

Rejection of Trace Organic Compounds by Reverse Osmosis and Nanofiltration Membranes

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I. INTRODUCTION

The objective of this study is to develop a mechanistic understanding of the rejection of trace organic compounds by high-pressure membranes, based on an integrated framework of compound properties, membrane properties, and operational conditions. High-pressure membranes, encompassing reverse osmosis (RO), low-pressure RO (LPRO), and nanofiltration (NF), may provide an effective treatment barrier for representative trace organic compounds including disinfection by-products (DBPs; e.g., trichloroacetic acid, bromoform), chlorinated solvents (e.g., trichloroethylene, carbon tetra chloride), endocrine disrupting chemicals (EDCs; e.g., 17 β -estrodial, bisphenol-A), and pharmaceutically active compounds (PhACs; e.g., ibuprofen, carbamazepine). These compounds are being emphasized during our research, for comparison purposes, based on considerations of compound properties, occurrence, and health effects.

About five RO membranes (e.g., LE-440, XLE-440) and about two NF membrane (e.g., NF-90), provided by several companies, were and will be characterized according to pure water permeability (PWP), molecular weight cutoff (MWCO), hydrophobicity (contact angle), and surface charge (zeta potential). In bench-scale experiments, solute rejections are determined with pure water (Milli-Q) as well as synthetic feed-waters with adjusted pH and ionic strength.

Stirred cell tests are being performed as dynamic adsorption tests, with results compared against static (isotherm) adsorption tests to describe solute partitioning into the membrane. The experimental approach of bench-scale cross-flow tests with flat-sheet specimens involves determining rejections from synthetic waters over a range of Jo/k ratios and/or recoveries. It is noteworthy that rejections of compounds of intermediate hydrophobicity by candidate membranes were observed to be less than salt rejections reported for these membranes, suggesting that transport of these solutes through these membranes is facilitated by solute-membrane interactions. Diffusion cell measurements are being performed using actual membrane specimens to determine “hindered” or “facilitated” diffusion coefficients that, when compared to solute diffusion coefficients in water, describe hindered or facilitated solute transport through a membrane.

Data derived from cross-flow and diffusion cell tests will be used as a basis in formulating a solute transport model, delineating transport by convection versus diffusion. In addition, the role of hydrogen bonding and the influence of membrane fouling are being further explored. To date, we have observed greater rejection of (negatively) charged compounds than neutral compounds, and greater rejection of non-polar than polar compounds.

II. BACKGROUND

In both drinking water treatment and wastewater reclamation, there are concerns about the occurrence and potential health effects of trace organic compounds including disinfection by-products (DBPs), pesticides, solvents, and new emerging contaminants such as endocrine disrupting compounds (EDCs) and pharmaceutically active compounds (PhACs). Enhanced coagulation can remove more hydrophobic polar and larger molecular weight compounds, but it is difficult to remove

more hydrophilic and smaller molecular weight compounds by chemical methods. Furthermore, compounds such as persistent organic pollutants (POPs) are often less biologically degradable and remain after biological wastewater treatment. High-pressure membranes, encompassing reverse osmosis (RO), low-pressure RO (LPRO), and nanofiltration (NF), may provide an effective treatment barrier for these compounds, occurring at $\mu\text{g/L}$ to ng/L levels. Of the indicated groups of compounds, a significant knowledgebase exists only for pesticides.

Relatively few studies have focused on DBPs removal by RO and NF. Some researchers have studied NF for removing organohalides or precursor compounds from drinking water (Ducom and Cabassud, 1999). Chellem and Taylor (2001) have reported that diffusion might play an important role in the transport of molecules across NF membranes based on rejection data for DBP precursors. Hofman *et al.* (1993) and Van der Bruggen *et al.* (1998) have studied the rejection of POPs by several NF membranes. Bonné *et al.* (2000) reported good results in pilot studies using RO membranes. Kiso *et al.* (2001) confirmed that molecular size parameters such as molecular width, Stokes radii and molecular mean size are better predictors of steric hindrance effects on the rejection of POPs by NF membranes than molecular weight. Agenson *et al.* (2003) recently examined rejection mechanisms by NF membranes for organic solutes including EDCs. They proposed a theory based on structural features and polarity of solute molecules. A pore model proposed and developed by Sourirajan and Matsuura (1985) was based on cellulose acetate (CA) rejection of PhACs; however, their use of membranes in a non-aqueous medium (e.g., methanol) is limited to prediction of solvent sorption and permeation. Koops *et al.* (2001) published rejection behavior in a non-aqueous medium using CA. Bhanushali *et al.* (2002) also examined the affinity of solute and solvent type for the membrane material and its impact on rejection for aqueous and non-aqueous systems.

III. MATERIALS AND EXPERIMENTAL METHODS

A. Materials and Chemicals

Environmental Protection Agency (EPA) sample vials (40 mL) with a screw cap lined with Teflon were used for sample collection and extraction. Autosampler vials used were 2.0 mL amber glass vials with a crimp cap and a Teflon-faced seal. Disposable Pasteur pipettes (9 inch) were used to transfer extracted samples. Micropipettes (10-100 μL , 100-1000 μL , and 1-5 mL) with disposable tips were obtained from Fisher Scientific (USA). A mini-vortexer (VWR Scientific, USA) was used as an orbital mixer. A Brinkmann bottle top dispenser was used for adding solvent. An analytical balance (Mettler Toledo AT201), capable of weighing to 0.01 mg, was used in weighing chemicals. A diazomethane reaction chamber was used in a step for HAAs analysis.

Bromoform (BF), Perchloroethene (PCE), Carbon tetrachloride (CT), Carbon tetrabromide (CTB), and Dichloroacetic acid (DCAA) were obtained from Aldrich (USA). Chloroform (CF), Trichloroethene (TCE), and Trichloroacetic acid (TCAA) were purchased from Fisher Scientific. Ibuprofen (α -Methyl-4-(isobutyl)phenylacetic acid) were purchased from Sigma. Standard stock solutions were prepared, for example, by dissolving 5 mL (7.46 mg) of CF and 1 mL (2.89 mg) of BF in 1 L Milli-Q water, respectively, until saturation. Relevant compound properties are summarized in Table 1; where property data are unavailable, a quantitative structure-activity relationship (QSAR) software package (e.g., EPI Suite developed by EPA (Log K_{ow}) or ChemOffice 2002 of Cambridge Soft (Dipole)) is being used to develop estimates. D_w (diffusion coefficient in water) values are calculated from the Hayduk and Laudie method (Schwarzenbach *et al.*, 1993):

$$D_w = \frac{13.26 \times 10^{-5}}{\mu^{1.14} \cdot (\bar{V})^{0.589}} \quad (\text{cm}^2/\text{s}) \quad (1)$$

where μ is the viscosity of water (1.002) at 20 °C, and \bar{V} is molar volume of compounds calculated by molecular weight (g/mol) divided by liquid density of compound (g/cm^3). Unknown liquid density values are calculated by Grain's Method (Lyman *et al.*, 1990).

Table 1. Properties of selected compounds

Compound	MW (g/mol)	Log K _{ow}	D _w (x 10 ⁻⁵ cm ² /s)	Dipole (Debye*)	Molar Volume (\bar{V}) (cm ³ /mol)	pK _a
CF	119	1.97	1.00	1.120	80	N/A
BF	253	2.40	0.95	0.995	87	N/A
TCE	131	2.29	0.94	0.946	90	N/A
PCE	165	3.40	0.87	0.108	102	N/A
DCAA	129	0.92	0.98	2.396	82	1.48
TCAA	163	1.33	0.89	1.499	100	0.70
CT	154	2.83	0.90	0.295	96	N/A
CTB	332	3.42	0.82	0.011	112	N/A
IBP	206	3.97	0.75	1.292	130	4.91

*Debye unit = 3.33564 x 10⁻³⁰ C-m

Anhydrous sodium sulfate and sodium chloride were obtained from Fisher Scientific. Potassium hydroxide, potassium chloride, and a buffer solution based on potassium phosphate, used for water quality maintenance, were also purchased from Fisher Scientific. 1-methyl-3-nitro-1-nitrosoguanidine (MNNG) and Silica gel (35-70 mesh) was obtained from Aldrich. Sulfuric acid was purchased from Mallinckrodt Chemicals (USA). Methyl tert-Butyl Ether (MtBE), used for analysis, and HPLC grade methanol were obtained from Fisher Scientific.

