

Coupled Effects of Salt Concentration Polarization and Colloidal Deposition on the Performance of Reverse Osmosis Membranes

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1. Introduction

The shrinking water supply together with our continuously increasing demand for this resource has stimulated a renewed interest in reverse osmosis (RO) as a water treatment unit process. A wider use of RO membranes, however, is impeded by a group of phenomena that lead to permeate flux decline, deterioration of permeate water quality, shortening of membrane life, and thus to a substantial increase in operational costs [1, 2]. The relevant physicochemical phenomena include concentration polarization, scaling, adsorptive and biological fouling, and colloidal fouling.

Although source waters usually undergo pretreatment that is designed to remove the colloidal fraction, in practice both dissolved and residual suspended phases are present in RO feed [3-5]. Because of their small size, these residual colloids can form membrane deposits with a high hydraulic resistance contributing to the permeate flux decline. Also, colloids deposited on the membrane surface can inhibit back-diffusion of dissolved species resulting in precipitation of sparingly soluble salts in the pores of the deposited layer and in the enhanced osmotic pressure [6, 7]. If the source water pretreatment is inadequate or fails, colloidal fouling can be especially egregious. The structure of the colloidal fouling layer is known to be a complex function of operational variables such as flow hydrodynamics, colloid size and charge, and solution chemistry [8-13]. The propensity of colloids to deposit affects the layer's hydraulic resistance both directly via the overall deposit thickness and indirectly via the accumulative drag force on deposited colloids that plays a role in determining the equilibrium distance between colloidal particles. Therefore, accounting for various mechanisms of particle transport to membrane surface in crossflow channels is essential for the accurate prediction of the permeate flux [14].

Solution chemistry-mediated interactions between particles within the deposited layer is another significant factor that determines the structure and, therefore, specific hydraulic resistance of the deposit [15]. Theoretical and experimental studies indicate that colloidal cakes can be stratified and can contain layers with dense and loose particle packing [9, 11, 12, 16]. There is also evidence for the existence of the concentrated flowing layer of colloids between the stagnant cake of deposited colloids and the bulk suspension [17-20]. One objective of this study is the direct experimental determination of (1) the effect of rejected salt on the structure of colloidal layer and (2) how the *two-way* coupling between

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salt concentration polarization and colloidal deposition influences permeate flux and salt rejection. Another objective is the evaluation of the effect of spacers on RO flux and rejection in the presence of colloidal particles in the feed.

2. Experimental Methods

The schematic of the bench-scale crossflow RO unit is shown in Fig. 1. Two identical Sepa CF II high pressure membrane modules in medium/high foulant configuration (GE Osmonics, Minnetonka, MN) were connected in parallel. The real-time data from the in-line digital flow meters (Models 101-8 and 101-3, McMillan Co., Georgetown, TX), pressure transducers, the weighing balance (ARC120, Ohaus Corp., Pine Brook, NJ), the conductivity meter (Orion 550, Thermo Electron Corp., Beverly, MA) were logged to the computer via the data acquisition module using a program written in LabView (version 7.1, National Instruments). The temperature of the feed water was maintained at $(20.0 \pm 0.5) ^\circ\text{C}$ using a programmable circulating chiller (Model 9512, PolyScience, Niles, IL) with an external temperature probe. Silica particles (SnowTex-XL, Nissan Chemical America Corp., Houston, TX) were chosen as the model colloidal foulant. Polyamide thin-film composite RO membrane (BW30-365, Dow-FilmTec, Minneapolis, MN) was used in all experiments.

The experimental protocol consisted of the following sequential steps: (1) Membrane compaction (48 hr). (2) Clean water flux test and measurement of membrane hydraulic resistance. (3) Membrane conditioning (12 hr). (4) Measurement of the initial osmotic pressure and salt permeability constant. Membrane fouling experiment (ca. 24 hr).

