

A Novel Method for Investigating the Influence of Feed Water Recovery on Colloidal and NOM Fouling of RO and NF Membranes

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ABSTRACT

A systematic investigation on the role of feed water recovery (or concentration factor) in colloidal and natural organic matter (NOM) fouling of reverse osmosis (RO) and nanofiltration (NF) membranes is reported. Fouling experiments were conducted using a laboratory-scale crossflow test unit with continuous permeate disposal to simulate concentration factor (CF) and feed water recovery as commonly observed in full-scale RO/NF systems. With this novel method, the deterioration in membrane performance due to fouling and recovery-related osmotic pressure buildup can be distinguished. For colloidal fouling of RO membranes, the so-called “cake enhanced osmotic pressure” is a key fouling mechanism resulting in severe decline in permeate flux and significant decrease in salt rejection with increasing CF. On the other hand, NOM–calcium complexation rather than enhanced osmotic pressure is the key mechanism for NOM fouling of NF membranes. The decline in permeate flux and decrease in solute rejection with increasing CF were significant under favorable conditions for fouling, namely at higher initial permeate flux, ionic strength, and calcium ion concentration.

Key words: concentration factor; colloidal fouling; NOM fouling; solute rejection; cake enhanced osmotic pressure; NOM–calcium complexation; EDTA; RO; NF

INTRODUCTION

ADVANCEMENTS IN MEMBRANE TECHNOLOGY and the pressing need for augmenting potable and industrial water supplies have accelerated the use of membrane-

based treatment processes. Of particular interest is the use of reverse osmosis (RO) and nanofiltration (NF) for sea water and brackish water desalination and for the removal of natural organic matter (NOM), the major precursor of disinfection byproducts. However, colloidal and

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NOM fouling is still a major obstacle for efficient operation of RO and NF plants, adversely affecting both the quantity (permeate flux) and quality (solute concentration) of the product water. Therefore, fundamental understanding of colloidal and NOM fouling mechanisms and the impact of fouling on membrane performance are of utmost importance.

Numerous studies have been carried out to elucidate colloidal (e.g., Cohen and Probst, 1986; Gilron and Hasson, 1987; Zhu and Elimelech, 1997; Yiantsios and Karabelas, 1998; Hoek *et al.*, 2002) and NOM (e.g., Hong and Elimelech, 1997; Braghetta *et al.*, 1998; Schafer *et al.*, 1998; Cho *et al.*, 1999, 2000; Lee *et al.*, 2002a; Seidel and Elimelech, 2002) fouling mechanisms. Among the factors investigated in these studies were feed water solution chemistry (pH, ionic strength, and divalent cations), foulant characteristics (size, structure, and charge characteristics), membrane properties (pore size, surface charge, roughness, and hydrophobicity), solute–solute and solute–membrane interactions (steric, hydrophobic, and electrostatic interactions), and hydrodynamic operating conditions (initial permeation rate and crossflow velocity).

The results of these laboratory-scale studies have demonstrated that there exist favorable conditions for fouling, namely high ionic strength, presence of divalent cations, low pH, high initial permeation rate, and low crossflow velocity. It has been suggested that membrane performance—permeate flux and solute rejection—can be optimized by avoiding these favorable conditions for fouling. These findings, however, were mostly obtained from filtration experiments performed with laboratory-scale crossflow setups utilizing flat sheet membrane coupons. Feed water recovery, one of the most important parameters in membrane plants, usually approaches zero in such laboratory-scale setups because of the very small area of the membranes used. In contrast, in real-world applications of RO/NF, solute or foulant concentration in spiral-wound modules increases downstream of the pressure vessel containing the modules (Mulder, 1996; Song *et al.*, 2002). The increase in salt concentration along the membrane affects the local membrane flux and salt rejection, and thus the overall membrane performance.

Despite the vast significance of membrane recovery in membrane performance, laboratory studies investigating the effect of feed water recovery and the resulting concentration factor on fouling behavior are limited. The paucity in such studies is mostly attributed to the limitation of laboratory-scale setups, that is, the relatively small surface area of the membrane, which results in negligible recovery or change in concentration factor. While the use of small membrane modules in laboratory studies is feasible, the cost is prohibitive as each fouling run would require a new, fresh membrane module.

Hasson *et al.* (2001) and Le Gouellec and Elimelech (2002) investigated the influence of feed water recovery and concentration factor on calcium sulfate (gypsum) scaling of RO and NF membranes. The results showed that permeate flux continuously decreased as concentration factor increased. Furthermore, a marked decrease in permeate flux was observed at a certain value of concentration factor (or feed water recovery) which corresponded to the onset of scale formation. However, the mechanisms of precipitate fouling are quite different from colloidal or organic fouling. Systematic studies on the role of feed water recovery on colloidal and NOM fouling are therefore of paramount importance.

The objective of this study is to systematically investigate the influence of feed water recovery on the fouling behavior of RO and NF membranes. Emphasis is placed on (1) developing an experimental method to simulate feed water recovery using a laboratory-scale plate-and-frame crossflow filtration unit and (2) differentiating membrane performance (permeate flux and salt rejection) changes due to fouling from those attributed to the increase in feed water recovery. The new method to investigate the influence of feed water recovery and concentration factor on fouling behavior is used to further verify and elucidate the fouling mechanisms governing colloidal and NOM fouling of RO and NF membranes.

MATERIALS AND METHODS

RO and NF membranes

Commercial thin-film composite RO and NF membranes were used—the RO membrane was LFC-1 (Hydranautics, Oceanside, CA) and the NF membrane was NF-70 (Dow-FilmTec, Minneapolis, MN). Average hydraulic resistances were determined to be $9.16 (\pm 0.11) \times 10^{13} \text{ m}^{-1}$ and $3.65 (\pm 0.07) \times 10^{13} \text{ m}^{-1}$ for the RO and NF membranes, respectively. Observed salt rejections (R_{obs}) of the RO and NF membranes were 97.5–98.2 and 84.5–86.4%, respectively (determined at an applied pressure of 100 psi, 10 mM NaCl, and a crossflow velocity of 8.1 cm/s). Other properties of the membranes can be found elsewhere (Childress and Elimelech, 1996; Hoek *et al.*, 2001; Seidel and Elimelech, 2002).

Reagents and chemical solutions

All chemicals used were ACS grade (Fisher Scientific, Pittsburg, PA) and were used without further purification. Chemical solutions and feed waters used for colloidal and NOM fouling experiments were prepared with deionized (DI) water (Nano Pure II, Branstead, Dubuque, IA) having a conductivity less than $0.7 \mu\text{S/cm}$ when in equilib-

rium with atmospheric CO₂. Salt stock solutions used to obtain desired feed ionic strength, divalent (calcium) ion concentration, and pH were prepared using NaCl, CaCl₂ · 2H₂O, and NaHCO₃, respectively. For further investigations of cake-enhanced osmotic pressure and NOM-calcium complexation, sucrose, lanthanum chloride (LaCl₃), and disodium EDTA (Na₂C₁₀H₁₄O₈N₂ · 2H₂O) stock solutions were prepared with DI water. Salt (NaCl) and Ca²⁺ concentrations of feed and permeate samples were measured during the course of the fouling tests with feed water recovery simulation using a conductivity meter (Model 32, YSI Co., Inc., Yellow Spring, OH) and a calcium selective electrode (Model 93-20, Orion Research Inc., Boston, MA) along with reference electrode (Model 90-01, Orion Research Inc., Boston, MA) connected to a pH/mV meter (Accumet, Fisher Scientific), respectively.

Colloidal particles and NOM

Commercial colloidal silica (SiO₂) particles with an average diameter of 300 nm (MP-3040, Nissan Chemical Industries, Ltd., New York, NY) and an initial concentration of 200 mg/L were used as the model colloidal foulant for the accelerated fouling tests. For the few dead-end filtration tests designed to further verify cake-enhanced osmotic pressure, the initial silica colloid concentration was 100 mg/L. The colloidal silica was supplied in the form of stable concentrated aqueous suspension at an alkaline pH, and was used as obtained with no further treatment. Gravimetric analysis revealed the density of the particles to be 2.30 g/cm³. The measured electrophoretic mobility (ZetaPALS, Brookhaven Instruments Corp., Holdsville, NY) of the silica colloids verified that the colloidal particles were negatively charged at the pH and solution chemistries used for the fouling tests. Feed colloid concentration was measured during the course of the fouling tests using a turbidity meter (Model 43900, Hach Company, Loveland, CO).