B. Experimental Methods

Membranes Properties Tests

To date, the four FilmTec membranes tested are BW-400, LE-440, XLE-440, and NF-90; the former three membranes are RO membranes. These membranes are composed of MPD (Metaphenylene diamine (Benzene-1,3-diamine)) and TMC (Trimesoyl chloride (1,3,5-Benzenetricarbonyl trichloride)). Membrane properties were determined by different methods. Membrane hydrophobicity was characterized by contact angle measurement. A stirred cell filtration unit (Amicon) was used to test disk specimens of membranes in a dead-end mode for determining the MWCO of membranes using polyethylene glycols (PEGs), done only for the NF membrane (NF-90). The PWP of each membrane was measured, reflecting the capacity for water to pass through the membrane normalized by transmembrane pressure. For study of electrokinetic properties, an electrophoresis method for zeta potential measurement has been used with ELS-8000 (Otsuka Electronics, Japan); in the electrophoresis cell consisting of membrane and quartz cells, asymmetric electroosmotic flow occurs due to the accumulation of ions on the membrane surface during the electrophoresis method (Shim *et al.*, 2002). A summary of membrane properties is presented in Table 2 and wider ranges of membranes are considered for the expanded scope (Table 3).

Table 2. Summary of FilmTec membrane properties

Membrane name		BW-400	LE-440	XLE-440	NF-90
Type		RO	RO	LPRO	NF
Rejection from manuf. (FilmTec)	NaCl (%)	98	98	98	90
Rejection from manuf. (FilmTec)	Sucrose (%)	99.9	99.9	99.9	99+
Net driving pressure from manuf.*	psi (kPa)	203 (1400)	203 (1400)	103 (710)	70 (480)
MWCO from manuf.		N/D	N/D	N/D	200
Operating press. (experimental)**	psi (kPa)	90 (620)	80 (550)	60 (410)	40 (280)
MWCO (PEG test)		N/D	N/D	N/D	400
Contact angle	Degrees (Stdev.)	56.8 (2.3)	41.5 (0.5)	39.8 (2.6)	59.8 (2.5)
Zeta potential at pH 8 (10mM KCl)	mV (Stdev.)	-4.49 (1.97)	-23.02 (1.25)	-19.42 (2.48)	-30.76 (0.78)
Pure water permeability (PWP)	L/day m ² kPa	0.68	0.77	0.92	2.23
Jo (based on operating pressure)	L/m ² hr	18	18	16	26

*Pressure at pilot or plant ** Basis for $Jo/k \approx 1$

Table 3. Additional Membranes

Company		Saehan		Toray
Membrane		RE-BLR	NE-90	UTC-70
Type		RO	NF	LPRO
Operating press. (experimental)*	psi (kPa)	70 (480)	35 (240)	50 (340)
Pure water permeability (PWP)	L/day m ² kPa	0.77	2.17	0.99
Jo (based on operating pressure)	L/m ² hr	15	22	14

*Basis for $Jo/k \approx 1$

Membrane Filtration Tests

Using a stirred cell (Figure 1) for dynamic adsorption tests, a 4 L feed reservoir was employed to provide a continuous supply of feed water, with pressure applied to the reservoir. Water flux was monitored until it became stable. Feed water was then introduced to the membrane filtration unit with 26 cm² membrane for 100 hrs. The permeate flux was monitored as a function of delivered solute, defined as a summation of feed mass per unit area of membrane. A 4 L Erlenmeyer flask was used for static adsorption tests (isotherm tests). A 57 cm² membrane was placed into 4 L water, simultaneously spiking target compounds (Figure 2). For example, initial concentrations of BF were 0, 0.08, 0.16, 0.25, and 1.12 mg/L, and contact time was 100 hrs.

A membrane filtration unit accommodating flat sheet specimens (Osmonics, USA) was used for cross-flow tests, being composed of a polymeric membrane, a membrane holder, pumps with a gear type pump head, needle valves (for the feed, retentate, and permeate streams), and pressure and flow meters. Either varying the pump head speed or controlling the needle valve in the retentate stream controlled the feed flow rate, the corresponding cross-flow velocity, and the trans-membrane pressure. The feed water temperature was maintained in the range of 20-25 °C. The cross-flow system shown in Figure 3 has been used to perform the bench-scale rejection experiments. The Osmonics system consists of a 120 L reservoir from which a small, variable speed gear pump provides feed to the test cell. The total membrane surface area in the test cell is approximately 135.8 cm² and the total cross flow area in the test cell is approximately 1.45 cm². Permeate and retentate are not recirculated but wasted in the experiments; thus, the experiments are performed on a once-through basis. Changes in pressure permitted variation of the Jo/k ratio, a hydrodynamic condition embodying initial flux (Jo) toward the membrane and back-diffusion (k , mass transfer coefficient, a function of diffusion coefficient and cross-flow velocity) away from the membrane (Cho *et al.*, 2000). The Jo/k ratio is also related to concentration polarization, with greater concentration polarization at higher Jo/k ratio.

$$J_o = \frac{Q_p}{A_h} \quad (\text{cm/s}) \quad (2)$$

$$U = \frac{Q_t}{A_v} \quad (\text{cm/s}) \quad (3)$$

$$k = 1.62 \left(\frac{UD_w^2}{2hL} \right)^{0.33} \quad (\text{cm/s}) \quad (4)$$

where Q_p is the permeate flux (cm³/s); A_h is the horizontal area of channel (the membrane surface area) (cm²); U is the cross-sectional velocity of feed; Q_t is total feed flux (cm³/s); A_v is the vertical area of channel (cm²); h is the channel height (cm); L is the channel length (cm); D_w is the diffusion coefficient of solute in water obtained by equation (1) (cm²/s). The system recovery ratio ($Q_p/Q_f = \sim 10\%$) was managed through the use of needle valves. The flow rate of retentate and permeate was monitored by measuring volume in a graduated cylinder over time. The pressures of the feed and retentate were assumed to be equal and were measured by a pressure sensor.

A diffusion cell (Figure 4) is being employed to determine solute diffusion coefficients through pores (D_p) in actual membrane specimens, with either hindered or facilitated transport compared to diffusion in water at room temperature. The diffusion cell is a two-chamber glass cell with a membrane separating the left (feed) and right (permeate) cells. The exposed membrane area in the cell is 54 cm^2 . At the beginning of the experiment, Cell A was filled with solute solution (e.g. BF) in the presence of $300 \text{ }\mu\text{S/cm}$ at pH 8, while Cell B was filled with water with the same properties. Solute-saturated (5 days) membranes were used due to adsorption. Samples were taken from the feed and permeate cells over the experimental period (every 5 days for 20 days) to measure solute concentration. The model used in analysis of diffusion experiment data is a pseudo steady state application of Fick's Law (Yoon *et al.*, 2003). The solution diffuses across the membrane from the feed cell to the permeate cell because of the concentration gradient. The diffusion coefficient of solute through the membrane (D_p) can be calculated by:

$$C_{B(t)} - C_{A(t)} = [C_{B(t_0)} - C_{A(t_0)}] \exp \left[-A \frac{D_p}{\delta_m} \left(\frac{1}{V_B} + \frac{1}{V_A} \right) t \right] \quad (5)$$

where C_B is the concentration in the fluid adjacent to the permeate surface of the membrane in diffusion cell (mol/L), C_A is the concentration in the fluid adjacent to the feed surface of the membrane in diffusion cell (mol/L), D_p is the hindered/facilitated diffusion coefficient of solute in/through membrane pores (cm^2/s), δ_m is the membrane thickness (cm), A is membrane area (cm^2), V_A is the volume of feed side of the membrane in diffusion cell (cm^3), V_B is the volume of the permeate side of the membrane in diffusion cell (cm^3), and t is the time during the test period (s).

