Flux decline during nanofiltration of naturally-occurring dissolved organic matter: effects of osmotic pressure, membrane permeability, and cake formation

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Received 17 April 2003; received in revised form 19 December 2003; accepted 30 December 2003
Available online 6 May 2004

Abstract
Nanofiltration of naturally-occurring dissolved organic matter (NOM) by an aromatic polyamide membrane was measured in a crossflow bench-scale test cell and modeled using a semi-empirical osmotic pressure/cake formation model. Our objective was to examine flux decline due to NOM fouling while explicitly accounting for flux decline due to osmotic effects and changes in membrane permeability. This approach allowed quantification of the effect of ionic composition on specific NOM cake resistance, and yielded insight into flux decline due to enhanced NaCl rejection by the NOM deposit. In the absence of NOM, increasing NaCl concentration reduced salt rejection and decreased membrane permeability. Flux decline was modeled by accounting for changes in osmotic pressure with time, and by employing an effective permeability. The addition of calcium significantly reduced rejection of sodium and feed conductivity, and thus mitigated flux decline. Increasing pH from 4 (near membrane pI) to 10 increased the effective permeability but also increased NaCl rejection, which resulted in greater flux decline. The presence of NOM caused greater flux decline resulting from a combination of NOM cake resistance and increased rejection of NaCl by negatively charged NOM functional groups. Increasing NaCl concentration had little effect on the mass of NOM deposited, but significantly increased the specific resistance of the NOM cake. Flux decline caused by NOM fouling in the presence of calcium was only significantly different than that caused by NOM in a solution of NaCl at the same ionic strength when the calcium concentration corresponded to saturation of NOM binding sites.

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Keywords: Nanofiltration; Fouling; Natural organic matter; Water treatment; Concentration polarization

1. Introduction
The use of membrane filtration as a drinking water treatment technology has increased in recent years, motivated in part by more stringent drinking water regulations [1]. Nanofiltration (NF), one of several alternative membrane filtration technologies, has been used to remove divalent cations and natural organic matter (NOM) from surface waters [2]. The removal of NOM has been motivated to control color, and in many cases, reduce the concentrations of halo-methanes and halo-acetic acids that form when NOM-containing water is disinfected with chlorine [3–5]. NF is a pressure-driven membrane process combining Donnan exclusion and sieving separation mechanisms. NF processes operate at pressures between 350 and 1000 kPa—much lower than reverse osmosis (RO) (1400–6800 kPa), but higher than ultrafiltration (UF) (<70 to 500 kPa). The molecular weight cut-off (MWCO) is generally between 300 and 1000 Da [6]. Rejection of monovalent ions by NF membranes is typically on the order of 70%.
2. Experimental

2.1. NOM isolation and characterization

Dissolved naturally occurring organic matter (NOM) was isolated from the Tomhannock Reservoir (TMK), a drinking water source for Troy, NY. NOM was quantified as dissolved organic carbon (DOC); the DOC of TMK water averaged about 3 mg C L\(^{-1}\). The Tomhannock watershed consists of upland forest and mixed agricultural/residential development. NOM was isolated using a field reverse osmosis system following the approach described previously [29,30]. NOM was pretreated using a 5 μm pre-filter, a sodium-form cation exchange softener, and two virgin polypropylene cartridge filters (1 and 0.45 μm) in series. The isolated NOM was kept in refrigerator at 4 °C before analysis and sample preparation.

Molecular weight and polydispersity were measured using high-pressure size exclusion chromatography (HPSEC) as described previously [31,32]. The HPSEC instrumentation (Hewlett-Packard 1100, Palo Alto, CA) included a Waters Protein Pak 125 modified silica column and variable wavelength UV detector. Benzoic acid and polystyrene sulfonate were used as standards.

The aquatic humic substance (humic and fulvic acids) content of NOM was quantified by applying NOM concentrations to a methyl methacrylate resin bed (Supelite DAX-8, Supelco, St. Louis, MO) at pH 2 employing a capacity factor (assuming frontal chromatography and neglecting mass transfer limitations) of 100 [33]. The adsorbed fraction, designated “hydrophobic” humic substances (HPO), was subsequently back-eluted from the column using a pH 11 solution while the non-retained fraction was designated “hydrophilic” organic acids (HPL) [34]. Early work on humic substance adsorption by synthetic resins established that adsorption was dominated by hydrophobic interactions [35]. Aiken et al. [36] compared several resins and identified the poly(methyl methacrylate) XAD 8 as having good sorption properties (rate, capacity, and reversibility) for humic substances. This resin is of relatively low polarity with low ion exchange capacity on the order of 10 \(^{-2}\) meq g\(^{-1}\) resin. Preparative isolation and fractionation schemes have been developed further by U.S.G.S. researchers [37,38]. The resin employed in this work was 40/60-mesh size with a mean surface area 160 m\(^2\) g\(^{-1}\) and a mean pore diameter of 225 Å. As-received resin was first washed in 0.1 M NaOH solution, then sequentially soxhlet extracted using acetonitrile and methanol for 24 h each, and exhaustively rinsed with reagent grade 1 water.