The NOM used in this study was concentrated from Nakdong River surface water (Changweon, Korea) by a presoftening step, followed by RO concentration. The concentrated NOM was further freeze dried to make a powder form. Dissolved organic carbon content (DOC) of the NOM powder was determined to be 0.462 g DOC/g NOM using a DOC analyzer (Model 820, SIEVERS, Ionics Instrument Business Group, Boulder, CO). NOM characteristics, including size (average molecular weight), structure (hydrophobic and hydrophilic content), and functionality (carboxylic and phenolic groups) can be found in our previous studies (Lee *et al.*, 2002a, 2002b). An initial concentration of 20 mg (NOM powder) per liter was used for the fouling tests. NOM concentration of feed and permeate samples was measured

during the course of the fouling tests using UV absorbance at 254 nm (Hewlett Packard 8453).

Crossflow test unit and fouling experiment with feed water recovery simulation

The two rectangular plate-and-frame membrane cells were configured in parallel. Each cell contains a flat membrane sheet, placed in a rectangular channel having dimensions of 7.7 cm length, 2.6 cm width, and 0.3 cm height. The calculated hydraulic diameter of the channel is 0.54 cm. Retentate flow rate was monitored by a floating disc rotameter (King Instrument, Fresno, CA), and feed pressure and crossflow velocity were controlled using a bypass valve (Swagelok, New Haven, CT) and a back pressure regulator (US Para Plate Co., San Jose, CA). The permeate flux was monitored continuously by a digital flow meter (Optiflow 1000, Humonics, Folsom, CA) interfaced with a PC. Crossflow velocity was fixed for all experiments (8.1 cm/s) and the feed water temperature was maintained at 20.0 (±0.3)°C by a recirculating heater/chiller (Model 633, Polysciences, Warrington, PA). Permeate was disposed continuously and the cumulative permeate volume was determined by integrating the permeate flux over time. Because the feed-water volume (initial volume 12 L) decreased continuously as permeate was discarded, the solute (salt, colloids, and NOM) concentration in the feed tank increased accordingly and was measured several times during the course of each experiment.

The experimental protocol for the colloidal and NOM fouling experiments involved: (1) 12-h stabilization with DI water with the permeate being disposed to compact membranes and remove possible impurities, (2) 12-h equilibration with DI water with the permeate being recycled to the feed tank, (3) 6-h equilibration with the salt solution to be used in the fouling experiment, and finally, (4) initiation of colloidal or NOM fouling by the addition of 200 mg/L silica colloids or 20 mg/L NOM to the feed tank, respectively. Prior to the fouling experiments, salt (NaCl) was used alone to determine the effect of concentration factor (CF) on salt rejection and permeate flux behavior due to osmotic pressure buildup ("osmotic run"). Colloids in salt-free deionized water and NOM in salt-free deionized water were also used to determine the extent of flux decline due to cake or gel formation. Such curves were used as baselines for further analysis of the influence of fouling and CF on solute (salt or NOM) rejection.

Feed water recovery and concentration factor

Due to the very small surface area (20 cm² per cell) of the membranes used in the crossflow plate-and-frame test unit, it was not possible to directly study the influ-

ence of feed water recovery on colloidal and NOM fouling behavior. To circumvent this problem, the product water permeate was disposed rather than recycled back to the feed tank, thus allowing the feed tank concentration to increase continuously with time. Increasing the concentration of feed water through permeate disposal (represented by the CF) is directly linked to the feed water recovery (Y) via (Sheikholeslami and Tan, 1999; Hasson *et al.*, 2001; Le Gouellec and Elimelech, 2002):

$$CF = 1 + \frac{R_{obs} V_p}{V_F - V_p} \quad (1)$$

$$Y = \frac{CF - 1}{CF - (1 - R_{obs})} \quad (2)$$

where R_{obs} is the observed solute rejection at the corresponding CF, V_p is the cumulative permeate volume, and

V_F is the feed water volume. For example, feed water recovery ranging from 0 to 0.7 is equivalent to an increase in concentration factor from 1.0 to 3.3 when solute is completely retained by a membrane (i.e., $R_{obs} = 1.0$). In this study, most fouling experiments were performed until concentration factor reached approximately 3.3.

Dead-end filtration for colloidal fouling

To further investigate the concept of cake-enhanced osmotic pressure (Hoek *et al.*, 2002; Hoek and Elimelech, 2003), dead-end RO filtration tests were carried out with feed solution containing sucrose (a neutral solute to produce osmotic pressure), silica colloids, and a small amount of trivalent salt ($LaCl_3$) to destabilize colloids and form a cake on the membrane surface. The NaCl used in the previously described crossflow fouling experi-

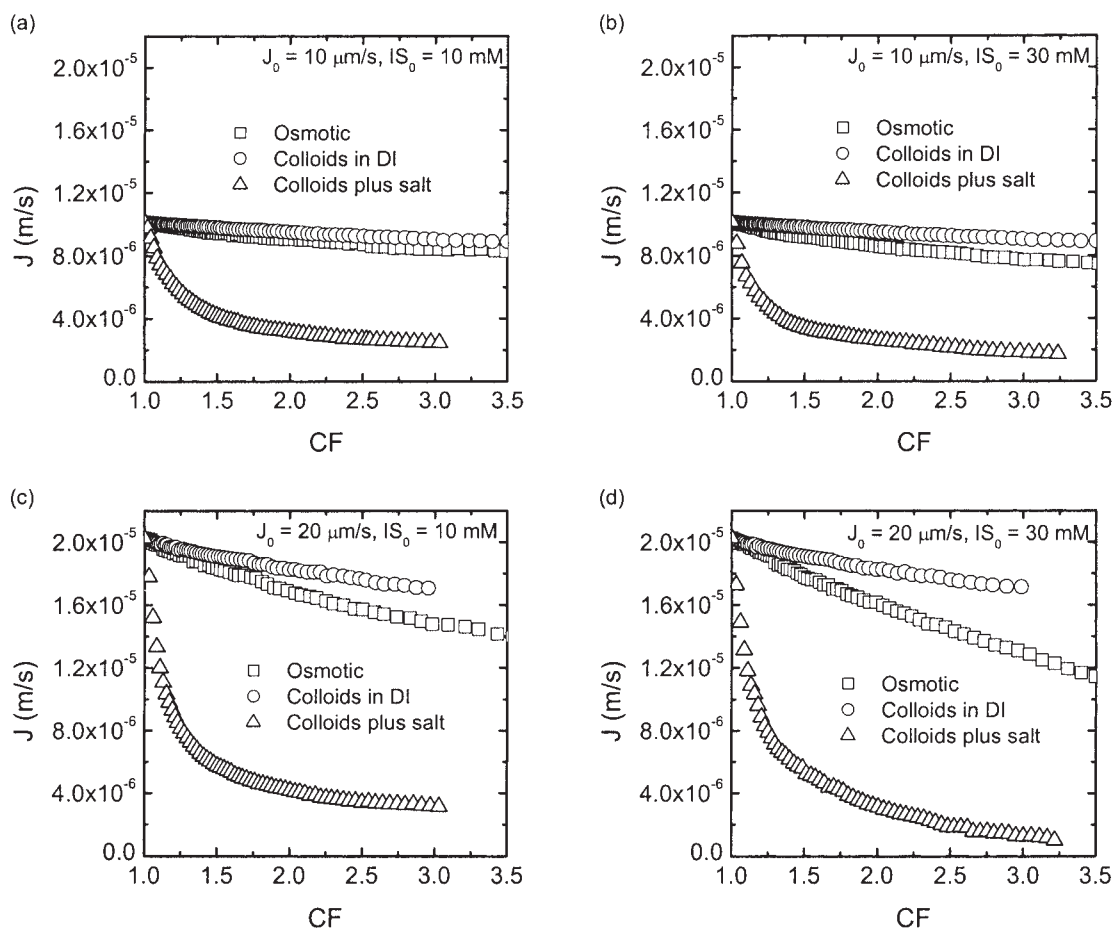


Figure 1. Permeate flux (J) as a function of concentration factor (CF) for different initial permeate fluxes (J_0) and ionic strengths (IS_0): (a) $J_0 = 10 \mu\text{m/s}$, $IS_0 = 10 \text{ mM}$; (b) $J_0 = 10 \mu\text{m/s}$, $IS_0 = 30 \text{ mM}$; (c) $J_0 = 20 \mu\text{m/s}$, $IS_0 = 10 \text{ mM}$; and (d) $J_0 = 20 \mu\text{m/s}$, $IS_0 = 30 \text{ mM}$. Experimental conditions: initial colloid concentration = 200 mg/L, crossflow velocity = 8.1 cm/s (Reynolds number = 434), temperature = $20.0 \pm 0.3^\circ\text{C}$, and pH = 5.95 ± 0.05 (ambient pH). The experiments labeled as “Osmotic” are for runs with only salt (i.e., with no colloids).