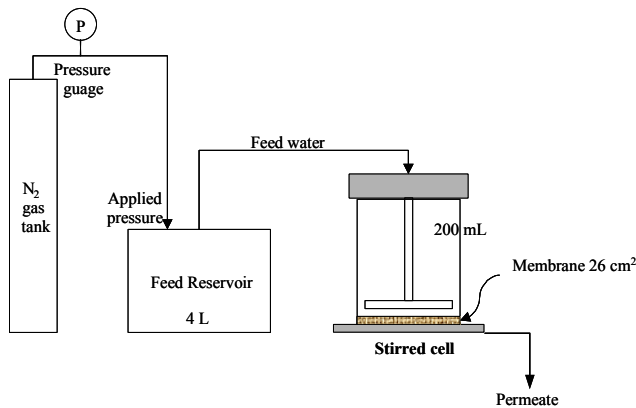


Figure 1. Stirred cell unit (Amicon)

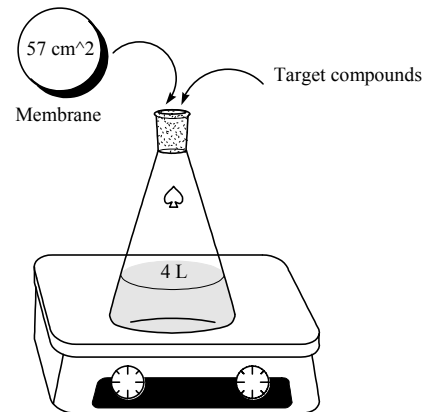


Figure 2. Isotherm tests unit

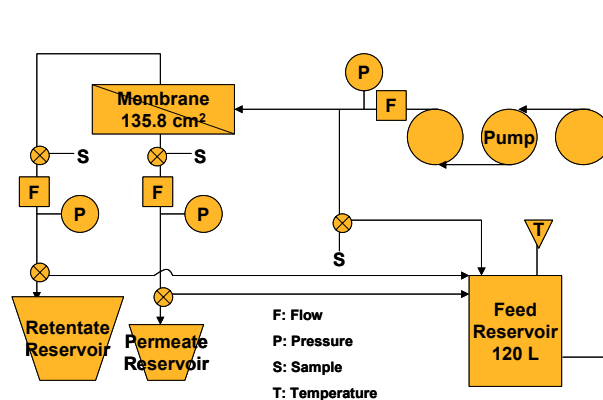


Figure 3. Cross-flow system (Osmonics)

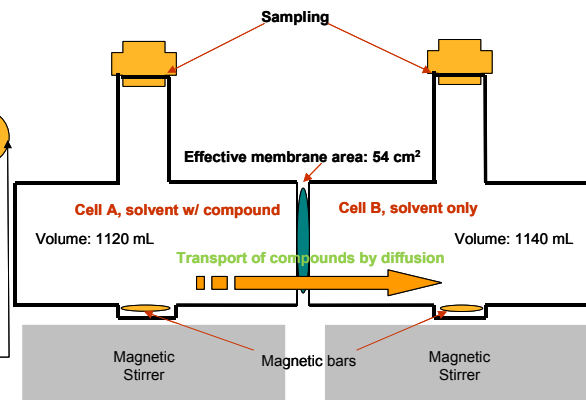


Figure 4. Diffusion cell unit

C. Estimation of Solute Transport by Thermodynamic Model

The non-equilibrium thermodynamic transport equation is composed of two driving forces, convection and diffusion, combining observations about molecular transport, osmotic pressure, molecular reflection, average bulk fluid, and solvent transport through membrane (Kedem and Katchalsky, 1958; Tandon *et al.*, 1997; Yoon *et al.*, 2003):

$$J_s = \text{Diffusion} + \text{Convection} = \omega \Delta \Pi + (1 - \sigma) C_{avg} J_v \quad (6)$$

where J_s is the solute flux (mol/m²-s) occurring due to diffusion and convection, ω is the molecular transport coefficient (solute permeability) (mol/m²-s-Pa), $\Delta \Pi$ is the osmotic pressure gradient (Pa), σ is the molecular reflection coefficient (dimensionless), C_{avg} is the bulk fluid interfacial concentration between feed and permeate side (mol/m³), and J_v is the solvent flux (m³/m²-s).

In the diffusion term, ω is a function of the hindered diffusion coefficient (D_p) measured by the diffusion cell tests. It is important to directly measure the hindered diffusion of target solutes by the diffusion cell because the D_p is significantly affected by ionic radius, ion charge, membrane surface charge, membrane pore size, membrane pore density, and membrane thickness. The molecular transport coefficient (solute permeability, ω) can be given by:

$$\omega = \frac{D_p}{\delta_m} \frac{1}{RT} = \frac{D_w H}{\delta_m} \frac{1}{RT} \quad (7)$$

where D_p is the hindered/facilitated diffusion coefficient in membrane pores (cm²/s), D_w is the diffusion coefficient in water (cm²/s) through non-charged porous material, H is the hindered/facilitated coefficient at the membrane interfaces (dimensionless), δ_m is the effective thickness of the membrane (m) (separation plus support layer), R is the gas constant (J/mole-K), and T is the absolute temperature (K).

The osmotic pressure influencing solute transport by diffusion arises when a semi-permeable membrane separates two solutions of different concentration. The osmotic pressure gradient, $\Delta \Pi$, is calculated by:

$$\Delta \Pi = RT \left(\sum C_s^{feed} - \sum C_s^{perm} \right) \quad (8)$$

where C_s^{feed} is the total solute concentration in feed side (mol/m³) and C_s^{perm} is the total solute concentration in permeate side (mol/m³) in diffusion cell tests.

The other factors are obtained from cross-flow tests. The average bulk fluid interfacial concentration, C_{avg} , between the feed at the membrane surface and the permeate is the mean logarithmic concentration and is given by:

$$C_{avg} = \frac{(C_m - C_p)}{\ln \left(\frac{C_m}{C_p} \right)} \quad (9)$$

where C_m is the feed concentration of the membrane surface (mol/m³) and C_p is the permeate concentration (mol/m³). The increase in concentration of solute at the membrane surface influences their transport through the membrane. The solute feed concentration on the membrane surface is calculated from the concentration polarization (Taylor and Jacobs, 1996) and given by:

$$\left(\frac{C_m - C_p}{C_b - C_p} \right) = \exp \left(\frac{J \cdot \delta}{D_w} \right) \quad (10)$$

where C_b is the feed (bulk) concentration (mol/m³), J is the pure water flux (m/s), δ is the thickness of the boundary layer (m), and D_w is the diffusion coefficient of the solute in pure water (infinite solution) (m²/s). δ is the boundary layer where the solute concentration increases and reaches a maximum value at the membrane surface. It is calculated by:

$$\delta = \frac{D_w}{k} \quad (11)$$

where k is membrane permeability coefficient for solute (m/s). This mass transfer occurs where solute concentration increases at the membrane surface.

The solvent flux, J_v , is experimentally measured and is described as:

$$J_v = L_p(\Delta P - \sigma_r \Delta \Pi) = \left(\frac{Q_p}{A \cdot \Delta P} \right) (\Delta P - \sigma_r \Delta \Pi) \quad (12)$$

where L_p is the filtration coefficient (hydraulic permeability) ($\text{m}^3/\text{m}^2\text{-s-Pa}$) and ΔP is the differential pressure (Pa). The time dependent rejection is used instead of σ_r .