Acidic functional groups in the NOM structure can play an important role in membrane processes due to electrostatic interactions with the membrane surface. The two major acidic functional groups are carboxylic groups, which are considered to be significantly ionized at pH values >6, and the phenolic groups, which are predominantly un-ionized at pH values <8 [39,40]. Proton dissociation of organic acid while rejection of color, organic carbon, and trihalomethane precursors can be much higher, generally between 90 and 95%. Rejection of hardness ions in membrane softening applications generally ranges from 85 to 95% [7–10].
components of NOM (organic acidity) was determined by titrating 70-mL NOM samples under positive CO_2-free N_2 pressure with CO_2-free NaOH solutions prepared by diluting concentrated NaOH solutions with CO_2-free (boiled) reagent grade I water. Samples were titrated from an initial pH of 3.00 ± 0.02, to assure protonation of carboxylic groups, to a final pH of 10. Solution pH was measured using an Orion Ross semi-micro combination epoxy body probe and a pH meter (Accumet Model 50, Fisher Scientific). Titrant was delivered to the sample using a Class A, 5 mL microburette, marked at 0.01 mL increments, with a 70-mL integral reservoir (Kimax, Fisher Scientific) which remained closed to the atmosphere except during buret refilling. For each incremental change in pH, the moles of base added to an NOM sample in excess of that necessary to effect the same change in pH for water only is attributed to buffering by NOM. Carboxyl groups were assumed to contribute all titratable charge up to pH 7, and phenolic groups were assumed to account for the additional titratable charge to pH 10 [39,41,42]. Oliver et al. [42] report that carboxylic acidity (to pH 7) of aquatic humic substances from nineteen different source waters throughout the United States ranged from 5.1 to 13.4 μeq mg⁻¹ C with an average value of 10.0 and standard deviation of 1.7 μeq mg⁻¹ C.

Binding of calcium by NOM was determined in batch reactors. NOM solutions (10 mg/L DOC, 50 mL) were amended with calcium ion (as CaCl₂) to produce total calcium concentrations ranging from 0.001 to 0.01 M. Reactors were mixed completely for 4 h, a time sufficient to assure equilibration based on constant free calcium concentrations. Free (non-complexed) calcium was measured using an ion-specific electrode (Thermo Orion) and a pH/ISE meter (Accumet Model 50, Fisher Scientific) calibrated with external standards. The complexed calcium was calculated by difference. Precision of such measurements (relative standard deviation) was within 5% except for the data corresponding to the lowest calcium concentration, for which the R.S.D. was within 14%.

NF characterization

An aromatic polyamide thin-film composite membrane (NF-70, Dow-FilmTec Inc., Minneapolis, MN) was chosen for this research as representative of a class of membranes used increasingly in water treatment applications. The thin-film composite NF-70 membrane has an isoelectric point near pH 4 [43,44] and a surface charge of about −25 mV at pH 7 with a background electrolyte of 0.01 M NaCl [44]. Vrijenhoek et al. [44] report an average roughness of 43.3 nm, defined as the average deviation of peaks and valleys from the mean plane, i.e., the average of all height values obtained by AFM analysis. A molecular weight cut-off of about 200 Da has been reported for this membrane [45], and contact angle of 28 ± 2° was measured using the captive bubble technique. The salt (NaCl) rejection is about 70% [9] and the magnesium sulfate rejection is 95%, as reported by the manufacturer (conditions: 2000 mg L⁻¹ MgSO₄, 70 psi (483 kPa), and 25°C).

Membrane sheets were cleaned and pre-compacted at 4000 kPa using tap water treated with a mixed bed ion-exchanger and activated carbon (DI water). After membrane compaction (indicated by a steady-state flux), DI water was used to determine the clean water permeability (Lp), which averaged 3.36 ± 0.28 × 10⁻⁶ m s⁻¹ kPa⁻¹ (0.121 L MH⁻¹ Pa⁻¹) at 23°C. Membrane sheets were stored in 1% sodium metabisulfite (Na₂S₂O₅) at 4°C to prevent microbial activity and oxidation.

Crossflow bench-scale test cell

Solution flux experiments were conducted using the cross-flow bench scale membrane test system depicted schematically in Fig. 1. Additional details of this system were described by Allgeier and Summers [46]. This system consists of a stainless steel cell (SEPA, Osmonics Inc. Minnetonka, MN), a high-pressure stainless-steel piston feed pump, and a high capacity booster (gear) pump to maintain high flow rates in a recycle loop. A 155 cm² (24 in²) membrane sheet and a feed channel spacer (0.086 cm high with three to four strands per cm) were mounted between stainless steel halves of the cell, and were sealed with an o-ring. A flow rate, Q, of 530 mL min⁻¹ was maintained in the recycle loop (independent of the feed flow rate and recovery). A crossflow velocity of 0.1 m s⁻¹ was estimated based on a cell cross-sectional area, A_c, of 1.23 × 10⁻⁴ m² and a spacer-filled porosity, ε, of 0.72 computed as described by Da Costa et al. [47]. A Reynolds number (N_Re) of approximately 104 was computed on the basis of the hydraulic diameter. Recovery was maintained at 85%, and inlet temperature was approximately 23°C during filtration experiments.

Flux experiments

NOM-free reagent-grade sodium chloride solutions (concentrations ranging from 0.004 to 0.10 M) were used to evaluate the effects of salt concentration polarization. The effects of fouling by NOM were evaluated using feed solutions containing 10 mg C L⁻¹. Solution pH was
adjusted to pH 7, and ionic strength was adjusted to 0.01 M as NaCl (i.e., corresponding to a conductivity of 1070 µS cm⁻¹ at 25 °C). Prior to filtration, the membrane system was flushed with feed solution. The initial solution flux was subsequently adjusted to 1.25 × 10⁻⁷ m s⁻¹ (45 L m⁻² h⁻¹) while the transmembrane pressure was kept constant during filtration. Permeate flow was continuously measured throughout the filtration run. Permeate and retentate (bleed) flows were periodically sampled to calculate rejection and mass balance.

2.5. Analytical methods

NOM concentrations were measured as dissolved, non-purgeable carbon using a carbon analyzer (Model 1010, OI Analytical, College Station, TX) employing high temperature wet oxidation. External standards (ranging from OI Analytical, College Station, TX) employing high temperature were made using an Advanced Portable Meter (AP50, Denver Instrument Co., Arvada, CO). Permeate and retentate (bleed) flows were periodically sampled to calculate rejection and mass balance.

