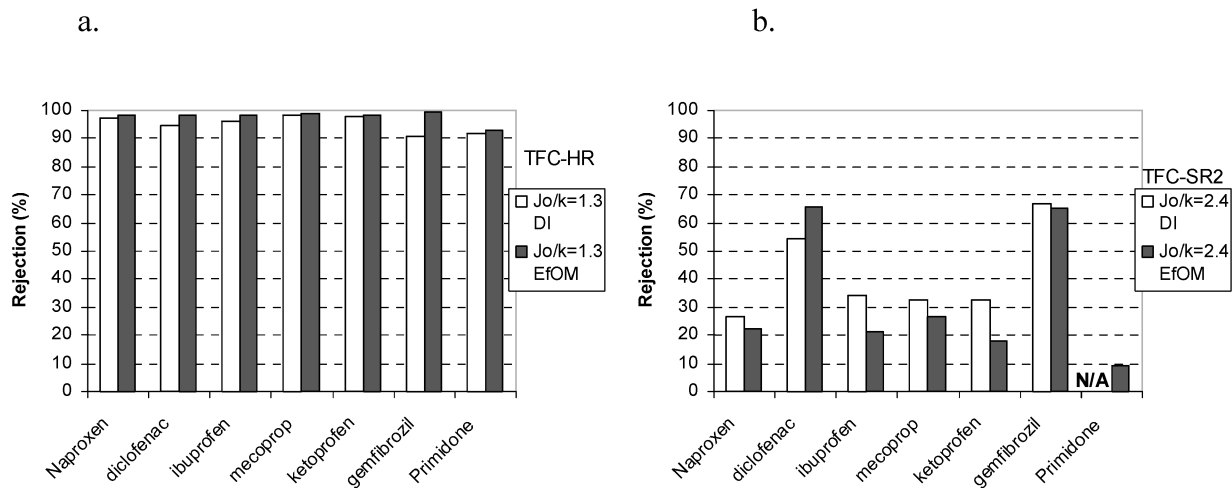


Figure 3—Rejection of trace-organic pollutants by TFC-HR and TFC-SR2 at varying Jo/k ratios and in type-II (deionized) and EfOM water matrix (nominal surrogate feed concentration 300 ng/L, pH 6.0, conductivity 750 μ S/cm, and hardness 120 mg/L as $CaCO_3$, TOC 5 mg/L for EfOM matrix).

membranes were used on surface water. Parallel bench-scale studies by the authors, using membrane specimens, demonstrated that, at pH 6.0, the zeta-potential of NF-200, NF-90, XLE, and TFC-HR membranes decreased to a similar level of -27.9 , -27.2 , -35.3 , and -29.3 mV, respectively, when the membranes were fouled by MF-treated secondary effluent.

At a Jo/k ratio of 1.3 in a type-II water matrix, experiments with negatively charged compounds of interest demonstrated that rejection and molecular solute weight or solute width are not correlated (Figure 4). This finding was expected, because electrostatic repulsion was the dominant rejection mechanism. Even though the NF-200 is considered a loose NF membrane, with a nominal MWCO of 300 Dalton, it could still achieve a reasonable rejection, exceeding 89% for low-molecular-weight compounds (such as ibuprofen with a molecular size of 206 Dalton), likely because of its highly negative surface charge (-15.3 mV at pH 6.0). This highly negative surface charge of the NF-200 and NF-90 was likely the reason why the rejection of almost all negatively charged compounds was similar to a rejection exhibited by RO membranes such as TFC-HR and XLE.

Rejection of Hydrophobic Nonionic Organic Solutes. Rejection experiments were conducted with two hydrophobic nonionic compounds (chloroform and bromoform), using the NF-90, XLE, and TFC-HR membranes. The nominal solute feed concentration was 100 μ g/L, added to an ion-strength-adjusted, type-II water matrix, and the Jo/k ratio for the experiments was kept at 1.1. Feed and permeate concentrations were monitored for 72 hours for the XLE and TFC-HR membranes and for 24 hours for the NF-90. Initially, the rejection of the two solutes was similar for all membranes tested, with the larger bromoform (253 Daltons) being rejected by 90% and chloroform (119 Daltons) by 80%, respectively (Figure 5). In addition, bromoform is more hydrophobic than chloroform, with a log K_{ow} value of 2.40, as compared to 1.97 for chloroform, which can also contribute to a higher initial removal, as a result of hydrophobic-hydrophobic solute-membrane interactions. After approximately five hours of operation, rejection of all three membranes decreased significantly and leveled off between 20 and 35% for chloroform and 35 to 45% for bromoform, respectively. The RO membrane, TFC-HR, exhibited the lowest rejection efficiency. Because the XLE membrane is more hydrophobic than the TFC-HR,