The reflection coefficient in Equation (6), σ , represents a measure of the selectivity of a membrane and usually has a value between 0 and 1. Solute transport by convection does not occur when σ is equal to one. There is no selectivity when σ is equal to zero. Experimentally determined parameters, measured J_s ($=J_{s\text{-measured}} = C_p \cdot Q_p/A$), C_{avg} , and J_v under varying pH and conductivity conditions, were used to determine the reflection coefficient by nonlinear estimation with a three dimensional plot of $J_{s\text{-measured}}$ versus C_{avg} versus J_v . The equation was solved using STASTICA (5.5 version, StatSoft, Inc.) (Yoon, 2001).

After comparing the calculated J_s with $J_{s\text{-measured}}$, the difference between them is indicative of the hindrance of solute flux by adsorption of compounds. The calculated J_s will be obtained by equation (6) with calculated σ and measured other factors.

D. Analytical Methods

Dissolved organic carbon was measured by a Sievers 800 portable total organic carbon analyzer (TOC) with auto sampler. The concentrations of IBP are determined by a fluorometer (Hitachi F-3010, Japan). For DBPs analysis, gas chromatography (GC) was used with an HP 6890 series GC system with a micro electron capture detector (GC-ECD), an HP 7683 autoinjector, an autosampler tray module, and an HP PC. A DB-1 capillary column coated with dimethylpolysiloxane ($30 \text{ m} \times 0.25 \text{ mm} \times 1 \text{ }\mu\text{m}$) was employed.

CF, BF, TCE, PCE, CT, and CTB were extracted and concentrated by using U.S. EPA method 551.1 (1995). The extraction and concentration of DCAA and TCAA followed standard method 6251B (1998).

As analytical conditions, nitrogen was used as the carrier gas at 30 cm/sec, the injection temperature of the GC-ECD for THMs and chlorinated solvents analysis 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 μL sample using the auto injector module. In the case of DCAA and TCAA, the oven temperature was programmed in the order of 44 °C (1 min), 95 °C at 3 °C/min, 140 °C at 5 °C/min, and 180 °C at 20 °C/min. The splitless mode was used in HAAs analysis with gas saver of 20.0 mL/min for 2 min. The electron capture detector was operated in the scan mode. Data collection was accomplished with HP Chemstation software.

IV. RESULTS AND DISCUSSIONS

Preliminary results have been derived from four (FilmTec) membranes and eight compounds (CF, BF, DCAA, TCAA, TCE, PCE, CT, and CTB). These results support some of our original hypotheses including: (i) a high rejection of DCAA and TCAA can be attributable to transport hindrance by electrostatic interaction (repulsion); (ii) higher rejection of BF over CF can be attributable to greater steric hindrance to transport based on MW; and (iii), however, lower rejection of CF vs. CT, BF vs. CTB, and TCE vs. PCE can be attributed to competition between hydrophobic-hydrophobic interaction and dipole-dipole interaction with the membranes.

A summary of 24hr-rejections with some chemical properties assembled to date is presented in Table 4. Figure 5 summarizes results for LE-440 and NF-90, for example, and six compounds at pH 8 and 300 $\mu\text{S/cm}$. Similar trends happened with other membranes. It can be seen that the trends of rejection of CT, CTB, and PCE are different from those of the other three compounds. Thus, it is

apparent that the trends of rejection of CT, CTB and PCE are better than those of the other three compounds, all of which contain a hydrogen. Graphs of 24 hour rejection versus log K_{ow} were drawn with a linear relationship observed, as shown in Figure 6.

Table 4. Summary of 24hr-rejection with chemical properties to date (at pH 8 and 300 $\mu\text{S}/\text{cm}$)

COMPOUND	MW	Log K_{ow}	D_w ($\times 10^{-9} \text{m}^2/\text{s}$)	pK_a	24hr- Rejection (%)						
					BW-400	LE-440	XLE-440	NF-90	RE-BLR	NE-90	UTC-70UB
CF (CHCl_3)	119	1.97	1.00	N/A	31	18	13	0	28	1	6
TCE (C_2HCl_3)	131	2.29	0.94	N/A	37	31	23	3	48	3	8
BF (CHBr_3)	253	2.40	0.95	N/A	40	45	42	17	68	35	44
CT (CCl_4)	154	2.83	0.82	N/A	89	77	79	55	92	57	84
PCE (C_2Cl_4)	165	3.40	0.87	N/A	94	95	91	78	98	87	71
CTB (C_2Br_4)	332	3.42	0.78	N/A	98	92	89	82	99+	79	79

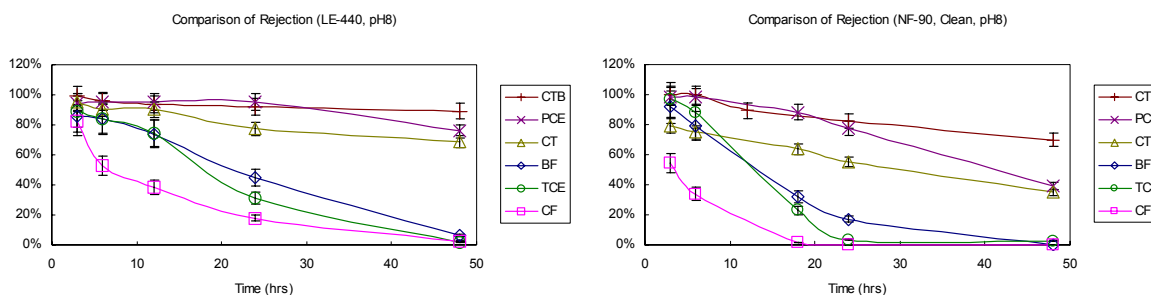


Figure 5. Comparison of cross-flow tests of six compounds at pH 8 and 300 $\mu\text{S}/\text{cm}$ according to LE-440 (Left) and NF-90 (Right)

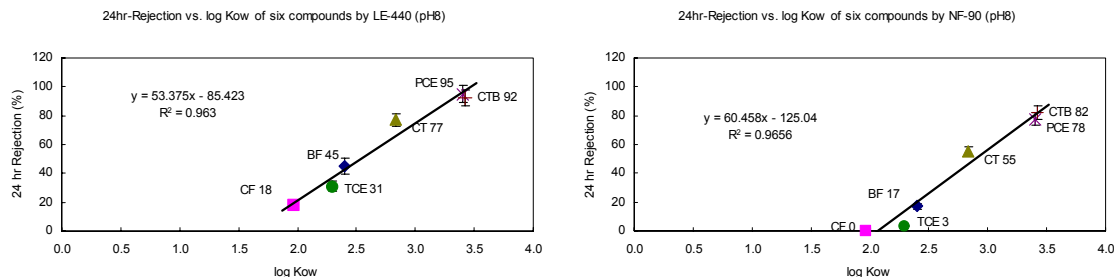


Figure 6. Comparison of 24 hr rejection of six compounds at pH 8 and 300 $\mu\text{S}/\text{cm}$ versus log K_{ow} according to LE-440 (Left) and NF-90 (Right)

Figure 7 illustrates 24hr rejection vs. Dipole (Debye) (at pH 8 and 300 $\mu\text{S}/\text{cm}$). The order of dipole is $\text{CTB} < \text{PCE} < \text{CT} < \text{TCE} \leq \text{BF} < \text{CF}$, but that of 24hr-rejections is $\text{CTB} > \text{PCE} > \text{CT} > \text{BF} \geq \text{TCE} > \text{CF}$ by four membranes at pH 8. Based on their Dipole, the compounds can be separated into two groups, CT, PCE, and CTB versus CF, BF, and TCE. In addition, 24hr rejections vs. molar (molecular) volume (cm^3/mol) are interpreted in Figure 8. Molar volume (cm^3/mol) is obtained by equation (1) on page 5. It can be used instead of molecular width as a molecular size parameter. The order of molecular volume is $\text{CTB} > \text{PCE} > \text{CT} > \text{TCE} \geq \text{BF} > \text{CF}$, and that of 24hr rejections is $\text{CTB} > \text{PCE} > \text{CT} > \text{BF} \geq \text{TCE} > \text{CF}$. It is noteworthy that the molar volumes of TCE and BF are very similar ($90 \text{ cm}^3/\text{mol}$: $87 \text{ cm}^3/\text{mol}$), while their MWs are quite different (MW of BF (253) is about twice than that of TCE (131)).