3. Theory

3.1. Solution flux

Flux of solutions containing salt (e.g., NaCl) is given by:

\[ J_0 = L_0(\Delta P - \sigma \Delta \pi) = \frac{\Delta P - \sigma \Delta \pi}{\mu(R_m + R_{loop})} \]  

where \( J_0 \) is the membrane permeability (m s⁻¹ kPa⁻¹), \( \Delta P \) the average transmembrane pressure (kPa), \( \sigma \) the osmotic reflection coefficient, and \( \Delta \pi \) the difference in osmotic pressure between the membrane and permeate stream, \( \Delta \pi = \pi_{mem} - \pi_{perm} \) (kPa). The reflection coefficient was estimated by the intrinsic membrane rejection, \( \pi_{mem} \), where \( \pi_{mem} = 1 - C_{perm}/C_{mem} \). \( C_{perm} \) and \( C_{mem} \) are the concentrations in the permeate and at the membrane surface, respectively. The solution flux can also be written in terms of membrane resistances, where \( R_m \) is the membrane hydraulic resistance (m⁻¹); \( R_{loop} \) the non-recoverable resistance that develops during filtration (m⁻¹); and \( \mu \) the dynamic viscosity of the solution (kg m⁻¹ s⁻¹).

Under constant-pressure operation, assuming constant membrane permeability, and in the absence of feed components that cause fouling by pore blockage or cake formation (e.g., NOM), the change in solution flux is related to the change in osmotic pressure as a result of solute (e.g., NaCl) accumulation at the membrane-solution interface. The osmotic pressure is correlated with NaCl concentration, with \( \pi \) (kPa) = \( aC \) (mol l⁻¹)), where \( a = 4815 \) (kPa mol⁻¹) at 25 °C under the ideal solution assumption [51]. Therefore, \( \Delta \pi = \sigma(C_{mem} - C_{perm}) \). Using the intrinsic rejection this can be written \( \Delta \pi = \sigma(\pi_{mem} - \pi_{perm}) \). The concentration at the membrane surface was eliminated in favor of \( \pi_{mem} \), the directly measurable bulk (retentate recycle loop) concentration, as follows. First, clean water flux \( (J_0) \) experiments were conducted in the absence of NaCl to obtain values for \( R_m \) (using Eq. (2) written in terms of resistances with \( \sigma \Delta \pi = 0 \)) and \( R_{loop} = 0 \). The additional fouling resistance \( R_{fouling} \) was measured by a second clean water flux measurement following filtration of a salt solution and subsequent membrane cleaning (using Eq. (2) with \( \sigma \Delta \pi = 0 \)). Solution flux in the presence of salt was then measured under steady-state conditions with different salt concentrations. Data from such experiments, shown in Fig. 2, were used to calculate \( \sigma \Delta \pi \) using Eq. (2) and \( \pi_{mem} \), using \( \sigma \Delta \pi = \text{our}(C_{mem} - C_{perm}) \). The ratio \( \beta = \pi_{mem} \) was correlated as a function of NaCl concentration, and the
linear driving force, where state is reached. This mass transport is approximated by a concentration polarization layer, which occurs before steady transfer from the bulk to the membrane surface, forming the cake (perm). The deposition of solute molecules on the membrane surface provides an additional resistance, $R_c$, to solution flux:

$$J_s = \frac{\Delta P - \Delta \pi}{\mu(R_n + R_{\text{mem}} + R_c)}$$

(5)

When the feed solution contains both salt and NOM, the change in solution flux is related to the change in osmotic pressure as a result of concentration polarization (assumed to be primarily caused by salt), and the change in the hydraulic resistance of the NOM cake that forms on the membrane surface:

$$\frac{dJ_s}{dt} = \frac{-\sigma \alpha_{\text{late}} R_{\text{mem}} \beta_s}{\mu(R_n + R_{\text{mem}} + R_c)} \left( \frac{dC_{\text{reten}}}{dt} \right)$$

(6)

where the subscript $s$ refers to NaCl (salt). In the cake formation model, the time rate of change in cake resistance is assumed to be proportional to the rate of change in cake mass, $m_{\text{cake}}$ (kg), which increases at a rate proportional to the net rate of convective mass transport toward the membrane surface:

$$\frac{dm_{\text{cake}}}{dt} = \alpha_{\text{cake}} \frac{1}{A_0} \left( \frac{dJ_v}{dt} \right)$$

(7)

where $\alpha_{\text{cake}}$ is the specific cake resistance (assumed constant) (m kg$^{-1}$), $C_{\text{reten,NOM}}$ is the NOM concentration in the retentate recycle loop ($kg m^{-1}$), and $J_v$ (m s$^{-1}$) is the effective flux associated with back-transport resulting from cross-flow. The development of cake resistance as a function of time, $R_c$ in Eq. (6), was evaluated by integrating Eq. (7), and the change in salt concentration, $dC_{\text{reten,salt}}/dt$, was determined using the overall material balance model, Eq. (4). Eqs. (6) and (7) were integrated using a fourth-order Runge-Kutta routine, using the specific cake resistance and the effective back-transports flux ($J_v$) as fitting parameters, determined by minimizing the sum of squared residuals (SSR) between the observed and fitted solution flux. Parameter search was done as described in Section 3.2.
4. Results and discussion