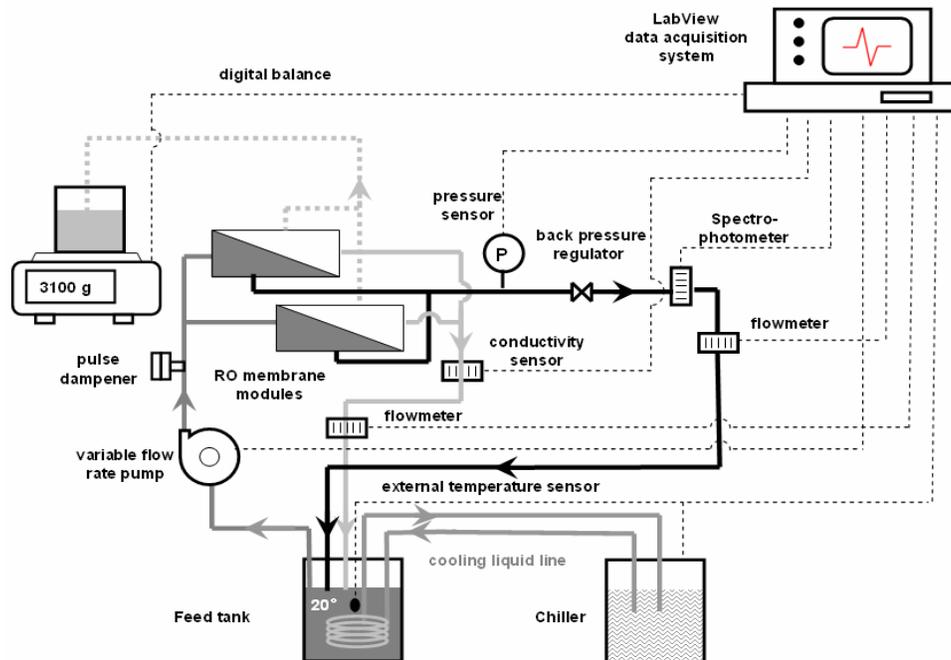


Fig. 1 Schematic of the experimental apparatus

3. Results and Discussion

3.1. Permeate flux, NaCl rejection, and structure of the deposited layer at different ionic strengths

Figure 2 illustrates transient behavior of permeate flux (J), observed salt rejection (R_{obs}), C_m , M_p , effective porosity (ϵ), and the resistance of the deposit layer (R_d) during colloidal fouling experiments with 200 mg/L silica suspension at three different ionic strengths. There was no appreciable permeate flux decline for the silica suspension in deionized water (Fig. 2a). While it is clear from M_p data that particles were depositing on the membrane surface (Fig. 2d), the resistance of the deposit was much smaller than that of the membrane itself and therefore the deposition did not lead to an observable increase in the overall resistance to the permeate flow.

For non-zero electrolyte concentrations, the permeate flux decreased significantly before a steady state value was reached. The steady state value of the permeate flux was smaller, while the time to reach the steady state was higher, for the higher ionic strength (Fig. 2a); the same trend for the steady state flux and the time to reach steady state flux as a function of ionic strength have been reported previously [12, 21]. Based on the permeate flux (Fig. 2a) and salt rejection (Fig. 2b) data, C_m as a function of filtration time was calculated (Fig. 2c, Table 1). In the course of the experiment, C_m increased to reach a maximum (after 6 h for 10^{-2} M and after 8 h for 10^{-1} M ionic strength) and then decreased slightly resulting in an overall increase with respect to the initial value. The initial increase and the resulting overall increase was attributed to the hindrance effect of the fouling layer on salt back diffusion [7]. Possible reasons for the decrease in C_m are discussed in section 4.5. Effective porosity ϵ of the particle deposit was calculated to be 0.41 and 0.27 for ionic strengths of 0.01 M and 0.1 M, respectively. This was much lower than that for the case of particles suspended in deionized water. The decrease in porosity was attributed to the lower surface charge and smaller repulsive forces between the particles with increasing ionic strength. It should be noted that although more particles were deposited on the membrane surface at 10^{-2} M than at 10^{-1} M (Fig. 2d) ionic strength, the deposited layer at 10^{-1} M had a considerably larger hydraulic resistance (Fig. 2f) because of the smaller effective porosity (Fig. 2e). Both $\Delta\pi_m$ and R_d were larger at 10^{-1} M, which resulted in a larger flux decline at 10^{-1} M (Fig. 2a).

