Rejection of organic micropollutants by high pressure membranes: comparison of bench-scale versus single element tests


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Abstract

There has been considerable information reported on rejection of trace organic compounds from pilot-scale and full-scale experiments with reverse osmosis (RO) and nanofiltration (NF), but this information has limited value in predicting the rejection of these compounds by high-pressure membranes. The goal of this research is to define relationships between compound properties, membrane properties, and operational conditions, e.g. pressure, recovery, affecting trace organic compound rejection, comparing bench-scale recirculation tests and bench-scale single-pass tests. In addition, bench-scale results are compared against single element tests to ascertain scale-up effects.

Keywords
Membrane treatment; nanofiltration; organic micropollutants; reverse osmosis; water reclamation

Introduction

There are concerns about the occurrence and potential health effects of trace organic compounds including disinfection by-products (DBPs), e.g. trihalomethanes (THMs) and haloacetic acids (HAAs), in both drinking water and wastewater treatment as well as other anthropogenic compounds such as, for example, halogenated solvents like trichloroethylene (TCE). 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 μg/L to ng/L levels. Some researchers have studied NF for removing organohalides or precursor compounds from drinking water (Ducom and Cabassud, 1999). Hofman et al. (1993) have studied the rejection of persistent organic pollutants by several NF membranes using pilot systems. Bonné et al. (2000) reported good results in pilot studies using RO membranes. However, the incomplete rejection of neutral compounds, e.g. trihalomethanes (THMs), has been reported during pilot-scale high-pressure membrane applications (Levine et al., 1999).

Bench-scale cross-flow tests with a stainless steel cell and flat-sheet specimens have been performed in two modes: (i) a recirculation mode in which the reject stream (the retentate) is recycled back into the feed tank; and (ii) a single pass mode in which the retentate and permeate are wasted after sampling. The former simulates an array in which the original feed is the feed to the first stage and the retentate (reject/concentrate) is the feed to the second stage; the latter simulates the first stage. One goal of this research is to define relationships between compound properties, membrane properties, and operational conditions, e.g. pressure, recovery, affecting trace organic compound transport. Single-elements tests, employing 6.25 cm × 100 cm (2.5 inch × 40 inch) modules, have also

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been performed on a recirculation basis, recycling both retentate and permeate, to confirm bench-scale results at a larger scale. In these experiments, given the large water volume requirements, deionized water was spiked with a cocktail of several compounds. In selected experiments, results from bench-scale versus single element tests were compared to ascertain scale-up effects. An advantage of bench-scale experiments is the lower volume of feed water required, but there is a fundamental question about whether bench-scale results simulate single element results. A second issue relates to the merits of a single pass versus recirculation mode; the former providing a clearer indication of steady-state rejection; the latter more clearly quantifying adsorption through a closed mass balance. A further advantage of the single pass mode is minimization of the volatilization losses of neutral compounds, e.g. bromoform.

**Methods**

**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 for solute measurements. 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 \( \mu \text{L} \), 100–1000 \( \mu \text{L} \) 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 for weighing chemicals. A diazomethane reaction chamber was used as a step for HAAs analysis.

Bromoform (BF) were obtained from Aldrich (USA). Chloroform (CF), trichloroethene (TCE), and trichloroacetic acid (TCAA) were purchased from Fisher Scientific (USA). 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 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 \( K_{\text{ow}} \)) or Chem3D Ultra 7.0 of Cambridge Soft (Dipole), was used to develop estimates. \( D_w \) (diffusion coefficient in water) values are calculated from the Hayduk and Laudie method (Schwarzenbach *et al.*, 1993):

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

where \( \mu \) 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).

Anhydrous sodium sulfate and sodium chloride were obtained from Fisher Scientific (USA). Potassium hydroxide, potassium chloride, and a buffer solution based on potassium phosphate, used for water quality maintenance, were also purchased from

**Table 1** Properties of selected compounds

<table>
<thead>
<tr>
<th>Compound</th>
<th>MW (g/mol)</th>
<th>Log ( K_{\text{ow}} )</th>
<th>( D_w ) ( (\times 10^{-6} \text{ cm}^2/\text{s}) )</th>
<th>Dipole (Dipole*)</th>
<th>Molar volume ( (\text{cm}^3/\text{mol}) )</th>
<th>pKa</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chloroform (CF)</td>
<td>119</td>
<td>1.97</td>
<td>1.00</td>
<td>1.120</td>
<td>80</td>
<td>N/A</td>
</tr>
<tr>
<td>Bromoform (BF)</td>
<td>253</td>
<td>2.40</td>
<td>0.95</td>
<td>0.995</td>
<td>87</td>
<td>N/A</td>
</tr>
<tr>
<td>Trichloroethene (TCE)</td>
<td>131</td>
<td>2.29</td>
<td>0.94</td>
<td>0.946</td>
<td>90</td>
<td>N/A</td>
</tr>
<tr>
<td>Trichloroacetic acid (TCAA)</td>
<td>163</td>
<td>1.33</td>
<td>0.89</td>
<td>1.499</td>
<td>100</td>
<td>0.70</td>
</tr>
</tbody>
</table>

*Debye unit = 3.33564 \( \times 10^{-30} \text{ C-m} \)
Fisher Scientific (USA). 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 (USA).