4.1. Overall system mass balance

The concentration of NaCl in the retentate stream of the bench scale system (in NOM-free solutions) as a function of time is shown in Fig. 2. Excellent fits of the Schmidt number, $N_k$, Average $l (m \cdot s^{-1})$ within confidence interval within $\pm 1\%$ of the stated value. The average value of the estimated mass transfer coefficient, $1.6 \times 10^{-3} \text{m}^{-1} \cdot \text{s}^{-1}$, is within 13\% of the value predicted by the Graetz–Leveque equation, and within 20\% of the value predicted by a correlation reported by DuCosta et al. [56] for their 80 MIL-2 spacer, although the Schmidt number, $N_k$, employed in that study was much higher than ours. The value predicted using a correlation reported by Schock and Miguel [57] for spiral wound RO applications is about 78\% higher than that found here, possibly because their correlation used exponents on higher than that found here, possibly because their correlation used exponents on $N_k$ and $N_p$ characteristic of turbulent flow, which was not the case here. Steady state retentate concentrations increased in a roughly linear manner proportional to feed concentration, while the overall mass transfer coefficients declined slightly with increased feed salt concentration.

4.2. Effects of NaCl concentration on flux decline

The measured change in $C_{\text{reten}}$ as a function of time was employed in Eq. (3) in an attempt to predict the effects of osmotic pressure on flux decline; such effects are illustrated by the data (shown as symbols) in Fig. 3. The model tended to under-predict flux decline; however, the data could be fitted after multiplying the right hand side of Eq. (3) by a constant factor, $\eta$:

$$\frac{dJ_v}{dt} = -\eta \frac{\sigma a R_{\text{mem}} \beta}{\mu (R_m + R_{\text{non-rec}})} \left( \frac{dC_{\text{reten}}}{dt} \right)$$

(8)

Because the parameters $\sigma$, $a$, $\beta$, and $R_{\text{mem}}$ were determined independently, the factor $\eta$ multiplies the clean water permeability, $L_p$:

$$\frac{1}{\mu (R_m + R_{\text{non-rec}})} = \eta L_p = L_{p,\eta}$$

(9)

Therefore, we interpret $\eta$ as a permeability reduction factor, with the product $\eta L_p$ representing an effective permeability in the presence of salt, $L_{p,\eta}$. This is equivalent to defining a membrane resistance in the presence of salt, $R_{m,\eta}$, where $R_{m,\eta} = 1/(\mu (R_m + R_{\text{non-rec}}))$ and

$$R_{m,\eta} = \frac{R_m + (1-\eta)R_{\text{non-rec}}}{\eta} = \frac{1-\mu R_{\text{non-rec}} L_p}{\mu L_{p,\eta}}$$

(10)

The effective permeability, $L_{p,\eta}$, was evaluated by fitting Eq. (8) to the experimental data shown in Fig. 3 using a Fourth-order Runge–Kutta routine, minimizing the sum of squared residuals (SSR) for each feed salt concentration, as described in Section 3.2.

The observation that membrane permeability was reduced in the presence of salt implies that osmotic pressure was overestimated when steady-state NaCl solution flux data were analyzed using Eq. (2) in conjunction with $R_p$. Hence, values of $C_{\text{mem}}$ and $\beta$ were also overestimated. Therefore, to obtain more accurate estimates of model parameters, an iterative approach was required. Fitted values of effective permeability were used to obtain new estimates of osmotic pressure, $C_{\text{mem}}$ and $\beta$. These were used with Eq. (8) to generate new estimates of effective permeability. These calculations were repeated until convergence (parameter value changed by less than 1\%), generally achieved in less than seven iterations.

Table 1

<table>
<thead>
<tr>
<th>Parameter</th>
<th>NaCl concentration (M)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$C_{\text{reten}}$ (M)</td>
<td>0.004 0.01 0.05 0.075 0.1</td>
</tr>
<tr>
<td>$J_{v,\text{mem}}$ (m/s)</td>
<td>0.224 0.218 0.209 0.203 0.207</td>
</tr>
<tr>
<td>$J_{v,\text{non-rec}}$ (m/s)</td>
<td>1.69 1.65 1.58 1.53 1.56</td>
</tr>
<tr>
<td>Average $l_1$</td>
<td>$1.60 \times 10^{-3} \text{m}^{-1} \cdot \text{s}^{-1}$</td>
</tr>
</tbody>
</table>

The product $k_{o,d}$ is the fitted overall mass transfer coefficient, where $a_{os}$ is the volumetric specific surface area (m$^2$ m$^{-3}$) equal to the effective membrane surface area divided by the reactor (recycle loop) volume. The product $k_{o,d}$ was determined with an approximate 95\% confidence interval within $\pm 1\%$ of the stated value.

The concentration of NaCl in the retentate stream of the bench scale system (in NOM-free solutions) as a function of time is shown in Fig. 2. Excellent fits of the Schmidt number, $N_k$, Average $l (m \cdot s^{-1})$ within confidence interval within $\pm 1\%$ of the stated value. The average value of the estimated mass transfer coefficient, $1.6 \times 10^{-3} \text{m}^{-1} \cdot \text{s}^{-1}$, is within 13\% of the value predicted by the Graetz–Leveque equation, and within 20\% of the value predicted by a correlation reported by DuCosta et al. [56] for their 80 MIL-2 spacer, although the Schmidt number, $N_k$, employed in that study was much higher than ours. The value predicted using a correlation reported by Schock and Miguel [57] for spiral wound RO applications is about 78\% higher than that found here, possibly because their correlation used exponents on $N_k$ and $N_p$ characteristic of turbulent flow, which was not the case here. Steady state retentate concentrations increased in a roughly linear manner proportional to feed concentration, while the overall mass transfer coefficients declined slightly with increased feed salt concentration.