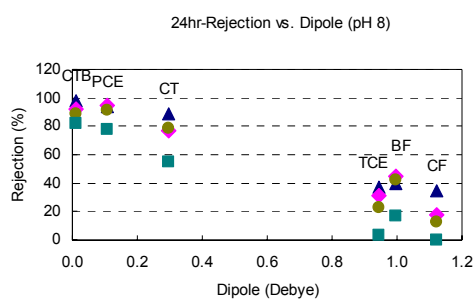


Figure 7. Comparison of 24hr-rejection vs. dipole of six compounds at pH 8 by four membranes

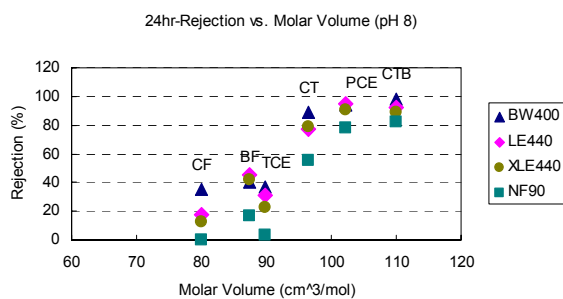


Figure 8. Comparison of 24hr-rejections vs. molar volume of six compounds at pH 8 by four membranes

Besides the neutral DBPs and chlorinated solvents, experiments were run with ionizable DBPs, DCAA and TCAA, for which electrostatic interactions embodied by membrane zeta potential are expected to be influential. Rejections of DCAA and TCAA (feed concentration of 0.1 mg/L) were high and consistent over time (Figure 9). To probe the rejection mechanism of electrostatic exclusion, experiments were also performed with IBP, anionic under typical pH conditions. High rejections were observed for all four negatively-charged membranes. As a reference, properties of IBP are: MW (206.29), D_w (0.52×10^{-5} cm²/s or 5.2×10^{-10} m²/s), and pK_a (4.91). In addition, standard operating conditions are pH 8, 300 μ S/cm, 10% Recovery, and 100 μ g/L feed concentration. Each sample was analyzed by Fluorescence Spectrophotometer (Hitachi F-3010) at excitation 222 nm and emission 288 nm. Figure 10 shows comparison of cross-flow test results by four membranes.

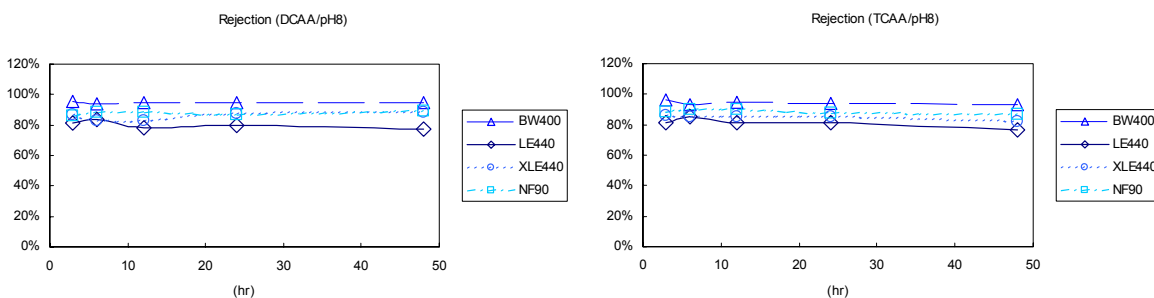


Figure 9. Comparison of cross-flow tests by four membranes at pH 8 according to DCAA and TCAA

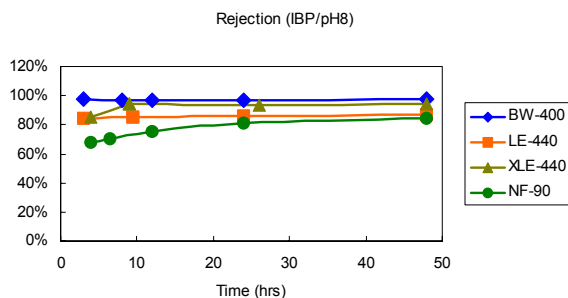


Figure 10. Comparison of cross-flow tests by four membranes at pH 8 according to IBP

It is noteworthy that rejections of compounds of intermediate hydrophobicity by the candidate membranes were observed to be less than salt rejections reported for these membranes, suggesting that transport of these solutes through these membranes is facilitated by solute-membrane interactions. Through diffusion cell tests, the diffusion coefficient of BF through membrane pores (D_p) was determined to be $6.5E-8$ cm^2/sec for the LE-440 (RO) membrane; for reference, the diffusion coefficient in water of BF is $9.5E-6$ cm^2/sec (Schwarzenbach *et al.*, 1993). With the same method, a D_p value of $4.1E-8$, $1.0E-8$ and $3.0E-9$ cm^2/sec was determined for CTB, IBP, and TCAA with a D_w value of $8.2E-6$, $7.5E-6$, and $8.9E-6$ cm^2/sec , respectively (Table 5 and Figure 11). Both BF and CTB exhibit adsorption phenomena, but CTB appears to adsorb only to the membrane surface, not being transported through the membrane. This is supported by a high-concentration feed experiment of CTB with good rejection even after 48 hrs. Therefore, it is evident that BF (neutral) is adsorbed into, transported through, and desorbed from the RO and NF membranes tested (Ducom and Cabassud, 1999) because of intermediate hydrophobicity and dipole-dipole interaction, while CTB (neutral) is adsorbed on surface but is not desorbed through membrane because of both a relative large molecular weight and hydrophobic-hydrophobic interaction, and IBP (negatively charged at pH 8) and TCAA (negatively charged) is rejected well because of charge. Meanwhile, D_p values of $7.8E-8$, $5.4E-8$, $9.2E-9$, and $5.5E-9$ cm^2/sec were determined for the NF-90 (NF) membrane in experiments with BF, CTB, IBP, and TCAA, respectively (the rejection order is $\text{BF} < \text{CTB} < \text{IBP} < \text{TCAA}$). Summary and comparison of D_p of BF, CTB, IBP, and TCAA by four membranes through diffusion cell tests are represented in Table 5 and Figure 11. In addition, Table 6 and Figure 12 interpret H (the hindrance factor) of BF, CTB, IBP, and TCAA by four membranes through diffusion cell tests.