Experimental methods

Membrane property tests. Two FilmTec membranes were tested: XLE-440 and NF-90. The former membrane is a low pressure RO (LPRO) membrane while the latter is a nanofiltration (NF) membrane. These membranes are composed of MPD (metaphenylenediamine (Benzene-1,3-diamine)) and TMC (trimesoyl chloride (1,3,5-Benzene trichloride)). Membrane properties were determined by different methods. Membrane hydrophobicity was characterized by contact angle measurements. A stirred cell filtration unit (Amicon) was used to test disk specimens of membranes in a dead-end mode for determining the molecular weight cut off (MWCO) of membranes using polyethylene glycols (PEGs), done only for the NF membrane (NF-90). The pure water permeability (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 was used (ELS-8000, Otsuka Electronics, Japan; Shim et al., 2002). A summary of membrane properties is presented in Table 2.

Membrane filtration tests. A membrane filtration unit accommodating flat sheet specimens (SEPA II, 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. By either varying the pump head speed or controlling the needle valve in the retentate stream, the feed flow rate, the corresponding cross-flow velocity, and the transmembrane pressure were controlled. The feed water temperature was maintained in the range of 20–25°C. The osmonics system consists of a 120L 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. Two modes of testing were employed: (i) single pass (once-through) experiments in which the permeate and retentate were not recirculated; and (ii) recirculation experiments in which the retentate, but not the permeate, was recycled to the feed reservoir. In the former mode, a steady-state rejection can be approached after adsorptive presaturation of the membrane, while in the latter mode, one can observe the depletion of solute from the system by adsorption as it

Table 2 Summary of FilmTec membrane properties

<table>
<thead>
<tr>
<th>Membrane name</th>
<th>XLE-440</th>
<th>NF-90</th>
</tr>
</thead>
<tbody>
<tr>
<td>Type</td>
<td>LPRO</td>
<td>NF</td>
</tr>
<tr>
<td>Composition</td>
<td>MPD/TMC</td>
<td>MPD/TMC</td>
</tr>
<tr>
<td>Rejection from manuf. (FilmTec) NaCl (%)</td>
<td>98</td>
<td>90</td>
</tr>
<tr>
<td>Rejection from manuf. (FilmTec) Sucrose (%)</td>
<td>99.9</td>
<td>99</td>
</tr>
<tr>
<td>Net driving pressure from manuf.* psi (kPa)</td>
<td>103 (710)</td>
<td>70 (480)</td>
</tr>
<tr>
<td>Operating press (experimental)** psi (kPa)</td>
<td>60 (410)</td>
<td>40 (280)</td>
</tr>
<tr>
<td>MWCO from manuf. N/D</td>
<td>200</td>
<td></td>
</tr>
<tr>
<td>Contact angle Degrees</td>
<td>39.8</td>
<td>59.8</td>
</tr>
<tr>
<td>Zeta potential at pH 8 (10 mM KCl) mV</td>
<td>−19.42</td>
<td>−30.76</td>
</tr>
<tr>
<td>Pure water permeability (PWP) L/day m² kPa</td>
<td>0.92</td>
<td>2.23</td>
</tr>
<tr>
<td>J₀ (based on operating pressure) L/m² hr</td>
<td>16</td>
<td>26</td>
</tr>
</tbody>
</table>

*Recommended pressure under pilot- or full-scale operation

**Basis for J₀/k = 1
approaches steady state (where retentate concentration ≫ permeate concentration). Changes in pressure permitted variation of the \( J_0/k \) ratio, a hydrodynamic condition embodying initial flux (\( J_0 \)) toward the membrane and back-diffusion (\( k \) is the mass transfer coefficient, a function of diffusion coefficient and cross-flow velocity) away from the membrane (Cho et al., 2000). The \( J_0/k \) ratio is also related to concentration polarization, with greater concentration polarization at a higher \( J_0/k \) ratio.