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$$\frac{dJ_v}{dt} = -\eta \frac{\sigma a R_{\text{mem}} \beta}{\mu (R_m + R_{\text{non-rec}})} \left( \frac{dC_{\text{reten}}}{dt} \right)$$

(8)

Because the parameters $\sigma$, $a$, $\beta$, and $R_{\text{mem}}$ were determined independently, the factor $\eta$ multiplies the clean water permeability, $L_p$:

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(10)

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An alternative explanation postulates an increase in the concentration of solute by a Donnan mechanism [26–28,59,60]. Decreased rejection of charged solutes by charged membranes with increasing feed ionic strength has been observed by others, and is consistent with ion exclusion by a Donnan mechanism [26–28,59,60].

Fig. 3 illustrates the effect of pH on flux decline; the solid lines are model fits using Eq. (8), fitted parameters are tabulated in Table 3. The rate and extent of flux decline increased with increasing pH, even though the effective permeability strength has been observed by others, and is consistent with ion exclusion by a Donnan mechanism [26–28,59,60].

4.3. Effects of pH on flux decline

To examine the effects of pH at constant ionic strength were investigated. Ionization of charged moieties with increasing pH will increase fixed charge and intramembrane electrostatic repulsion. A pH range from 4 (pH near the pI) to 10 was investigated, keeping the ionic strength constant with a feed NaCl concentration of 0.01 M. Fig. 4 illustrates the effect of pH on flux decline; the solid lines are model fits using Eq. (8), fitted parameters are tabulated in Table 3. The rate and extent of flux decline increased with increasing pH, even though the effective permeability strength has been observed by others, and is consistent with ion exclusion by a Donnan mechanism [26–28,59,60].

The intrinsic membrane rejection decreased significantly with increasing feed concentration, from about 90 to 73%. In part, this can be attributed to an increase in the concentration of salt at the membrane surface and an increase in solute flux relative to the solvent flux. However, electrostatic effects may also play a significant role. Increased ion concentration can cause a reduction in the electrical double layer thickness in membrane pores and thus increase the solute partition coefficient, causing a reduction in the rejection of ionic species [55,58]. Decreased rejection of charged solutes by charged membranes with increasing feed ionic strength has been observed by others, and is consistent with ion exclusion by a Donnan mechanism [26–28,59,60].

<table>
<thead>
<tr>
<th>Salt concentration as NaCl (M)</th>
<th>0.004</th>
<th>0.01</th>
<th>0.05</th>
<th>0.075</th>
<th>0.1</th>
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</thead>
<tbody>
<tr>
<td>ΔP (kPa)</td>
<td>408 (59.3 psi)</td>
<td>519 (75.3 psi)</td>
<td>825 (97.3 psi)</td>
<td>881 (127.8 psi)</td>
<td>1172 (170 psi)</td>
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<tr>
<td>σΔP (kPa)</td>
<td>93 (13.4 psi)</td>
<td>186 (26.9 psi)</td>
<td>414 (60.1 psi)</td>
<td>560 (81.2 psi)</td>
<td>723 (104 psi)</td>
</tr>
<tr>
<td>ΔP − σΔP (kPa)</td>
<td>315 (45.9 psi)</td>
<td>333 (48.4 psi)</td>
<td>256 (37.2 psi)</td>
<td>321 (46.9 psi)</td>
<td>449 (66.9 psi)</td>
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<tr>
<td>Jc (m s⁻¹) × 10⁶</td>
<td>10.4</td>
<td>9.26</td>
<td>6.80</td>
<td>6.19</td>
<td>6.19</td>
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<tr>
<td>Cmem (M)</td>
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<td>0.050</td>
<td>0.153</td>
<td>0.214</td>
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<tr>
<td>Cfeed (M)</td>
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<td>0.037</td>
<td>0.114</td>
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<tr>
<td>Creten (M)</td>
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<td>0.038</td>
<td>0.056</td>
<td>0.079</td>
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<td>β</td>
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<td>σ</td>
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<td>66.8</td>
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<td>88.0</td>
<td>75.1</td>
<td>73.7</td>
<td>72.5</td>
</tr>
</tbody>
</table>

* Average membrane permeability (Jmem) was 3.36 ± 0.28 × 10⁻⁸ m s⁻¹ kPa⁻¹ (0.121 LMH kPa⁻¹).
* Operating conditions: initial solution flux = 1.25 × 10⁻¹ (Mc)⁻¹, crossflow velocity = 0.1 m s⁻¹, recovery = 95%, temperature = 23°C.
* The permeability reduction factor, η, was determined with an approximate 95% confidence interval within ±4% of the stated value.
* Rmem = 1 - Cmem/Cfeed, Cfeed and Cmem are the permeate and feed reservoir DOC concentrations, respectively.
* Rreten = 1 - Creten/Cfeed, Cfeed and Cmem are the permeate and recycle loop retentate DOC concentrations, respectively.
within membrane pores, or both. The concentration at the membrane surface also increased, but not to the same extent as $C_{\text{reten}}$ increased; therefore the ratio $\beta = C_{\text{mem}}/C_{\text{reten}}$ decreased with increasing pH.

The effect of pH on rejection is consistent with the findings of Childress and Elimelech [43] for pH values above the membrane isoelectric point. The results presented here are also consistent with the model invoked by Braghetta et al. [14] to interpret their data. However, in contrast to the findings of this study, they found that solution flux increased with increasing pH, as a result of increases in membrane permeability. In their system the effects of membrane permeability, characterized here by $\eta$, were more important than the effects of solute rejection. Whereas the value of $\eta$ also increased with increasing pH in this work, the effects of pH on solute rejection, not membrane permeability, were most important. Possible explanations for these different observations include (1) the larger molecular weight cutoff of the membrane used by Braghetta et al. [14], which was on the order of 1000 Da, as compared to about 200 Da for the membrane in this work; (2) different membrane material and surface charge; or both.