ments has two important roles in cake-enhanced osmotic pressure. First, it produces elevated osmotic pressure near the membrane surface, resulting in flux decline by reducing the net driving force. Second, NaCl destabilizes colloidal particles, thus inducing the formation of a cake layer on the membrane surface, which is essential for the development of cake-enhanced osmotic pressure. The use of sucrose and LaCl_3 will decouple the dual role of NaCl because the neutral sucrose molecules will only contribute to osmotic pressure, while the 0.1 mM trivalent LaCl_3 salt will effectively destabilize colloidal particles but will have a negligible effect on osmotic pressure buildup.

EDTA treatment for NOM fouling

The use of a strong chelating agent as a means to lessen NOM fouling resulting from NOM–calcium complexa-

tion was investigated. A strong chelating agent, disodium EDTA ($\text{Na}_2\text{C}_{10}\text{H}_{14}\text{O}_8\text{N}_2 \cdot 2\text{H}_2\text{O}$), was selected. In these experiments, the NF membrane was first stabilized and equilibrated for 24 h with DI water, followed by 6-h equilibration with the 10-mM ionic strength salt solution (0.3 mM CaCl_2 along with 8.1 mM NaCl and 1.0 mM NaHCO_3). NOM was then introduced to the feed water, and the crossflow filtration was operated under continuous permeate disposal. The EDTA (0.3 mM) was added at two different times (or CF values) during the fouling test. In one experiment, the 0.3 mM EDTA was added to the feed water simultaneously with NOM addition (i.e., $\text{CF} = 1.0$), and in another test, 0.3 mM EDTA was added after a marked flux decline was observed. The first test investigates the competition between NOM and EDTA for free calcium ions, and the latter test examines the ligand exchange reaction mediated by EDTA for

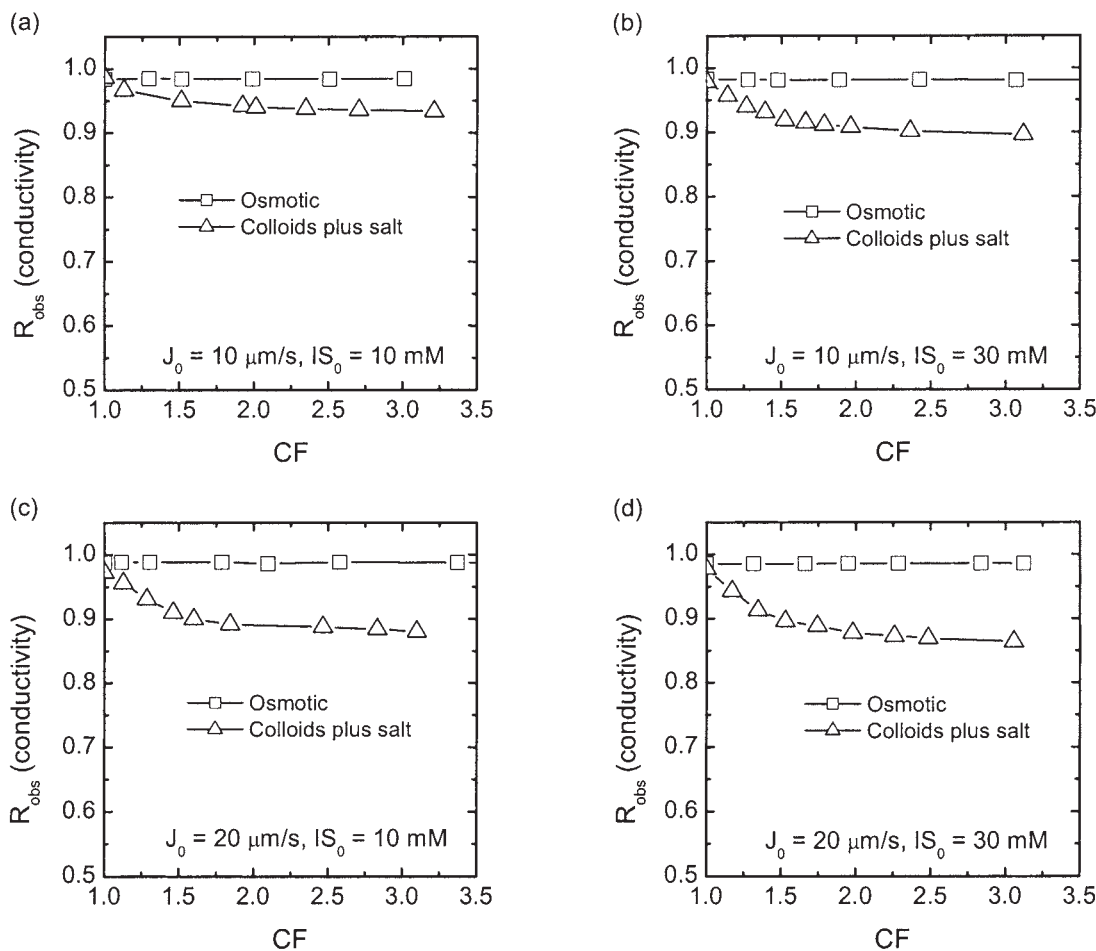


Figure 2. Observed salt rejection (R_{obs}) as a function of concentration factor for different initial permeate fluxes (J_0) and ionic strengths (IS_0): (a) $J_0 = 10 \mu\text{m/s}$, $IS_0 = 10 \text{ mM}$; (b) $J_0 = 10 \mu\text{m/s}$, $IS_0 = 30 \text{ mM}$; (c) $J_0 = 20 \mu\text{m/s}$, $IS_0 = 10 \text{ mM}$; and (d) $J_0 = 20 \mu\text{m/s}$, $IS_0 = 30 \text{ mM}$. Data are shown for runs with two different feed solutions. Experimental conditions are identical to those in Figure 1. The experiments labeled as “Osmotic” are for runs with only salt (i.e., with no colloids).

NOM–calcium complexes in the gel (fouling) layer (Hong and Elimelech, 1997).

RESULTS AND DISCUSSION

Colloidal fouling of RO membranes

Permeate flux behavior. To investigate the influence of concentration factor on colloidal fouling of the RO membrane, experiments were carried out with different feed solution ionic strengths and initial permeate fluxes. The results presented as permeate flux vs. CF are shown in Fig. 1. Permeate flux declined linearly as CF was increased for both the “osmotic” (i.e., only electrolyte) run and the run with colloids suspended in deionized water. Comparing the slopes of these linear flux decline curves showed that osmotic pressure buildup at the membrane surface was more

influential than colloidal cake layer resistance. Furthermore, the linear flux decline with respect to CF was more severe for higher solution ionic strength and initial permeate flux due to the greater buildup of osmotic pressure or colloidal cake at the membrane surface. It should be noted, however, that cake accumulation for fouling runs with deionized water is expected to be very small due to the strong electrostatic repulsion between particles and between particles and the membrane surface.