Analysis of the permeate flux and rejection data at the very early stages of colloidal fouling can help to elucidate how newly deposited particles interact with the concentration polarization layer of salt. To record such data, a series of RO experiments with silica suspension of two solid fractions (200 mg/L and 500 mg/L) was conducted in laminar flow. The experimental sequence for each test was: (1) complete membrane compaction (60 h); (2) membrane conditioning (10^{-2} M, 12 h); (3) introduction of silica stock solution to achieve the desired silica particle loads, (4) colloidal fouling experiment. Transmembrane pressure was maintained at 300 psi (2.068 MPa) without any adjustments of system pressure. This ensured that the salt concentration profile was well stabilized before the introduction of particles, and that any changes in permeate flux and

rejection were due to the presence of silica particles. As Fig. 3 demonstrates, the introduction of colloids resulted in a short term increase in R_{obs} . For 200 mg/L silica concentration, the initial rejection increased from 97.5% to 97.9%; for 500 mg/L silica concentration, the increase was from 98.3% to 99.2%. Similar increase in the initial rejection during nanofiltration (NF) of 200 mg/L colloidal loading, 10^{-2} M NaCl feed suspension was reported earlier [7]. Because the conductivity measurement interval (2 min for filtration stage) was larger than the conductivity cell hydraulic detention time (0.6 min), the real initial increase in R_{obs} was even larger than the data suggest.