### 4.4. NOM characteristics

The characteristics of the Tomhannock Reservoir NOM, tabulated in Table 4, are representative of many surface water sources in the Northeast US. The organic acidity contributed by carboxylic groups measured by titration from pH 3 to 7 was 11.2 meq (g DOC)$^{-1}$; this compares to a mean value of 9.1 meq (g DOC)$^{-1}$ for fulvic acids as reported by Schnitzer [61]. This may contribute, in part, to the predominance of the polar (hydrophilic) components (63.6%) in this water.

### 4.5. Effect of NOM concentration on NaCl rejection and solution flux

Feed solutions having three different NOM concentrations, 5, 10, and 25 mg DOC$^{-1}$, were prepared from TMK isolate. The ionic strength (0.01 M as NaCl) and pH (7) of all feed solutions was the same. Fig. 5 shows the effect of NOM concentration on flux decline. The solid lines represent model fits to Eq. (6); directly measured process parameters and fitted model parameters are tabulated in Table 5. As expected, the presence of NOM caused greater flux decline than solutions of NaCl alone; normalized solution flux ($J/J_{\text{o}}$) decreased from 0.74 to 0.35 as NOM concentration increase from 0 to 25 mg DOC$^{-1}$. The increased flux decline resulted from a combination of resistance from an NOM deposit and an increased osmotic effect. The osmotic effect increased because the presence of NOM significantly increased NaCl rejection, which can be explained by electrostatic repulsion between Cl$^-$ ions and charged functional groups on the NOM molecules, and which caused an increase in the change of $C_{\text{reten}, x}$ with time (Eq. (6)).
Two factors contributed to an increase in the resistance of the NOM deposit with increasing NOM concentration. First was the mass of NOM deposited, which was 6.5, 10.5 and 39.8 mg for feed solutions concentrations of 5, 10 and 25 mg l\(^{-1}\), respectively. In addition, the specific resistance of the cake increased by a factor of almost two when the NOM concentration was increased from 5 to 10 mg l\(^{-1}\). The increase was statistically significant, because the specific resistance was determined with an approximate 95% confidence interval within ±10% of the stated value. However, the specific resistance appears to have reached a limiting value because further increases were not observed when the NOM concentration was increased to 25 mg l\(^{-1}\). The increase in cake resistance can be explained by a decrease in cake porosity with increasing NOM concentration, possibly resulting from a reconfiguration of NOM molecules to adopt more compact arrangements. (Whereas this would also imply an increase in the cake density, which would have the opposite effect, the specific resistance is more sensitive to changes in porosity.) The sharp decrease in solution flux observed with the 25 mg l\(^{-1}\) feed solution appears to be related primarily to an increase in the NOM mass deposited, because the salt rejection and specific resistance of the cake (as judged from a sensitivity analysis on fitted parameters) were not significantly different from the values obtained for the 10 mg l\(^{-1}\) solution. Cohen and Probstein [62] observed similar behavior for a colloidal solution of ferric hydroxide, when the colloidal dispersion was unstable, which resulted in rapid aggregation. The relatively constant value of the specific resistance observed may reflect an increased rate or extent of aggregation, and a balance between increases in porosity and decreases in cake density.

### 4.6. Effect of NaCl concentration in the presence of NOM

Careful examination of the data in Table 5 shows that the trends in specific resistance parallel those in the NaCl rejection. The role of NaCl concentration was further investigated by amending solutions of TMK NOM (10 mg l\(^{-1}\), pH 7) with varying amounts of NaCl to yield a range of ionic strength. Fig. 6 illustrates the effect of ionic strength on...
solution flux. The solid lines represent model fits to Eq. (6); directly measured process parameters and fitted model parameters are tabulated in Table 6. Increased ionic strength from 0.004 to 0.05 M NaCl decreased relative solution flux ($J = 10$) from 0.65 to 0.44; in all cases flux reductions were significantly greater than in the presence of salt alone. The amount of NOM deposited averaged 12.9 ± 2.5 mg and did not show any significant trend with ionic strength. However, as shown in Fig. 7, increases in flux decline correlate with statistically significant increases in the specific resistance of the cake; this parameter increased by a factor of about three over the range of ionic strength studied. It is likely that the increase in salt concentration in the cake layer reduced charge repulsion between ionized functional groups on single NOM molecules, allowing them to adopt more compact configurations, and between NOM molecules, increasing the compactness of the cake, resulting in lower cake porosity. A change in NOM configuration with increasing ionic strength is consistent with a model of NOM structure proposed by Ghosh and Schurz [63] and has been shown to influence mass transfer in sorption processes [64]. Kilduff and Weber [49] explained the effect of ionic strength on the rejection of humic acid by ultrafiltration membranes in terms of changes in humic acid molecular size. A similar approach was used here provide evidence that increases in specific cake resistance result from changes in NOM configuration and/or size.