A marked decrease in permeate flux was observed for the runs with colloids suspended in electrolyte solution. The permeate flux decline deviated significantly from the linear dependence on CF observed for colloidal fouling runs with no electrolytes. We attribute this severe flux decline to “cake-enhanced osmotic pressure,” as suggested by Hoek *et al.* (2002) and Hoek and Elimelech (2003). The reduction in interparticle electrostatic dou-

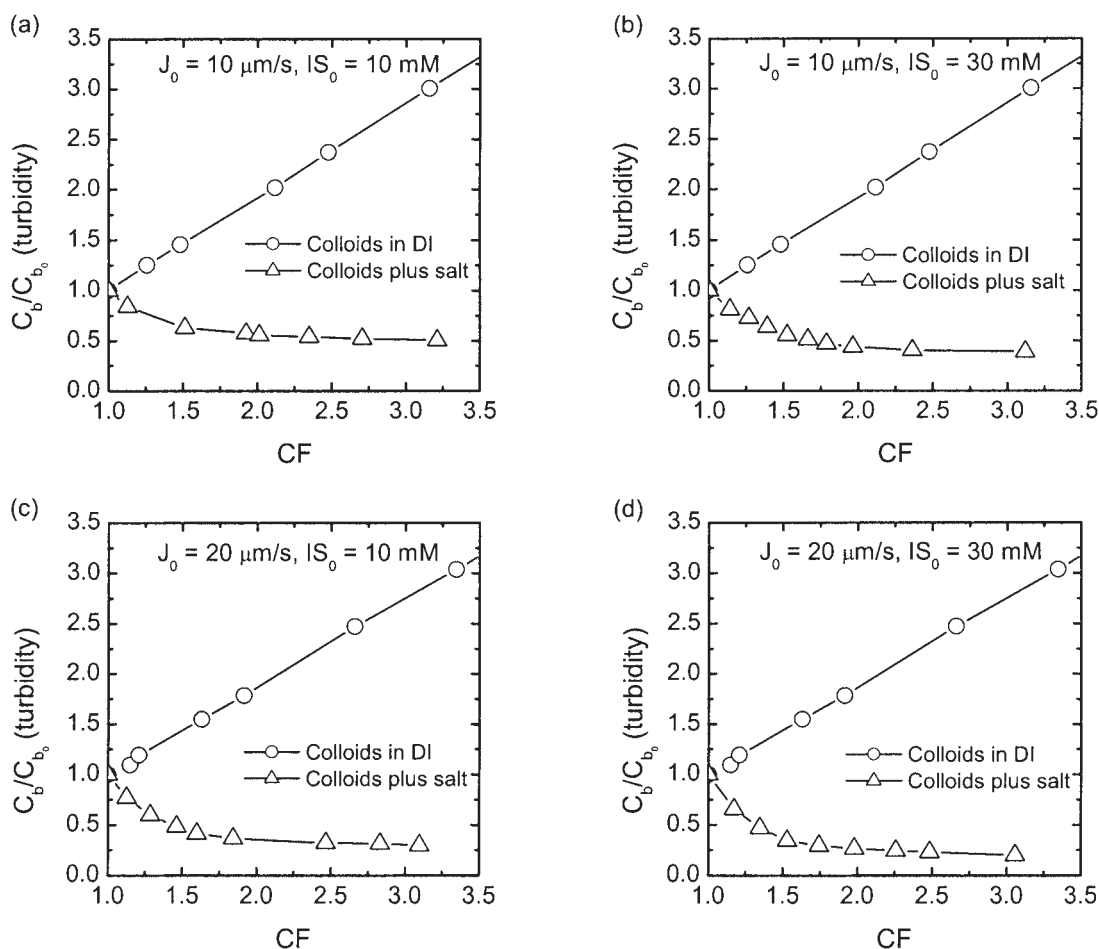


Figure 3. Variation of the measured RO feed colloid concentration (C_b) scaled with its initial value (C_{b0}) as a function of concentration factor (CF) for different initial permeate fluxes (J_0) and ionic strengths (IS_0): (a) $J_0 = 10 \mu\text{m/s}$, $IS_0 = 10 \text{ mM}$; (b) $J_0 = 10 \mu\text{m/s}$, $IS_0 = 30 \text{ mM}$; (c) $J_0 = 20 \mu\text{m/s}$, $IS_0 = 10 \text{ mM}$; and (d) $J_0 = 20 \mu\text{m/s}$, $IS_0 = 30 \text{ mM}$. Experimental conditions are identical to those in Figure 1.

ble layer repulsion by the electrolyte (NaCl) results in the formation of a thick cake layer on the membrane surface, which significantly hinders the back diffusion of accumulated salt. The marked increase in osmotic pressure at the membrane surface caused a substantial reduction in the driving force and hence severe flux decline. Much more severe flux decline was observed for runs at higher ionic strength and initial permeate flux due to accumulation of a thicker cake layer and the greater osmotic pressure buildup at the membrane surface.

Influence of CF and fouling on salt rejection. To investigate the influence of feed water recovery (or concentration factor) and colloidal fouling on salt rejection, salt concentrations in feed and permeate samples were measured several times during the course of the fouling runs described earlier. The change in the observed salt rejection (R_{obs}) with CF at various combinations of initial ionic strengths and permeate fluxes is shown in Fig. 2. Without the colloidal foulant (“osmotic” run), salt rejection was nearly constant. This implies that, in absence of fouling, the increase in feed water recovery along a membrane module dose not affect salt rejection, despite the decrease in permeate flux.

In contrast, in the presence of colloidal particles, salt rejection by the RO membrane decreased noticeably as colloidal fouling progressed. This implies that colloidal fouling of RO membranes results not only in permeate flux decline but also in deterioration of the permeate water quality. Figure 2 further shows that increasing the solution ionic strength and initial permeate flux results in greater reduction of salt rejection with CF. For the most favorable fouling conditions investigated—30 mM ionic strength and initial permeate flux of 20 $\mu\text{m/s}$ —salt rejection decreased from 98.5% (at CF = 1) to 85.2% (at CF = 3.0).

Change of feed particle concentration with CF. During the course of the fouling runs shown in Fig. 1, the particle concentration in the feed solution was measured at several time intervals. The scaled particle concentration (i.e., particle concentration, C_b , divided by initial feed concentration, C_{bo}) as a function of CF is shown in Fig. 3. For the runs with colloids suspended in DI water, the feed particle concentration increased as CF was increased due to the continuous decrease in feed water volume as permeate was disposed. In fact, for this case C_b/C_{bo} increased linearly (slope is almost unity) with increasing CF. This implies that, in DI water, the amount of particles deposited on the membrane surface is negligible due to the strong interparticle electrostatic repulsion at such very low ionic strength.

Unlike the case with DI water, C_b/C_{bo} for the runs with

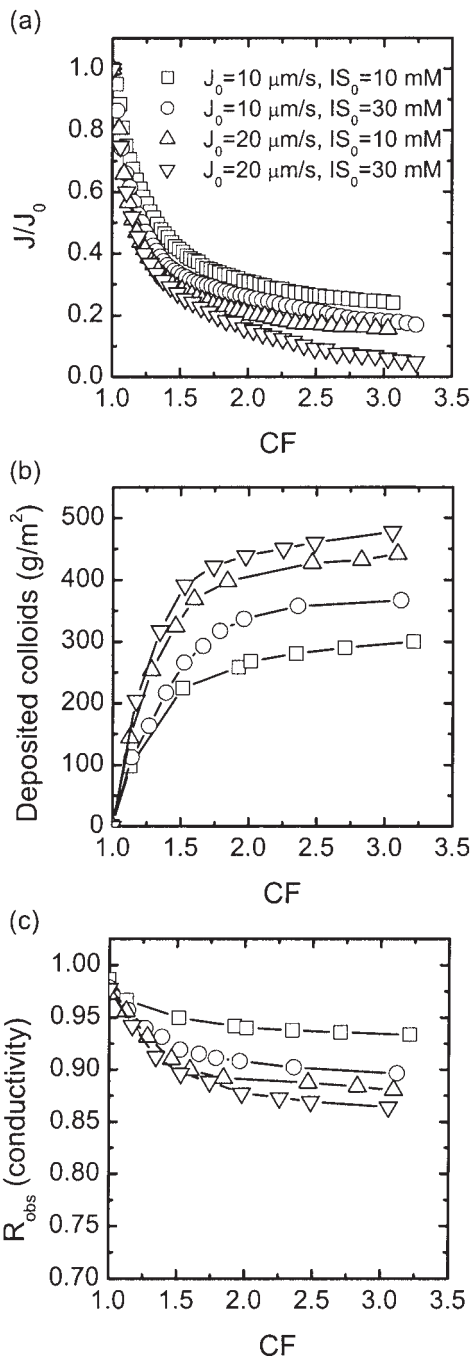


Figure 4. RO membrane performance (flux, deposited colloid mass, and observed salt rejection) as a function of concentration factor (CF) for feed solutions containing silica colloids and salt: (a) normalized flux, J/J_0 , vs. CF; (b) deposited colloid mass per unit membrane area versus CF; and (c) observed salt rejection, R_{obs} , vs. CF. Data are shown for runs at different initial permeate fluxes (J_0) and ionic strengths (IS_0). Experimental conditions are identical to those in Figure 1.