Table 5. Summary of D_p of BF, CTB, IBP, and TCAA by four membranes through Diffusion cell tests

(cm^2/sec)	D_w	D_p (BW-400)	D_p (LE-440)	D_p (XLE-440)	D_p (NF-90)
BF	9.5E-06	6.3E-08	6.5E-08	7.1E-08	7.8E-08
CTB	8.2E-06	4.1E-08	4.1E-08	4.4E-08	5.4E-08
IBP	7.5E-06	9.6E-09	1.0E-08	1.1E-08	9.2E-09
TCAA	8.9E-06	3.7E-09	3.0E-09	3.1E-09	5.5E-09

Table 6. Summary of H of BF, CTB, IBP, and TCAA by four membranes through Diffusion cell tests

	D_p/D_w (BW-400)	D_p/D_w (LE-440)	D_p/D_w (XLE-440)	D_p/D_w (NF-90)
BF	6.6E-03	6.8E-03	7.5E-03	8.2E-03
CTB	5.0E-03	5.0E-03	5.4E-03	6.6E-03
IBP	1.3E-03	1.3E-03	1.5E-03	1.2E-03
TCAA	4.2E-04	3.4E-04	3.5E-04	6.2E-04

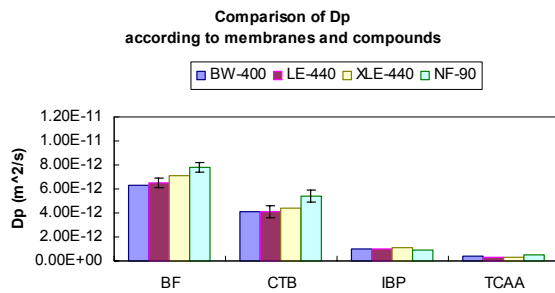


Figure 11. Diffusion cell tests – Comparison of D_p of BF, CTB, IBP, and TCAA by four membranes

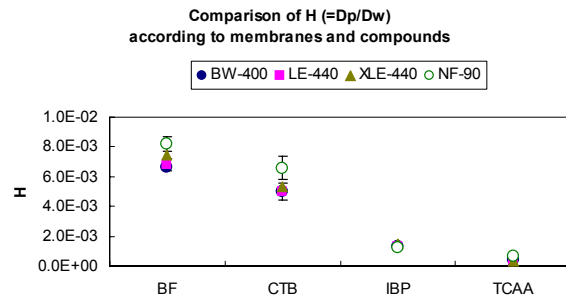


Figure 12. Diffusion cell tests – Comparison of H of BF, CTB, IBP, and TCAA by four membranes

After cross-flow tests and diffusion cell tests of BF (hydrophobic and polar), CTB (hydrophobic and neutral), IBP (hydrophobic and charged at pH 8), and TCAA (hydrophilic and charged), modeling efforts were performed, following equation (6). Figures 13 to 16 show comparisons of predicted solute flux ($J_{s\text{-predicted}}$) and measured solute flux ($J_{s\text{-measured}}$). It is a challenge to determine a third term to account for the difference between $J_{s\text{-predicted}}$ and $J_{s\text{-measured}}$, especially, in BF and CTB experiments even though, for example, the difference is as low as $1.3\text{E-}9$ mol/m²-sec (2.9 μg/cm²-day) for 24 hrs in case of BF by LE-440. The difference is expected to include adsorption because the adsorbed mass of BF in cross-flow tests by LE-440 was 3.3 μg/cm²-day after 24 hrs.

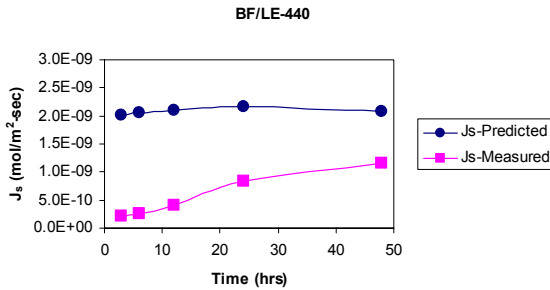


Figure 13. Comparison of predicted and measured J_s of BF by four membranes

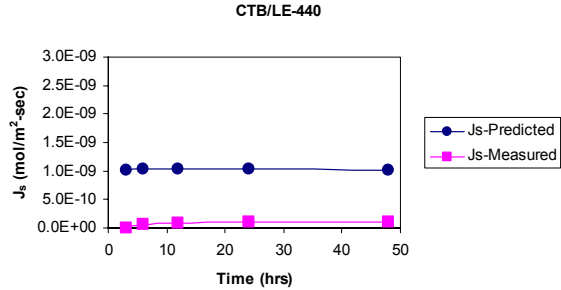


Figure 14. Comparison of predicted and measured J_s of CTB by four membranes

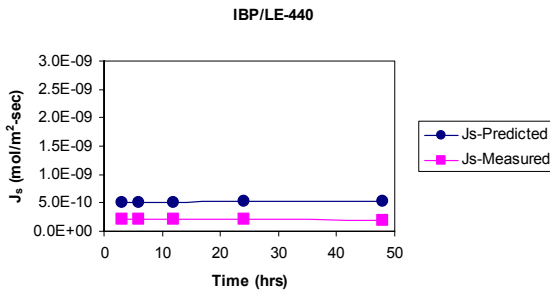


Figure 15. Comparison of predicted and measured J_s of IBP by four membranes

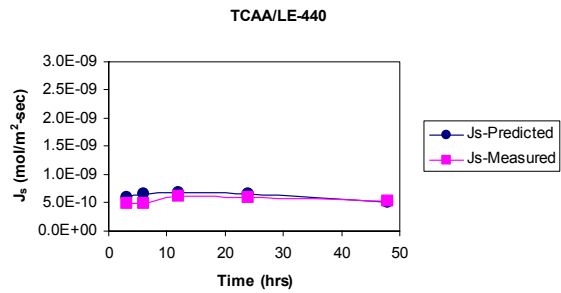


Figure 16. Comparison of predicted and measured J_s of TCAA by four membranes

In addition, other modeling efforts have been done in Figures 17 to 20, which show the percentage of convection ($J_{s\text{-convection}}$) and diffusion ($J_{s\text{-diffusion}}$) in the total solute flux ($J_{s\text{-predicted}}$) for four membranes at pH 8 and 300 μS/cm with KCl. If results for BF vs. CTB and IBP vs. TCAA are compared, diffusion is dominant in cases of more hydrophobic compounds (CTB and IBP). Meanwhile, predictions of (BF and CTB) vs. (IBP and TCAA) can explain that charged compounds are relatively more convection dominant. Comparing these efforts according to membranes, the looser the membrane is, the more dominant convection is.

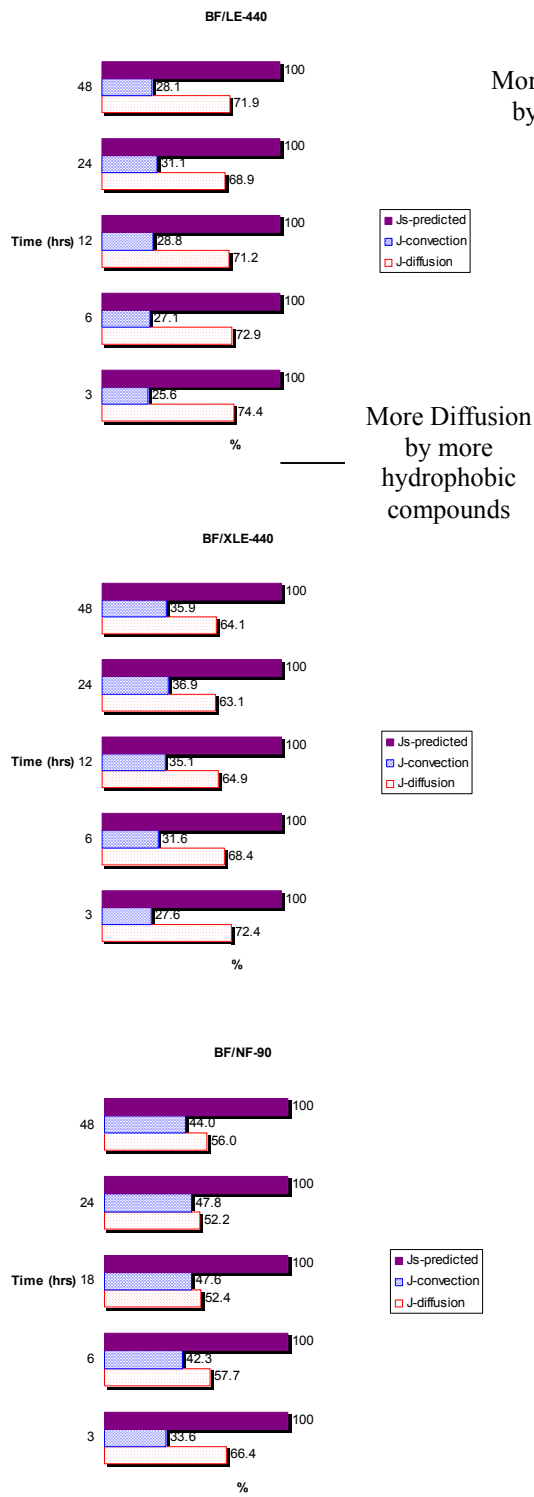


Figure 17. Percentage of convection and diffusion in the total solute flux of BF for three membranes