The effect of ionic strength on NOM macromolecular configuration was investigated by measuring transport across a 5 kDa molecular weight cut-off ultrafiltration membrane. The 5 kDa MWCO was selected because it exhibited near zero rejection of salt, thus preventing changes in ionic strength upstream of the membrane during the experiment. Also, a very small fraction of the TMK water was retained on the 5 kDa membrane, allowing that changes in molecular size resulting from changes in ionic strength could be readily detected. Solutions of TMK NOM (10 mg l$^{-1}$, pH 7) were prepared with a range of ionic strengths varying from 0.01 to 0.1 M as NaCl. Fig. 7 illustrates a decrease in NOM rejection by the UF membrane from 0.44 to 0.12 with an increase in ionic strength from 0.01 to 0.10 M. One explanation for the observed decrease in rejection is that NaCl screened charge on the UF membrane pore walls, reducing charge repulsion. This explanation was ruled out because ionic strength had no effect of the flux of NaCl solutions (data not shown), suggesting the membrane surface charge was small, consistent with manufacturer data. Therefore, we interpret the decrease in rejection with increasing ionic strength as evidence of a more compact NOM configuration (possibly becoming more a rigid, coiled, and spherical) with increasing ionic strength. This conclusion is supported by the data shown in Fig. 8, illustrating that the weight-averaged molecular weight of NOM components permeating the UF membrane (measured using size exclusion chromatography) is significantly higher for the feed having an ionic strength of 0.10 M as compared to 0.01 M. Therefore, the observed increases in specific resistance of the cake formed during filtration are attributed to a reduced cake porosity resulting from a reduction in NOM size or size distribution, and hence a more densely compacted NOM layer. It appears that the specific resistance approaches a limiting value as the reduction in NOM size reaches a limiting value at ionic strengths ranging from 0.08 to 0.10.

Fig. 9 combines selected flux data from Figs. 3 and 6 to illustrate the contributions of salt concentration polarization and NOM cake formation on solution flux. Data correspond-
Table 7

<table>
<thead>
<tr>
<th>pH</th>
<th>J(0) (LMH)</th>
<th>c,(mg/L)</th>
<th>(J_o)</th>
<th>(R_{feed} ), DOC</th>
<th>(R_{feed} ), conductivity</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>0.613</td>
<td>2.32</td>
<td>28.5</td>
<td>74.6–87.4 (81.1)</td>
<td>21.0–27.9 (25.5)</td>
</tr>
<tr>
<td>7</td>
<td>0.606</td>
<td>2.15</td>
<td>27.8</td>
<td>70.6–81.8 (80.2)</td>
<td>21.0–23.8 (22.2)</td>
</tr>
<tr>
<td>10</td>
<td>0.561</td>
<td>2.38</td>
<td>25.6</td>
<td>92.6–93.5 (93.0)</td>
<td>46.1–56.7 (49.5)</td>
</tr>
</tbody>
</table>

Solution conditions: NOM concentration = 14 mg l\(^{-1}\), ionic strength = 0.01 M NaCl. Operating conditions: initial solution flux = 1.25 x 10\(^{-5}\) m s\(^{-1}\), crossflow velocity = 0.1 m s\(^{-1}\), recovery = 85%, temperature = 23°C. The average of seven rejection values is shown in the parenthesis.

The specific cake resistance, \(\alpha\), was determined with an approximate 95% confidence interval within ±10% of the stated value.

The effective back transport flux, \(J_o\), was determined with an approximate 95% confidence interval within ±2% of the stated value.

4. Effect of pH in the presence of NOM

Fig. 10 illustrates the effect of pH on solution flux. The solid lines represent model fits to Eq. (6); directly measured process parameters and fitted model parameters are tabulated in Table 7. For these experiments, a separate batch of concentrated TMK-NOM was diluted to 14 mg l\(^{-1}\) DOC and ionic strength was adjusted to 0.01 M as NaCl. After 10 h
filtration, the normalized solution flux of pH 3, 4, 7, and 10 were approximately 0.62, 0.61, 0.56, and 0.57, respectively. These results show a reduced effect of pH in the presence of NOM as compared with results obtained in the absence of NOM. Surprisingly, the lowest pH values (3 and 4) exhibited somewhat less fouling than the higher pH values; at low pH, NOM molecules are more protonated, and a greater fouling potential would be expected. However, negative charge on the membrane is also more effectively screened; Vrijenhoek et al. [44] report that the NF-70 membrane carries a small positive charge at pH 1 (∼3 mV) and a small negative charge (∼−8 mV) at pH 4. Therefore, salt rejection is low as compared to higher pH values, and overall flux decline is less severe. As the pH increases, NOM functional groups become ionized, membrane charge becomes more negative, and membrane permeability increases (i.e., η approaches unity). At pH 7 specific cake resistance is statistically similar to the lower pH values; however, the increase in salt rejection becomes significant; therefore, flux decline is most severe at this pH. As the pH increases further to 10, the reduction in specific cake resistance is statistically significant, and salt rejection declines somewhat. These factors combine to reduce the magnitude of flux decline. The reduction in cake resistance is expected, based on ionization of, and charge repulsion between, NOM functional groups within the cake. A decrease in rejection at pH values above 8 was not expected, but similar behavior has been observed previously for the FT-30 membrane [59]. It is possible that the reduction observed here was related to the increase in membrane permeability.

4.8. Effect of calcium on NOM fouling

Multivalent cations (calcium) have been shown to significantly affect membrane fouling [2,15,24]. Process performance parameters for several runs in the presence of CaCl2 are tabulated in Table 8; these are compared to parameters determined in the absence of CaCl2 (reported above). Calcium has the ability to interact strongly with weak acid groups in the membrane phase, thus reducing fixed charge density [26]. Such a reduction in charge density would be expected to reduce membrane permeability; potentially increasing flux decline. However, in the absence of NOM, flux decline caused by a feed solution of NaCl was more pronounced (Jf/J0 = 0.74) than the decline caused by a solution composed of NaCl and CaCl2 (Jf/J0 = 0.81) having the same ionic strength. The ability of calcium to mitigate flux decline appears to be related primarily to a reduction in osmotic pressure. The major effect seems to be related to the significant reduction in sodium rejection observed when calcium was present. In addition, the ideal osmotic pressure of the solution containing calcium is about 15% lower than the 0.01 M NaCl solution. A minor effect (on the order of a few percent over the concentration range studied here) may be related to the somewhat lower osmotic coefficient exhibited by CaCl2 solutions as compared with NaCl solutions; e.g., at a concentration of 0.01 mol kg−1, the molal osmotic pressure coefficient for CaCl2 is 0.908 while that of NaCl is 0.968.