colloids suspended in electrolyte solution decreased as CF was increased. This means that particle concentration in the feed decreased continuously due to particle deposition at the membrane surface and formation of a cake layer. Cake formation is induced by the destabilization of colloidal particles due to charge screening and reduction in the magnitude and range of the interparticle electrostatic double layer repulsion. As expected, greater accumulation of particles (or greater reduction in C_b/C_{bo}) is observed for higher ionic strength (30 vs. 10 mM) and initial permeate flux (20 vs. $10 \mu\text{m/s}$). The results in Figs. 1–3 provide a comprehensive understanding of cake-enhanced osmotic pressure (CEOP) as well as its causes and consequences. As fouling progresses, colloidal particles deposit on the membrane surface (Fig. 3) resulting in enhanced salt concentration near the membrane surface. The enhanced salt concentration results in a marked flux decline (Fig. 1) and greater salt transport across the membrane, which results in deterioration of salt rejection (Fig. 2).

Effect of initial flux and salt concentration on CEOP. Figure 4 demonstrates the influence of initial permeate flux and solution ionic strength on permeate flux, deposited colloidal particles at the membrane surface, and salt rejection. The increase in initial flux and ionic strength results in a more rapid growth of the fouling cake layer (Fig. 4b) due to the effect of permeation drag (Zhu and Elimelech, 1997). The thicker cake layer as well as the higher permeate flux results in more severe cake-enhanced osmotic pressure buildup at the membrane surface and thus greater flux decline (Fig. 4a). The more severe enhanced concentration polarization at higher ionic strength and permeate flux also results in greater deterioration of salt rejection (Fig. 4c). The latter is in accord with our recent findings regarding the influence of CEOP during colloidal fouling on salt (Lee *et al.*, 2004) and trace organic (Ng and Elimelech, 2004) rejection by NF and RO. The continuous decrease in permeate flux and salt rejection with CF when colloidal fouling takes place due to CEOP underscores the importance of preventing colloidal fouling in RO operations as the water quality can be seriously compromised by the deterioration of salt rejection.

Further verification of CEOP. Previous work (Hoek *et al.*, 2002; Hoek and Elimelech, 2003) as well as the preceding results suggest that CEOP is induced by the hindered back diffusion of salt due to the presence of the colloidal cake layer. Our results described above also indicate that the electrolyte (NaCl) plays a dual role, namely promoting the accumulation of a cake layer on

the membrane surface and creating an elevated osmotic pressure at the membrane surface. To further verify the concept of CEOP, dead-end filtration tests were carried out with sucrose and lanthanum chloride (LaCl_3). In these experiments, 0.1 mM tri-valent salt (LaCl_3) was added to destabilize the colloidal particles, yet not to significantly influence the osmotic pressure. Sucrose (10 mM), on the other hand, was added to serve as the solute inducing the osmotic pressure buildup within the deposited cake layer.

The results in Fig. 5 support our earlier conceptual model for cake-enhanced osmotic pressure. The runs with colloids and colloids plus LaCl_3 resulted in very little flux decline because cake-enhanced osmotic pressure is negligible with LaCl_3 (only 0.1 mM) and the cake layer resistance is much smaller than the RO membrane resistance. Comparing the runs of sucrose and sucrose plus colloids reveals similar flux decline. This flux decline is attributed to the increased bulk sucrose concentration as permeate is disposed, similar to the “osmotic” runs described earlier. Cake-enhanced osmotic pressure is also negligible here because particles were very stable (no salt present) and did not form a cake layer on the membrane surface. However, the run with colloids plus sucrose and LaCl_3 resulted in severe flux decline. The flux decline in this case is attributed to cake-enhanced osmotic pressure. LaCl_3 destabilized the silica particles to induce the formation of a thick colloidal cake layer on the membrane surface. This, in turn, resulted in elevated sucrose con-

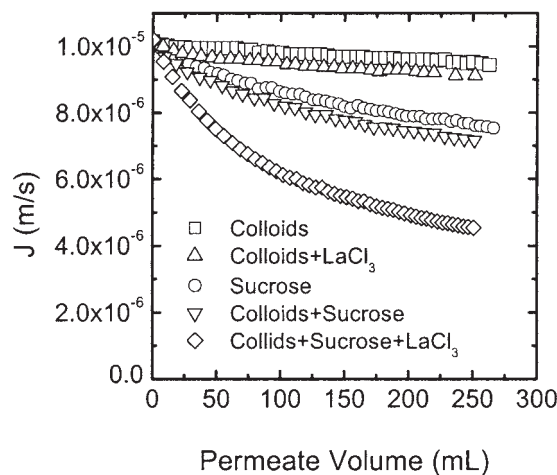


Figure 5. Verification of the role of cake-enhanced osmotic pressure (CEOP) in colloidal fouling through dead-end filtration. Data are shown for runs with five different feed solutions. Initial concentrations of colloids, sucrose, and LaCl_3 are 100 mg/L, 10 mM, and 0.1 mM, respectively. Other experimental conditions are: initial permeate flux (J_0) = $10 \mu\text{m/s}$, temperature = $23.0 \pm 0.5^\circ\text{C}$, and pH = 5.95 ± 0.05 (ambient pH).

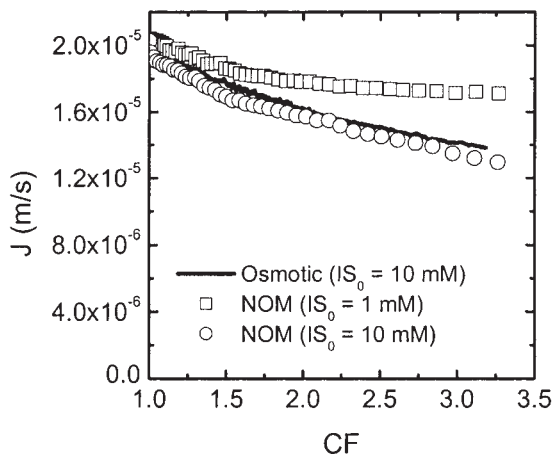


Figure 6. Permeate flux (J) as a function of concentration factor (CF) for feed solutions containing NOM. Data are shown for runs with different initial ionic strengths (IS_0). The “osmotic” line (i.e., with only indifferent monovalent salt in the feed solution) included in the figure is used as a baseline for the osmotic pressure contribution to flux decline. Experimental conditions are: initial NOM concentration = 20 mg/L, initial permeate flux (J_0) = 20 $\mu\text{m/s}$, crossflow velocity = 8.1 cm/s (Reynolds number = 434), temperature = 20.0 \pm 0.3°C, and pH = 8.05 \pm 0.05.

centration (or osmotic pressure) at the membrane surface and thus severe flux decline. These results verify the important role of salt in both promoting the accumulation of a cake layer on the membrane surface and creating an elevated osmotic pressure at the membrane surface.