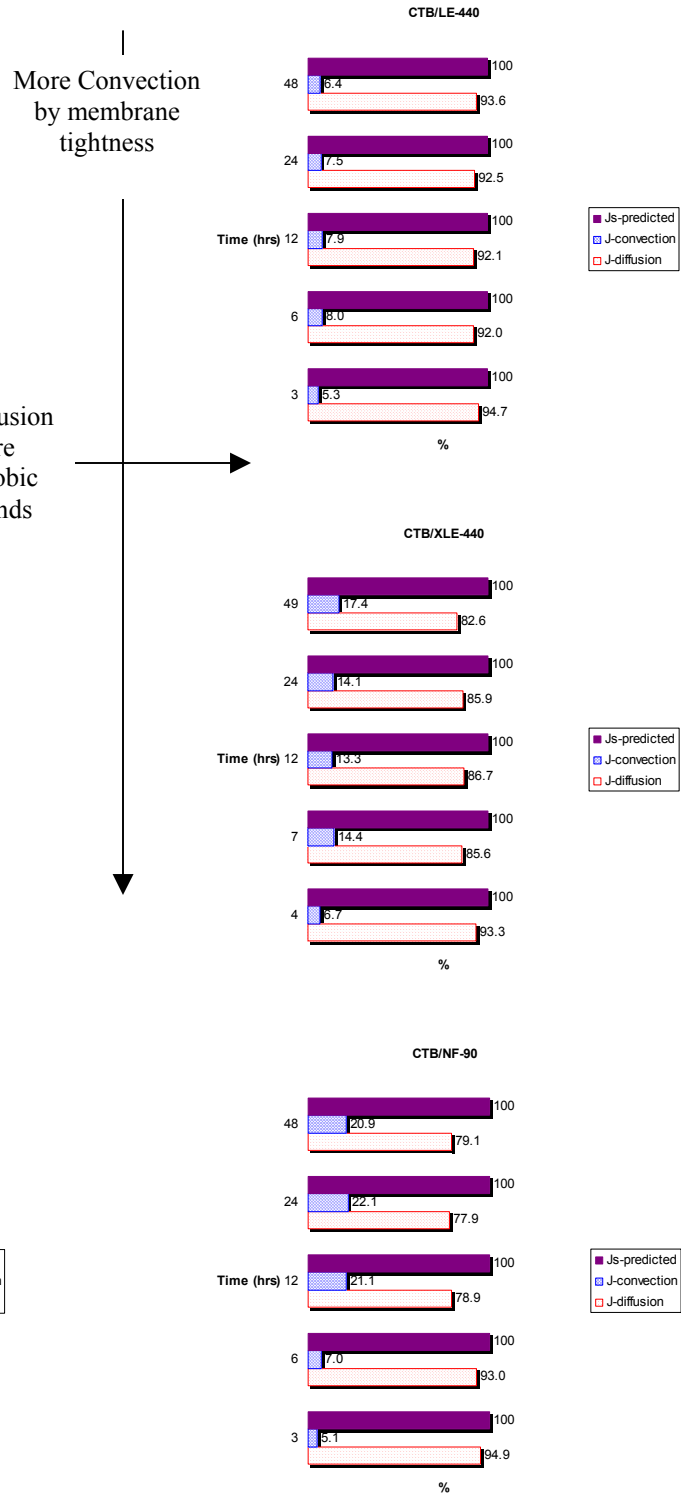


Figure 18. Percentage of convection and diffusion in the total solute flux of CTB for three membranes

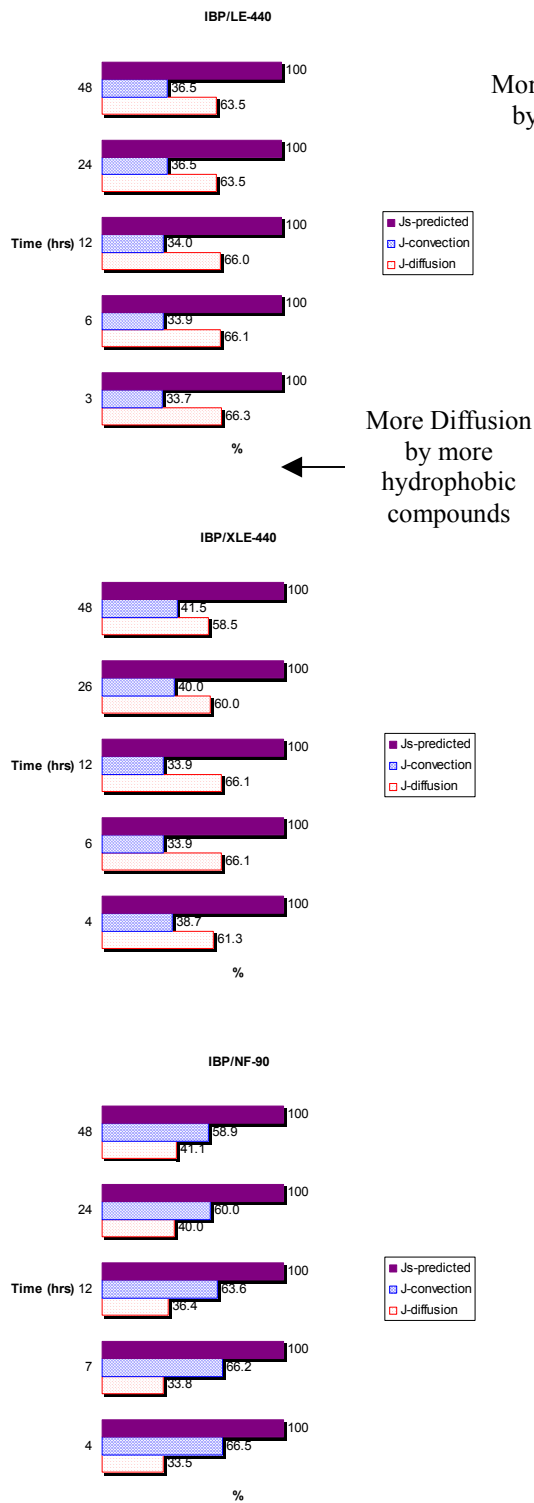


Figure 19. Percentage of convection and diffusion in the total solute flux of IBP for three membranes