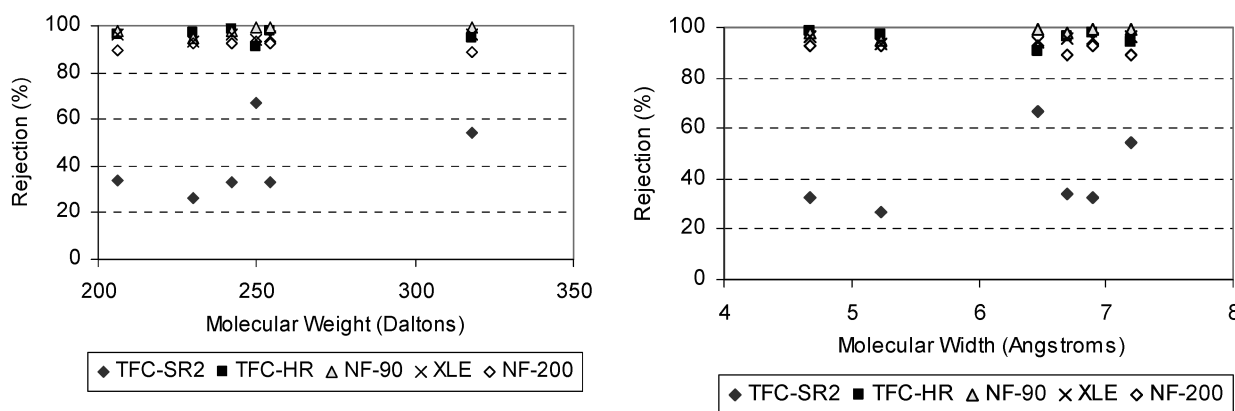


Figure 4—Rejection of negatively charged compounds vs. molecular weight and width at Jo/k ratio 1.3 in type-II water matrix (pH 6.0, conductivity 750 μ S/cm, and hardness 120 mg/L $CaCO_3$).

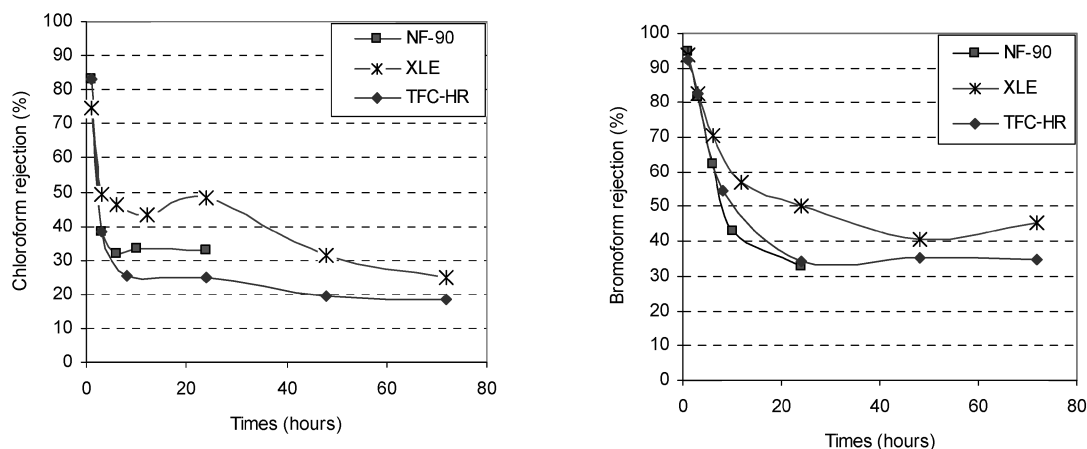


Figure 5—Rejection of chloroform and bromoform by XLE, NF-90, and TFC-HR, at varying Jo/k ratio of 1.1 and in type-II (deionized) water matrix (nominal surrogate feed concentration 100 $\mu\text{g/L}$, pH 8.0, and conductivity 600 $\mu\text{S/cm}$).

hydrophobic nonionic compounds could potentially adsorb more easily onto the XLE membrane, resulting in a higher rejection.

Similar results were reported by Schäfer et al. (2003), who found that both size exclusion and adsorption were essential to initial high retention of the hormone estrone by NF membranes. However, removal mechanisms of hydrophobic nonionic trace-organic pollutants are not well-understood when the adsorption reaches equilibrium. Bromoform had a higher rejection than chloroform, after reaching equilibrium, because of its larger molecular weight and width. The RO membrane, TFC-HR, exhibited a poorer rejection of the two solutes, as compared to the XLE, probably because of its more hydrophilic-membrane surface. A hydrophilic-membrane active layer can retain more water molecules, which might play an important role in facilitating hydrogen bonding of hydrophobic nonionic species to the membrane functional groups. Partitioning and diffusion of solutes through the membrane can, therefore, result in a lower rejection than expected, based on the solute's molecular size. These findings are consistent with Nghiem et al. (2004), who reported a low retention of natural hormones by two NF membranes at extended filtration stages, suggesting partitioning of solutes into the permeate.

Conclusions

Many trace organics, such as pharmaceutical residues, pesticides, or haloacetic acids, are dissociated at membrane-operating pH range of 6 to 8. Findings from this laboratory study indicate that *tight* NF and ULPRO membranes (MWCO of 200 Dalton and less), while operating at lower feed pressure, perform similar to conventional RO membranes, with regard to removal of emerging trace-organic pollutants. For *tight* high-pressure membranes, the membrane surface charge is more important for rejection than the MWCO, although a minimal MWCO is necessary. The presence of EfOM resulted in an improved removal of negatively charged compounds, as a result of increased membrane surface charge. Hydrophobic nonionic compounds, such as chloroform and bromoform, were only partially removed by a conventional RO membrane, such as TFC-HR. *Tight* NF and ULPRO membranes can achieve a similar and elevated degree of rejection for hydrophobic nonionic compounds dependent on the membrane surface properties.

Although it is commonly believed that an increased recovery should result in elevated permeate concentration, as a result of an

increased concentration gradient across the membranes, findings from this study imply a rather neutral or positive effect of hydrodynamic-operating conditions on the rejection of hydrophilic negatively charged and nonionic compounds in a Jo/k range of 1.3 to 2.4. This range corresponds to a recovery range of 10 to 25%, typically achieved by individual spiral-wound-membrane element used in two- and three-stage trains at full-scale applications. Furthermore, the presence of EfOM seems to completely neutralize the influence of hydrodynamic conditions on rejection performance of high-pressure membranes.

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