NOM fouling of NF membranes

Role of CF in fouling with 1:1 (NaCl) electrolyte. The influence of concentration factor on the permeate flux behavior of the NF membrane was investigated at a fixed foulant (NOM) feed concentration (20 mg/L). Continuous permeate disposal runs were performed at two different concentrations of an indifferent salt (1 and 10 mM). The results shown in Fig. 6 also include the baseline (osmotic) run with an NOM-free electrolyte solution. The difference between the permeate flux in the presence of NOM and the osmotic run represents the net contribution of NOM to permeate flux decline.

Figure 6 shows that permeate flux declined almost linearly with increasing CF for the runs with NOM feed solutions at both the lower and the higher ionic strengths. This implies that the increase in CF is the major cause for flux decline. Increasing the ionic strength from 1 to 10 mM results in more flux decline due to either the increase in salt osmotic pressure or the increase in NOM deposition on the membrane surface. It is noteworthy that the differ-

ence in permeate flux in the presence of NOM and the osmotic run was negligible. This suggests that the increase in CF rather than NOM fouling contributes to permeate flux decline in the presence of indifferent salts.

The change in NOM concentration in the feed solution during the above fouling runs is depicted in Fig. 7. Comparing Figs. 7 and 3 indicates that NOM accumulation near the membrane surface with increasing CF is much smaller than the deposition of colloidal particles (Fig. 3) in the presence of indifferent salt. Figure 8a demonstrates that, when flux decline mainly results from the increase in CF rather than NOM fouling, salt rejection by the NF membrane is nearly constant. This implies that salt concentration near the membrane surface did not increase significantly, unlike the case with colloidal fouling where cake-enhanced osmotic pressure plays a major role (Fig. 2). In the absence of severe NOM fouling, NOM rejection by the NF membrane also remains nearly constant with CF (Fig. 8b). The slight decrease in NOM rejection at higher ionic strength is attributed to the increase in NOM accumulation near the membrane surface (Hong and Elimelech, 1997), which results in diffusive transport through the membrane.

NOM-calcium complexation controls fouling. The effect of divalent cations (Ca^{2+}) on NOM fouling during the continuous permeate disposal runs is illustrated in Fig. 9. In these experiments, total ionic strength is kept constant (10 mM) by varying NaCl concentration. Other experimental conditions including NOM concentration, initial flux, crossflow velocity, pH, and temperature are identical to those for the runs shown in Fig. 6.

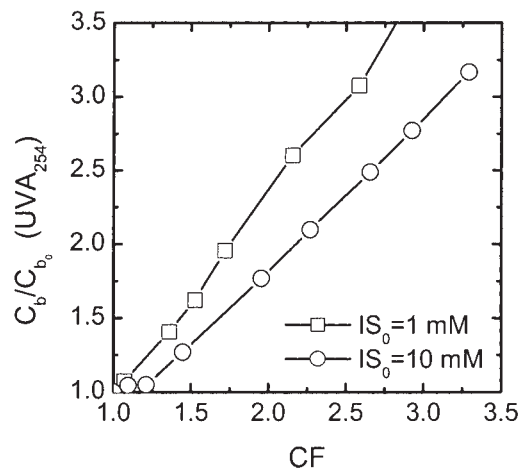


Figure 7. Variation of the measured NF feed NOM concentration (C_b) scaled with its initial value (C_{b0}) as a function of concentration factor (CF) for feed solutions containing NOM. Data are shown for runs with different initial ionic strengths (IS_0). Experimental conditions are identical to those in Figure 6.

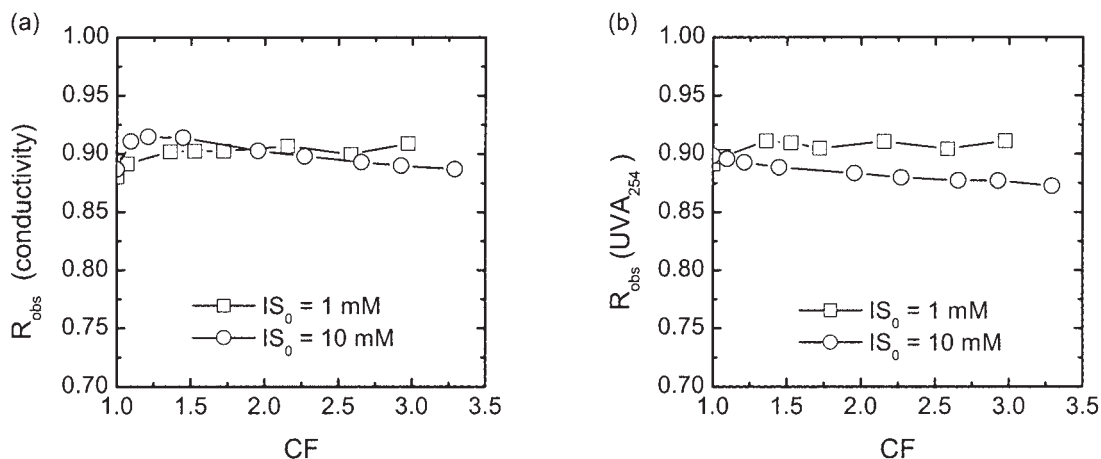


Figure 8. Solute observed rejection (R_{obs}) as a function of concentration factor for feed solutions containing NOM: (a) observed salt rejection versus CF and (b) observed NOM rejection vs. CF. Experimental conditions are identical to those in Figure 6.

The results clearly show that permeate flux decreases dramatically, and significantly deviates from the linear dependence on CF as calcium concentration increases. This implies that the main cause for the severe flux decline in the presence of calcium ions is NOM fouling rather than the increase in CF. In other words, the increase in the resistance of the NOM fouling layer to water permeation is much more significant compared to the decrease in the net driving force due to osmotic pressure at the membrane surface. The acceleration of NOM fouling in the presence of calcium ions is well documented in the literature (e.g., Hong and Elimelech, 1997; Braghetta *et al.*, 1998; Schafer *et al.*, 1998). NOM–calcium complexation results in a compact, dense NOM fouling layer on the membrane surface, which dramatically decreases the water permeability. The results shown in Fig. 10 further support our conclusion regarding the increased accumulation (deposition) of NOM and, thus, the more severe fouling with increasing calcium concentration. The higher the calcium concentration, the more NOM (Fig. 10a) and calcium (Fig. 10b) are associated in the formation of the NOM fouling layer. The formation of NOM–calcium complexes and their deposition on the membrane surface result in a decrease in bulk (feed tank) NOM and calcium concentrations as indicated by the slopes of the curves in Fig. 10.

Influence of CF and fouling on salt and NOM rejection. Previously, it was demonstrated that colloidal fouling of the RO membrane results not only in permeate flux decline (Fig. 1) but also in deterioration of the permeate water quality (Fig. 2). Similarly, the influence of the concentration factor and NOM fouling on salt and NOM rejection by the NF membrane is delineated in this

subsection. Salt and NOM concentrations in feed and permeate samples were measured several times during the course of the fouling (Fig. 9). The change in the observed salt and NOM rejection with CF at different calcium concentrations is shown in Fig. 11.

Unlike the case with colloidal fouling, salt rejection (Fig. 11a) as a function of CF at different calcium concentrations remains nearly constant except for the run with 1.0 mM calcium. This suggests that CEOP associated with NOM fouling is much less pronounced compared to colloidal fouling. For the latter, enhanced salt

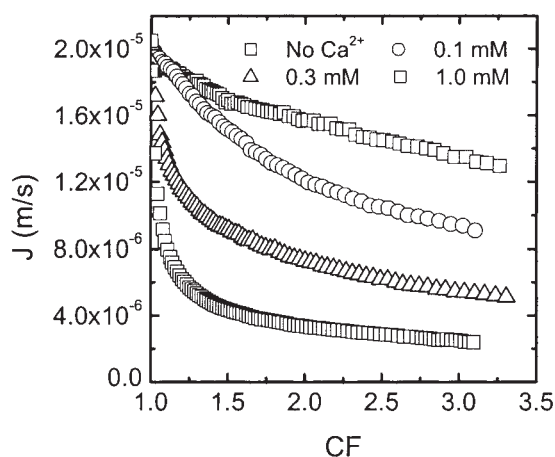


Figure 9. Effect of calcium ion concentration on NOM fouling of the NF membrane. The total initial ionic strength (IS_0) of the feed solution was fixed at 10 mM by varying NaCl concentration. Experimental conditions are: initial NOM concentration = 20 mg/L, initial permeate flux (J_0) = 20 $\mu\text{m/s}$, crossflow velocity = 8.1 cm/s (Reynolds number = 434), temperature = 20.0 \pm 0.3°C, and pH = 8.05 \pm 0.05.