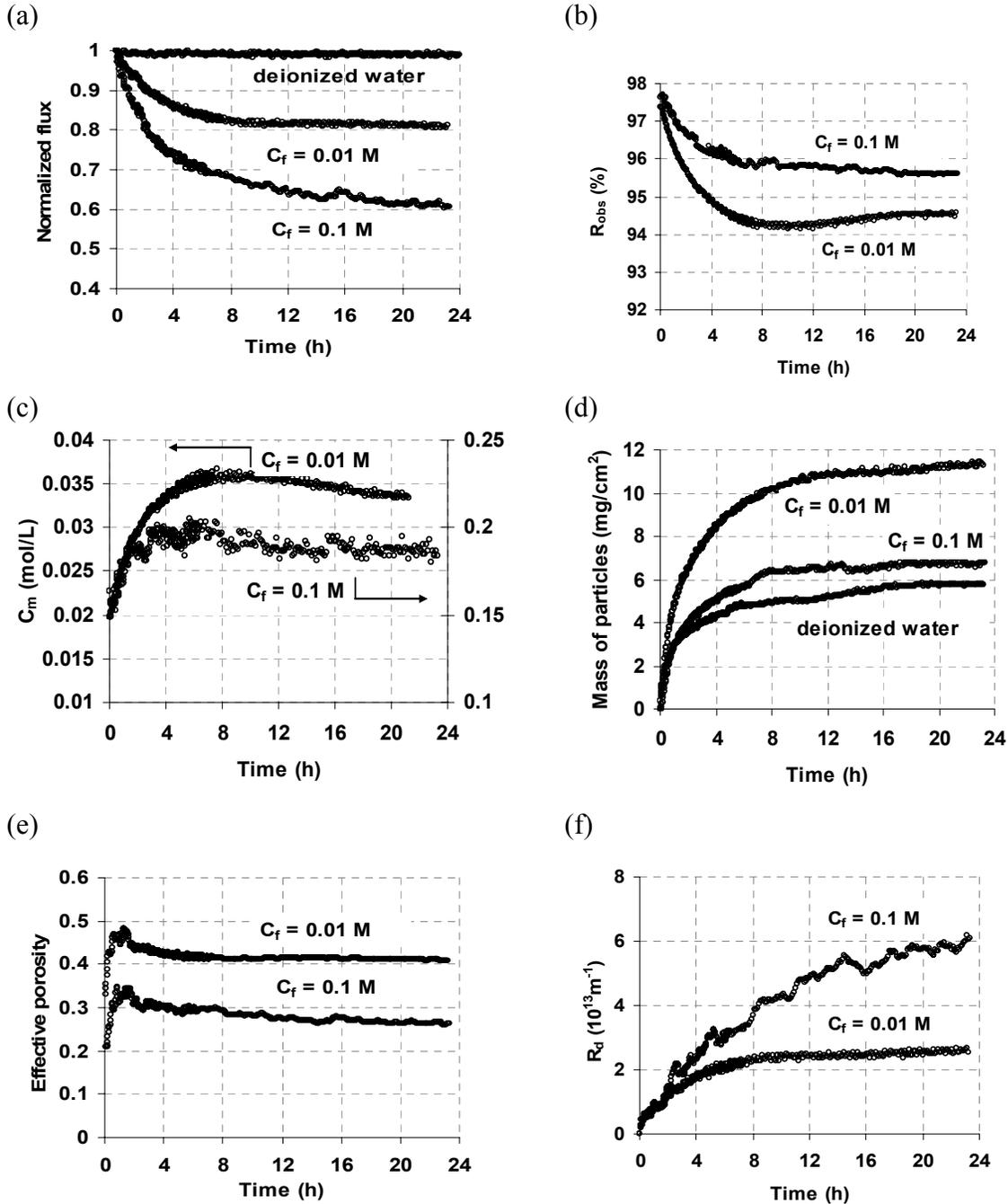


Fig. 2. (a) Normalized permeate flux at three ionic strengths; (b) observed salt rejection, R_{obs} ; (c) salt concentration at membrane surface, C_m ; (d) mass of deposited particles, M_d ; (e) effective porosity, ε , and (f) hydraulic resistance of deposited colloidal layer, R_d . No spacers were used in these experiments.

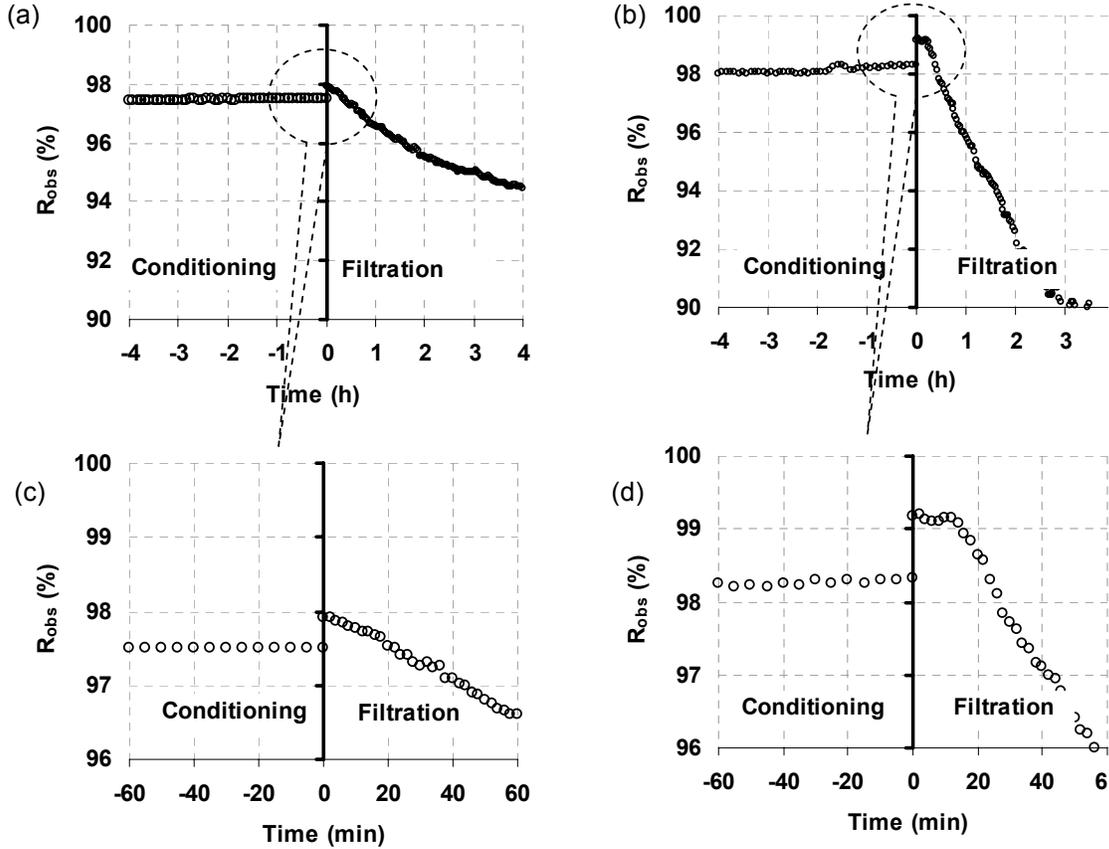


Fig. 3. Effect of introduction of silica particles on initial observed salt rejection at 10^{-2} M: (a) 200 mg/L silica particles; (b) 500 mg/L silica particles. (c) and (d) show the initial filtration in detail for (a) and (d), respectively.