\[
J_0 = \frac{Q_p}{A_h} \text{(cm/s)}
\]

\[
U = \frac{Q_t}{A_v} \text{(cm/s)}
\]

\[
k = 1.62 \left( \frac{UD_{w}^{2}}{2hL} \right)^{0.33} \text{(cm/s)}
\]

where \( Q_p \) is the permeate flux (cm\(^3\)/s); \( A_h \) is the horizontal area of channel (the membrane surface area) (cm\(^2\)); \( U \) is the cross-sectional velocity of feed (cm/s); \( Q_t \) is total feed flux (cm\(^3\)/s); \( A_v \) is the vertical area of channel (cm\(^2\)); \( h \) is the channel height (cm); \( L \) is the channel length (cm); and \( D_{w} \) is the diffusion coefficient of solute in water obtained by Equation 1 (cm\(^3\)/s). The system recovery ratio \( (R = Q_p/Q_t) \) was managed through the use of needle valves, and was maintained at \(~10\%\). 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.

One-stage membrane experiments were carried out with one 2540 spiral wound membrane element (2.6 m\(^2\) area and 3.2 m\(^3\)/day capacity) in a 6.25 × 100 cm pressure vessel. The feed flow rate for the one-stage membrane experiments was 7.3 L/min and was generated by a Procon vane pump head (Murfreesboro, TN, USA). The feed pressure for the tested two membranes was set at about 480 (XLE-440) and 410 (NF-90) kPa; the corresponding bench scale conditions (Table 2) were 410 and 280 kPa, respectively. Flow rates of feed, retentate and permeate were monitored by rotary flow meters. Feed and retentate pressures were monitored with pressure gauges. Feed pressure and permeate flux were controlled by adjusting a needle valve located on the retentate line to establish a recovery of approximately 10\%, and a hydrodynamic \( J_0/k \) ratio of 1.0; experiments were performed in a recirculation mode with recycle of both retentate and permeate. Membrane elements were first flushed with approximately 100 L of deionized water before rejection experiments with target compounds. After each membrane experiment, the membrane elements were cleaned with a 0.01 N NaOH solution for 10 minutes to remove any adsorbed organics and subsequently rinsed with at least 100 L of deionized water. All experiments were performed at room temperature (25 °C) (Xu et al., 2005).

**Analytical methods**

The target solutes corresponded to disinfection by-products (DBPs) and halogenated solvents. For DBP 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 m × 0.25 mm × 1 μm) was employed.

Chloroform (CF), bromoform (BF), and trichloroethylene (TCE) were extracted and concentrated by using USEPA method 551.1 (1995). The extraction and concentration of trichloroacetic acid (TCAA) followed **Standard Method 6251B** (1998).
Results and discussion

Comparison of bench-scale (cross-flow) experiments

Generally, for an ionisable (negatively charged) compound such as TCAA, the concentration of the solute in the retentate is higher than that in the feed, as illustrated in Figure 1 (compared with Figure 2). However, for non-ionic compounds such as BF, the concentration of the solute in the retentate is lower than that in the feed because of adsorption (Figure 2). Additionally, for neutral solutes, the concentration of solute in the permeate increases up to that of the retentate as time increases, in contrast to negatively-charged solutes. Figure 3 shows similar results (lower retentate concentration and increasing permeate concentration) even though XLE-440 is an RO membrane. Meanwhile, comparing single pass experiments (Figure 2) and recirculation experiments (Figure 4), the concentration of permeate in recirculation experiments was stable and lower than that in single pass experiments because the concentration of solute in the feed was decreased by more adsorption under recirculation than under single pass conditions.

Experiments were run with ionizable TCAA, for which electrostatic interactions (repulsion) embodied by membrane zeta potential are expected to be influential, and rejections of TCAA (feed concentration of 0.1 mg/L) were high and consistent over time (Figure 5). In this case, the rejection \( r \) can be defined by Equation 5:

\[
r = 1 - \left( \frac{C_p}{C_f} \right)
\]

where \( C_p \) is the permeate concentration; and \( C_f \) is the feed concentration.

Meanwhile, the rejection trends of BF, TCE, and CF with NF-90 (Figure 6) were slightly lower than those of XLE-440 (Figure 7) due to pore size of the membranes. Figure 8 illustrates that the rejection trends in recirculation experiments were stable and higher than those in single pass experiments as stated above. In this case, Equation 6

\[
r = 1 - \left( \frac{C_p}{C_f} \right)
\]
should be considered in defining the rejection ($r$):

$$r = 1 - \frac{C_p}{C_r(1-R) + C_pR}$$  \hspace{1cm} (6)$$

where $C_r$ is the retentate concentration; and $R$ is the recovery ratio. When the recovery ratio was 10%, as in our experiments, $r$ approximately equals $1 - C_p/C_r$.