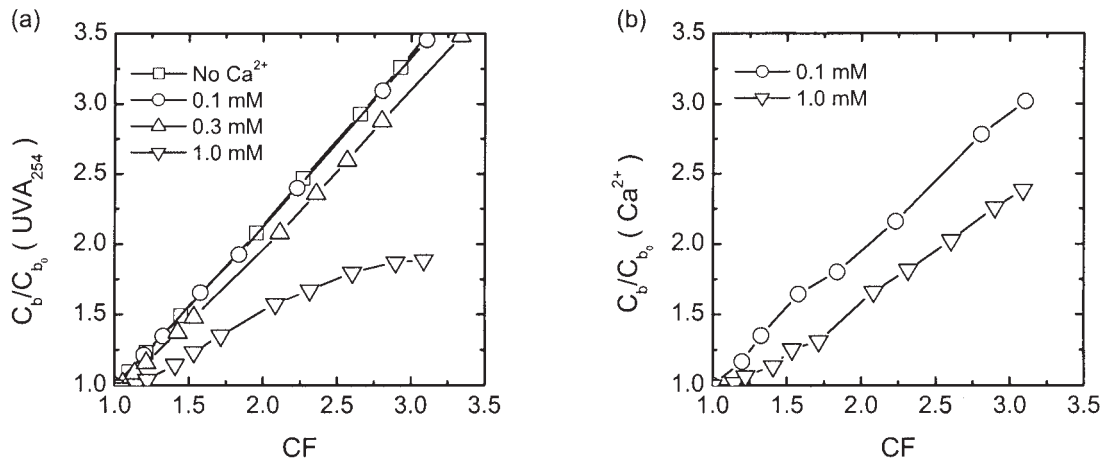


Figure 10. Variation of the NF feed solute concentration (C_b) scaled with its initial value (C_{b_0}) as a function of concentration factor (CF) for feed solutions containing NOM: (a) feed NOM concentration scaled with its initial value and (b) feed calcium concentration scaled with its initial value. Experimental conditions are identical to those in Figure 9.

concentration near the membrane surface results in a greater salt transport across the membrane and, hence, larger deterioration in salt rejection. Based on the run with 1.0 mM calcium, it is likely that at such high divalent ion concentration, a compact, dense NOM fouling layer forms on the membrane surface. The cake layer hinders salt back-diffusive transport away from the membrane surface, which results in the continuous decrease in salt rejection with CF. In addition, Fig. 11b indicates that NOM rejection by the NF membrane decreases with increasing calcium concentration. This behavior implies that NOM accumulation at the membrane surface increases as calcium ion concentration is increased, result-

ing in favorable conditions for NOM transport across the membrane. Furthermore, neutralization of the NOM molecule charge by complexation of calcium ions with carboxylic functional groups reduces the extent of NOM rejection by charge exclusion. Therefore, it can be concluded that NOM fouling in the presence of calcium ions results in both permeate flux decline and deterioration of permeate water quality.

Effect of initial flux on fouling. The effect of initial permeation rate on NOM fouling behavior at different calcium ion concentrations is shown in Fig. 12. It is clearly shown (Fig. 12a–c) that increasing initial perme-

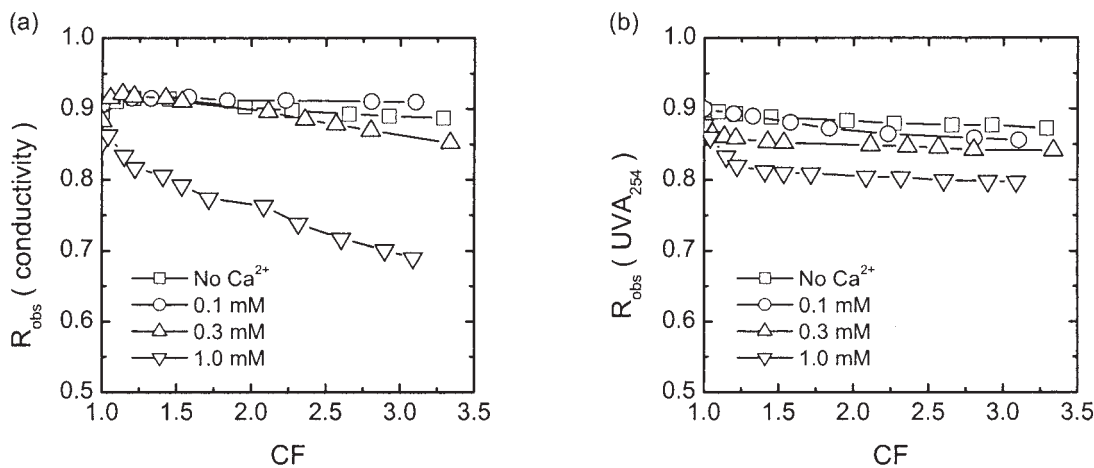


Figure 11. Solute rejection (R_{obs}) as a function of concentration factor for feed solutions containing NOM: (a) observed salt rejection vs. CF and (b) observed NOM rejection vs. CF. Experimental conditions are identical to those in Figure 9.