More Convection
by membrane
tightness

More Diffusion
by more
hydrophobic
compounds

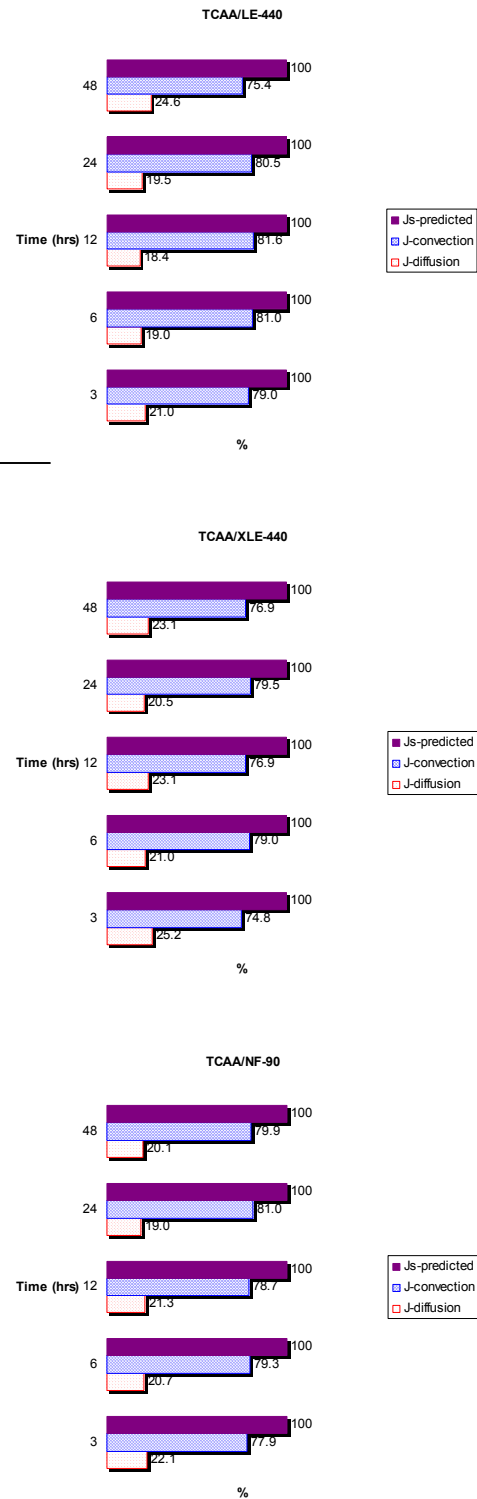


Figure 20. Percentage of convection and diffusion in the total solute flux of TCAA for three membranes

V. CONCLUSIONS AND FUTURE WORK PLAN

The membranes tested so far, similar in material composition, exhibit a significant adsorption (partitioning) capacity for solutes of intermediate hydrophobicity (CF, BF, and TCE). Observations of solute rejections indicate a time-dependent behavior, with shorter time frames indicating an overestimation of solute rejection because of solute adsorption/partitioning. Poor rejections of CF, BF, and TCE were observed, but good rejections of CT, CTB, and PCE were obtained. Good rejection was also seen in case of more polar/charged compounds (e.g., DCAA, TCAA, IBP) where (electrostatically) hindered transport enhanced solute rejection. Studying a more hydrophilic membrane (e.g. Koch CTA), less adsorption/partitioning of more hydrophobic solutes was observed along with poorer rejection (results not shown). The results of this research can be applied to polymer modification of membranes to decrease solute-membrane affinity and promote rejection, and to membrane selection based on compound properties.

In the future directions, a wider range of membranes from other manufacturers will be evaluated, and a knowledgebase on more PhACs (more polar, some charged) and EDCs (more non-polar) is being developed. Diffusion cell measurements are being continued to describe solute-membrane interactions by estimation of diffusion coefficients through membranes pores, either hindered or facilitated. In addition, the role of hydrophobic-hydrophobic interactions and dipole-dipole interactions will be probed, and the influence of membrane fouling is being further explored. Ultimately, a transport/rejection model will be more developed, based on compound and membrane properties.

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REFERENCES

- Agenson, K. O., Oh, J. I., and Urase, T. (2003). Retention of a wide variety of organic pollutants by different nanofiltration/reverse osmosis membranes: controlling parameters of process. *J. Mem. Sci.*, **225**, 91-103.
- Bhanushali, D., Kloos, S., and Bhattacharyya, D. (2002). Solute transport in solvent-resistant nanofiltration membranes for non-aqueous systems: experimental results and the role of solute-solvent coupling. *J. Mem. Sci.*, **208**, 343-359.
- Bonné, P. A. C., Beerendonk, E. F., Van der Hoek, J. P., and Hofman, J. A. M. H. (2000). Retention of herbicides and pesticides in relation to aging of RO membranes. *Desalination*, **132**, 189-193.
- Chellam, S. and Taylor, J. S. (2001). Simplified analysis of contaminant rejection during ground- and surface water nanofiltration under the information collection rule. *Wat. Res.*, **35**(10), 2460-2474.
- Cho, J., Amy, G., and Pellegrino, J. (2000). Membrane filtration of natural organic comparison of flux decline, NOM rejection, and foulants during filtration with three UF membranes. *Desalination*, **127**, 283-298.
- Ducom, G. and Cabassud, C. (1999). Interests and limitations of nanofiltration for the removal of volatile organic compounds in drinking water production. *Desalination*, **124**, 115-123.
- Hofman, J. A. M. H., Noij, Th. H. M., and Shippers, J. C. (1993). Removal of pesticides and other organic micropollutants with membrane filtration. *Water Supply.*, **11**, 129-139.
- Kedem, O. and Katchalsky, A. (1958). Thermodynamic analysis of the permeability of biological membranes to non-electrolytes, *Biochem. Biophys. Acta*, **27**, 229.

- Kiso, Y., Sugiura, Y., Kitao, T., and Nishimura, K. (2001). Effects of hydrophobicity and molecular size on rejection of aromatic pesticides with nanofiltration membranes. *J. Mem. Sci.*, **192**, 1-10.
- Koops, G. H., Yamada, S., and Nakao, S.-I. (2001). Separation of linear hydrocarbons and carboxylic acids from ethanol and hexane solutions by reverse osmosis. *J. Mem. Sci.*, **189**, 241-254.
- Lyman, W. J., Reehl, W. F., and Rosenblatt, D. H. (1990). *Handbook of chemical property estimation methods*, American Chemical Society, McGraw-Hill Inc., pp. 19.1-19.24.
- Reddersen, K. and Heberer, T. (2003). Multiple methods for the detection of pharmaceutical residues in various waters applying solid phase extraction (SPE) and gas chromatography with mass spectrometric (GC-MS) detection. *J. Sep. Sci.*, **26**, 1-6.
- Schwarzenbach, R. P., Gschwend, P. M., and Imboden, D. M. (1993). *Environmental Organic Chemistry*, John Wiley & Sons, pp. 182-214.
- Shim, Y., Lee, H.-J., Lee, S., Moon, S.-H., and Cho, J. (2002). Effects of natural organic matter and ionic species on membrane surface charge. *Environ. Sci. Technol.*, **36**, 3864-3871.
- Sourirajan, S. and Matsuura (1985). *Reverse Osmosis/Ultrafiltration Principles*, National Research Council of Canada, Ottawa, Canada.
- Standard Methods for the Examination of Water and Wastewater* (1998). 20th edn, American Public Health Association/American Water Works Association/Water Environment Federation, Washington DC, USA.
- Tandon, A., Gupta, S. K., and Agarwal, G. P. (1994). Modeling of protein transmission through ultrafiltration membranes, *J. Mem. Sci.*, **97**, 83-90.
- Taylor, J. S. and Jacobs, E. P. (1996) Reverse Osmosis and Nanofiltration. *Water Treatment Membrane Process*. McGraw-Hill, Chapter 9.
- U.S. EPA Methods 551.1* (1995). U.S. Environmental Protection Agency, Cincinnati, USA.
- Van der Bruggen, B., Schaep, J., Maes, W., Wilms, D., and Vandecasteele, C. (1998). Nanofiltration as a treatment method for the removal of pesticides from ground waters. *Desalination*, **117**, 139-147.
- Yoon, J., Amy, G., Yoon, Y., Brandhuber, P., and Pellegrino, J. (2003). Rejection of target anions; hexavalent chromium (CrO_4^{2-}), perchlorate (ClO_4^-), and arsenate ($\text{H}_2\text{AsO}_4^-/\text{HAsO}_4^{2-}$); by negatively charged membranes. *Membrane Technology Conference Proceedings*, American Water Works Association, Atlanta, USA.
- Yoon, Y. (2001). Rejection of perchlorate by reverse osmosis (RO), nanofiltration (NF), and ultrafiltration (UF) membranes: mechanisms and modeling, Ph.D. Thesis, Dept. of Civil, Environmental, and Architectural Engineering, University of Colorado at Boulder, USA.