The presence of NOM increased flux decline, reducing Jf/J0 from 0.74 to 0.64 in the absence of calcium and from 0.81 to 0.61 in the presence of calcium. Therefore, while the increase was greater, the flux decline caused by NOM fouling in the presence of calcium was only slightly lower than that caused by NOM in a solution of NaCl at the same ionic strength. Flux decline caused by NOM in the absence of calcium was caused, in part, by a significantly increased rejection of NaCl; in the presence of calcium, the rejection of conductivity was lower. In addition, as discussed above, the feed osmotic pressure is lower in the presence of calcium at constant ionic strength. However, it is likely that calcium is more effective at reducing charge repulsion between ionized functional groups on NOM molecules, as a result of complex or ion pair formation, with subsequent lowering of cake porosity (an increase of cake resistance) through decreased electrostatic repulsion or increased cross-linking [15].

Table 8

| CaCl2 (M) | NaCl (M) | NOMa (%DOC) | Jf/J0 | Rejection | Rejection | Rejection | Rejection |
|----------|----------|-------------|-------|-----------|-----------|-----------|
| 0.0      | 0.01     | 0          | 0.74  | ND        | 45-55 (46) | –         |
| 0.0      | 0.01     | 10         | 0.64  | ND        | 70-80 (73) | (98)      |
| 0.007    | 0.0      | 0           | 0.81  | 64-71 (68)| 30-42 (37) | 42-46 (43)| –         |
| 0.007    | 10       | 0.61        | 87-94 (91)| 63-79 (72)| 62-67 (64) | (95)      |

Solution conditions: ionic strength = 0.001, temperature = 23 °C, recovery = 85%, crossflow velocity = 0.1 m s−1, recovery = 0.85, temperature = 23 °C. The average of seven rejection values is shown in parenthesis. ND: not determined.

*Rejection values varied over a range less than 1% of stated value.

**Table 8**

cant effect only after the binding sites on the NOM became saturated. As discussed by Hong and Elimelech [15], part of the flux decline is likely related to the ability of calcium to reduce NOM charge density, reduce electrostatic repulsion between humic macromolecules, and thus create a denser NOM cake on the membrane surface.

The effect of calcium in the presence of 0.001-M phosphate buffer (HPO\(_4^{2-}\) + H\(_2\)PO\(_4^{-}\)) = 1 \times 10^{-4} M (added as sodium salt) is also shown in Fig. 12. Significant flux decline due to fouling was observed during this experiment, despite a low calcium concentration of 0.001 M CaCl\(_2\). Equilibrium calculations suggest the likelihood that the solution was unstable (oversaturated) with respect to a hydroxyapatite solid phase. While direct measurements were not made, it is possible that the formation of such an inorganic precipitate formation caused the extensive flux decline observed, which was significantly different from the flux decline caused by NOM cake formation. It was also observed that the conductivity rejection decreased significantly from 73 to 39% during filtration. This is consistent with the effect of calcium in the absence of NOM. One explanation for this observation is that the precipitate was involved in the co-adsorption or complexation of NOM, reducing its ability to enhance salt rejection by charge repulsion.

5. Conclusions

Feed solution chemistry and natural organic matter influenced flux decline during nanofiltration using a negatively charged aromatic polyamide membrane. The effects of solution chemistry on solute and solution flux were modeled conceptually in terms of the effects of ions shielding charge on the membrane surface. For the negatively charged membrane studied here, shielding occurred at low pH and high ionic strength; small amounts of calcium were also effective. When membrane charge was neutralized or shielded...
the membrane permeability was reduced, possibly due to a reduction in membrane porosity or pore size. Solute rejection was also reduced, consistent with Donnan exclusion. Both mechanisms can have a significant effect on solution flux. Flux decline was modeled by accounting for changes in osmotic pressure with time, and by employing an effective permeability. With increasing ionic strength, the dominant mechanism was a reduction in effective permeability. With increasing pH (at constant ionic strength), the effective permeability increased, but solution flux still decreased as a result of increased osmotic effects resulting from increased solute rejection. This behavior is in contrast to looser membranes having low salt rejection, for which solution flux increases with increasing pH as a result of increases in membrane permeability.

The presence of NOM caused greater flux decline resulting from a combination of NOM cake resistance and increased rejection of NaCl by negatively charged NOM functional groups. Increasing NaCl concentration had little effect on the mass of NOM deposited, but significantly increased the specific resistance of the NOM cake. The effect of ionic strength on specific resistance correlated with a reduction in NOM size, estimated by separate UF permeation experiments and size exclusion chromatography analysis of UF permeate. Therefore, increased specific cake resistance is consistent with a more compact, less porous cake. Flux decline by NOM solutions showed a maximum at pH 7, where salt rejection was also a maximum. Flux decline caused by NOM fouling in the presence of calcium was only significantly different than that caused by NOM in a solution of NaCl at the same ionic strength when the calcium concentration corresponded to saturation of NOM binding sites.

Acknowledgements

This research was supported by the US Department of the Interior, Bureau of Reclamation, Desalination Research and Development Program (Grant 98-FC-81-0061); the National Science Foundation, Division of Chemical and Thermal Systems (Grants CTS-9400610 and Division of Bioengineering and Environmental Systems (Grants BES-9871241 and BES-9984709); and the US Department of Energy, Basic Chemical Sciences Division (Grant DE-FG02-90ER14114). No agency review was done, and no official endorsement should be inferred. J.E. Kilduff also gratefully acknowledges support from the Eastman Kodak Company.

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