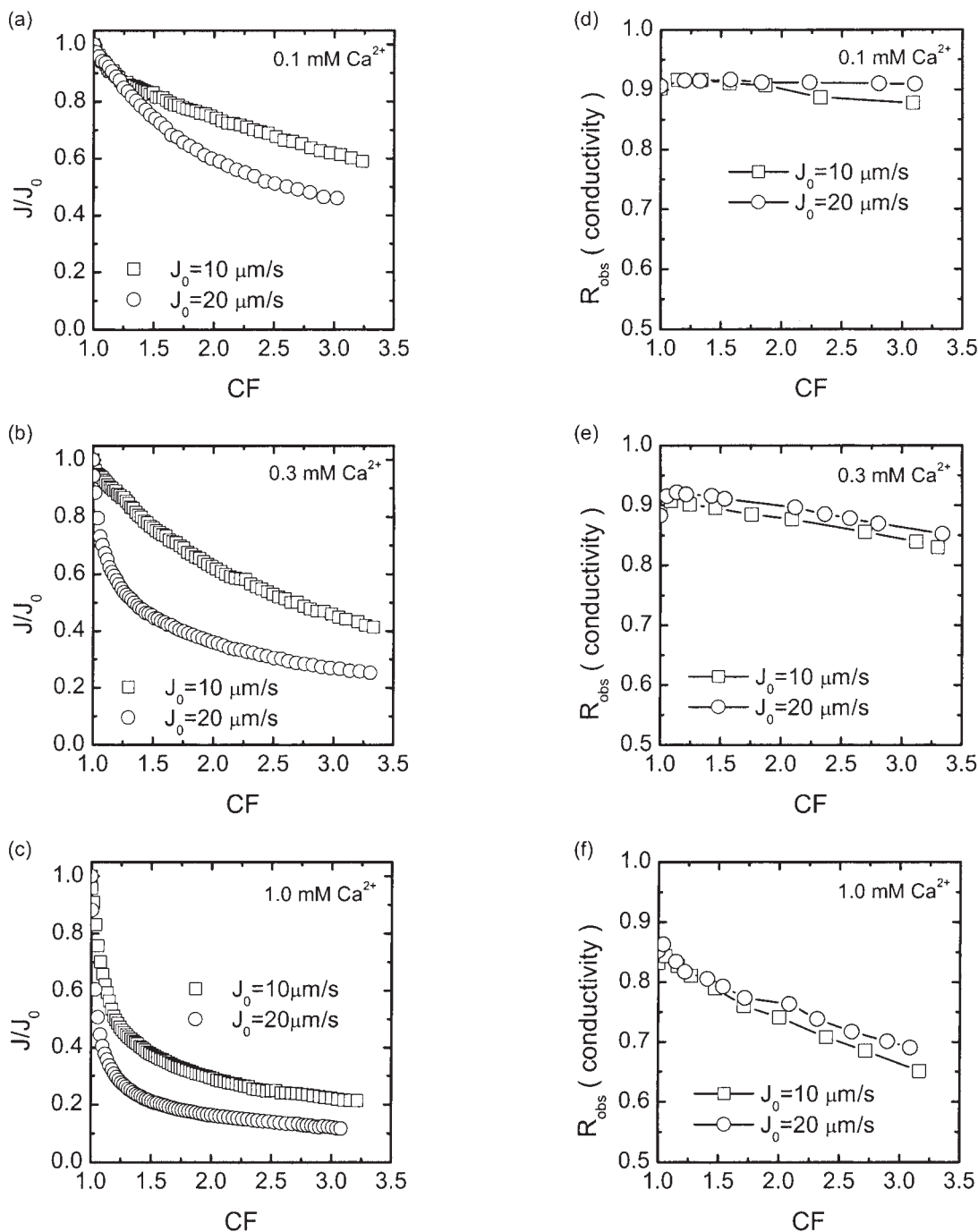


Figure 12. Effect of initial permeate flux (J_0) on NF membrane performance (permeate flux and observed solute rejection) for feed waters containing NOM and different concentrations of calcium ions: (a) normalized flux vs. CF at 0.1 mM Ca^{2+} ; (b) normalized flux vs. CF at 0.3 mM Ca^{2+} ; (c) normalized flux vs. CF at 1.0 mM Ca^{2+} ; (d) observed salt rejection vs. CF at 0.1 mM Ca^{2+} ; (e) observed salt rejection versus CF at 0.3 mM Ca^{2+} ; and (f) observed salt rejection vs. CF at 1.0 mM Ca^{2+} . Data are shown for runs with different initial permeate fluxes (J_0). Experimental conditions are: initial NOM concentration = 20 mg/L, total ionic strength = 10 mM, crossflow velocity = 8.1 cm/s (Reynolds number = 434), temperature = $20.0 \pm 0.3^\circ\text{C}$, and pH = 8.0 ± 0.05 .

ate flux (from 10 to 20 $\mu\text{m/s}$) results in more severe flux decline. This behavior is attributed to the formation of a thicker and more compressed NOM fouling layer at the higher permeation rate (Ho and Zydney, 2000; Seidel and Elimelech, 2002). The results also confirm previous studies (e.g., Hong and Elimelech, 1997) demonstrating that NOM fouling is governed by an interplay between chemical (i.e., divalent cation concentration) and physical (initial permeation rate) interactions. In addition, Fig. 12d-f shows that variation in calcium ion concentration rather than initial permeate flux is more influential on the decline of NF salt rejection with CF. The slight increase in salt rejection at the higher permeation rate is attributed to the so-called "dilution effect" (Seidel and Elimelech, 2002; Lee *et al.*, 2002b).

Further verification for the role of NOM-calcium complexation. The discussion in the preceding subsections has shown that NOM-calcium complexation rather than the increase in CF controls NOM fouling of the NF membrane. In this subsection, the role of NOM-calcium complexation in NOM fouling is further investigated by demonstrating the influence of EDTA treatment on NOM-calcium complexation. Hong and Elimelech (1997) demonstrated that EDTA lessens NOM fouling by reducing the concentration of free calcium ions through complexation as well as removing calcium ions from NOM-calcium complexes through a ligand exchange reaction. EDTA treatment during continuous permeate disposal fouling runs was performed in two ways. First, to demonstrate the role of EDTA in preventing NOM fouling by reducing the concentration of free (bulk) calcium ions through complexation, 0.3 mM EDTA was introduced to the feed solution immediately after NOM addition (injected at CF = 1.00). Second, 0.3 mM EDTA was introduced when significant flux decline was observed, assuming that NOM-calcium complexes have been formed and contributed to the formation of a thick and dense NOM fouling layer (injected at CF = 1.25). The aim of this delayed EDTA injection is to observe the effectiveness of EDTA in removing calcium ions from NOM-calcium complexes through a ligand exchange reaction mediated by EDTA. The EDTA treatment results are shown in Fig. 13, along with the previous fouling runs (Fig. 9) with and without 0.3 mM calcium.

The flux decline behavior when 0.3 mM EDTA was added to a feed solution containing 0.3 mM CaCl_2 at CF = 1.00 is very similar to that of the run obtained when calcium was not used (i.e., feed water contains NOM and 10 mM of indifferent electrolyte). This demonstrates that EDTA reduces the concentration of free calcium ions in feed solution through EDTA- Ca^{2+} complexation prior to the formation of NOM- Ca^{2+} complexes. It is also shown

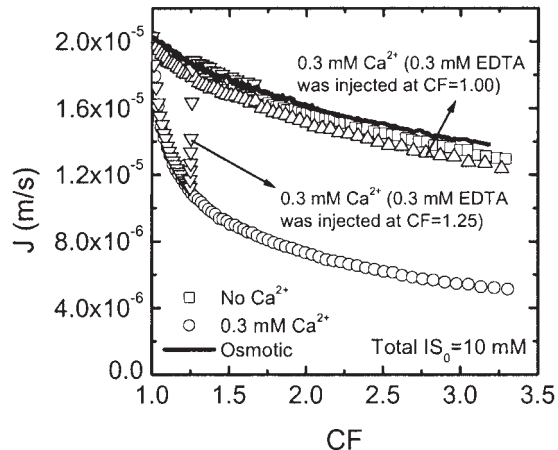


Figure 13. Effect of a strong chelating agent (0.3 mM $\text{Na}_2\text{-EDTA}$) on NOM fouling. Data are shown for runs with different feed solutions as indicated in the figure. The osmotic line is also included as a baseline. Experimental conditions are: initial NOM concentration = 20 mg/L, total ionic strength = 10 mM (see caption of Fig. 9), initial permeate flux = 20 $\mu\text{m/s}$, crossflow velocity = 8.1 cm/s (Reynolds number = 434), temperature = $20.0 \pm 0.3^\circ\text{C}$, and pH = 8.05 ± 0.05 .

in Fig. 13 that EDTA is effective in removing complexed calcium ions from NOM-calcium complexes by a ligand exchange reaction. Before EDTA injection, permeate flux declined severely due to NOM-calcium complexation; however, after EDTA injection (at CF = 1.25) the flux was recovered and reached the permeate flux level observed at CF = 1.25 when calcium was not used. The reason for the continuous decrease in water flux after the EDTA treatment is the continuous increase in CF rather than NOM-calcium complexation. Also note that the flux decline behavior is nearly similar to that of the osmotic run.

CONCLUSION

The influence of feed water recovery (or concentration factor) on colloidal and NOM fouling of RO and NF membranes was investigated using a laboratory-scale crossflow test unit with continuous permeate disposal. It was shown that the method for simulating feed water recovery, as commonly observed in full-scale RO/NF systems, was useful to investigate colloidal and NOM fouling mechanisms as well as solute rejection behavior. Permeate flux declined linearly with increasing CF as long as there was no fouling, that is, in the absence of cake-enhanced osmotic pressure for colloidal fouling and NOM-calcium complexation for NOM fouling. Furthermore, when no fouling took place, salt rejection by RO and salt/NOM rejection by NF were stable during the course of the permeate disposal runs. This im-

plies that the permeate water quality of RO/NF modules does not change when fouling is absent, even though the amount of permeate produced from each spiral-wound module decreases with CF. Our study further verified that cake-enhanced osmotic pressure is the major mechanism of colloidal fouling of salt rejecting membranes, whereas NOM-calcium complexation governs NOM fouling. When colloidal or NOM fouling takes place, the permeate water quality of RO/NF membranes severely deteriorates. The results suggest that successful operation of full-scale RO/NF plants can be achieved by optimizing water recovery (or concentration factor) as well as preventing membrane fouling.

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