Therefore, these results support some of our hypotheses including higher rejection of BF over CF, attributable to greater steric hindrance to transport based on MW, and lower rejection of BF, TCE, and CF, attributable to different magnitudes of hydrophobic-hydrophobic interactions and dipole–dipole interactions between the solute and the membrane (Kim et al., 2005a; b).

Comparison of single element vs. bench scale (cross-flow) experiments

The variation of BF feed concentration over time significantly decreased in single element tests due to adsorption, as shown in Figure 9; these tests were performed with
recirculation of both retentate and permeate. The retentate concentration also decreased following the feed concentration decrease. The single element membrane area (26,000 cm$^2$) was much larger than the bench scale membrane area (136 cm$^2$), so the variation in feed concentration could have been similar to that of the cross-flow recirculation.

**Figure 6** Variation of BF, CF, and TCE rejection vs. time: cross-flow tests by NF-90 (single pass)

**Figure 7** Variation of BF, CF, and TCE rejection vs. time: cross-flow tests by XLE-440 (single pass)

**Figure 8** Variation of BF, CF, and TCE rejection vs. time: cross-flow tests by NF-90 (recirculation)

**Figure 9** Variation of BF concentration vs. time: single element tests with NF-90 (recirculation)
tests shown Figure 4, if about 200 times larger volume of feed water (20,000 L) was used. As it is, the single pass experiments have the benefits of easier temperature control and mass balance calculations. Meanwhile, the feed concentration of TCAA was stable over the time frame similar to the bench scale tests because of no adsorption (Figure 10).

Through results like the single element tests shown in Figure 9, the rejection variations of BF and CF were obtained (Figure 11). These rejections were calculated based on retentate and permeate concentrations at each point in time. If initial feed concentration was used instead of retentate concentration, the rejection assumes a higher value. For example, the 24 hour rejection of BF in the single element test is 33% when the retentate concentration at each time is used, while it is 87% using the initial feed concentration (0.1 mg/L). Meanwhile, BF rejection is slightly higher than CF rejection.

Figure 12 illustrates BF rejection by NF-90, comparing single element tests (recirculation), bench scale (recirculation) tests, and bench scale (single pass) tests. There is little difference between single element rejection and bench-scale (recirculation) rejection at 24 hours. This result supports one of the hypotheses; most past studies have often overestimated rejection, not allowing for presaturation of the membrane due to adsorption and partitioning. In other words, the relation between membrane area and feed volume should be considered. Moreover, both modes of bench scale experiments (recirculation and single pass) with longer time (48 hours) and larger feed volume (120 L) can explain well the rejection phenomena of THMs (BF and CF) and chlorinated solvents, e.g. TCE, without single element experiments. Similar to BF rejection results, CF rejection results are illustrated in Figure 13. It is noteworthy that the ultimate rejections of both compounds were 0% in bench-scale single-pass tests. Based on these results, it is estimated that there is no rejection of BF and CF in full scale experiments if there are no other factors because it has been reported that different pH levels and different conductivities have little effect on BF rejection (Kim et al., 2005a; b). However, Amy et al. (2005) and
Xu et al. (2006) reported that membrane fouling resulted in an increase in rejection of these hydrophobic non-ionic compounds due to reduced mass transport by characteristic changes to the membrane surface. Drewes et al. (2005) also reported that rejections of CF and BF in a tertiary effluent and a secondary effluent varied from about 50–85% and about 70–95%, respectively, depending on feed water conditions in full scale investigations using a three-stage membrane train configuration.

One difference between the bench-scale and single element tests were slightly higher pressures in the latter; all factors equal, solute rejection increases with an increase in pressure, consistent with the results shown in Figures 12–14.

**Conclusions**

Synthesizing these results, it is evident that CF, BF, and TCE absorb into, diffuse through, and then desorb from, the RO and NF membranes tested (Ducom and Cabassud, 1999).
because of intermediate hydrophobicity and dipole–dipole interactions, while TCAA (negatively-charged) is rejected well because of charge. From reported results from pilot-scale and full-scale experiments with RO and NF, there is much rejection information available for trace organic compounds, but this information has limited value in predicting the rejection of those compounds by high-pressure membranes. Nevertheless, we suggest that similar rejection behaviour between bench scale cross flow tests and individual spiral-wound elements can be expected. A quantitative understanding of the rejection of trace organic compounds by RO and NF and an ability to predict rejection will improve process economics and expand drinking water/wastewater reclamation membrane applications.

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References