At 0.1 M ionic strength, the depolarizing effect of the concentrated flowing layer is less pronounced. With C_m (Fig. 2c) and M_p (Fig. 2d) remaining almost constant after 8 h of the experiment, the gradual decrease in permeate flux (Fig. 2a) appears to be due entirely to the gradual changes in cake porosity (Fig. 2e)

3.2. Effect of the feed channel spacers on NaCl rejection and permeate flux

To shift the balance from the formation of the (undesirable) stagnant layer of deposited particles to the formation of the (desirable) concentrated *flowing* layer, additional mixing in the vicinity of membrane surface is needed. An accepted method of providing such mixing in membrane systems is the use of membrane spacers. This goal as well as the need to test our hypothesis in the context of industrial applications motivated the part of this study where feed channel spacers were used.

Figure 4 shows the normalized flux and observed salt rejection as a function of filtration time when a spacer was placed in the feed channel. Filtration of silica suspension in deionized water was not conducted because there was no flux decline observed even when spacers were not used (Fig. 3a). When the spacers were used, no flux decline was observed at 10^{-2} M, and the flux decline was much smaller at 10^{-1} M compared with runs without the spacers (Fig. 3). Importantly, after the initial increase caused by the introduction of particles into the feed, R_{obs} remained stable at this elevated level. This was despite a decrease of particle concentration in the feed as detected by UV absorbance. It appears that the effect of spacers is that of “trapping” of particles in the interfilament domain of feed channel spacers where particles remain without depositing on the membrane surface. In terms of the concentrated flowing layer model, introducing a spacer inhibits the formation of the stagnant deposit so that mixing by colloidal particles in the flowing layer becomes the dominating effect of particles on the salt concentration polarization.

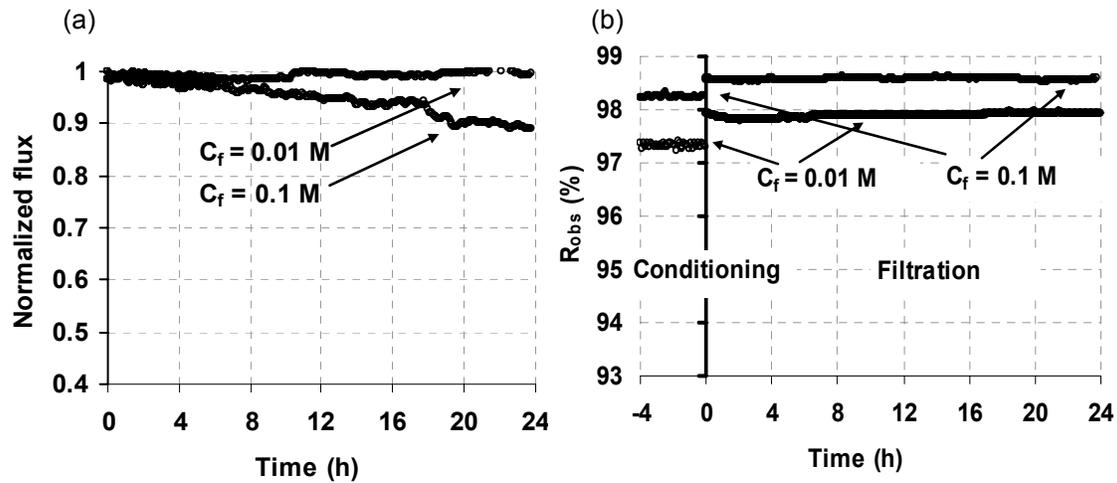


Fig. 4. Effect of the feed channel spacers on membrane performance: (a) Normalized permeate flux; (b) Observed salt rejection. Silica particle loading: 200 mg/L; Operating transmembrane pressure: for 10^{-2} M, $\Delta P = 250$ psi (1.723 MPa), and for 10^{-1} M, $\Delta P = 330$ psi (2.274 MPa); Initial flux: for 10^{-2} M, $J = 55.7$ L/(m²h) ($1.54 \cdot 10^{-5}$ m/s) and for 10^{-1} M $J = 60.0$ L/(m²h) ($1.55 \cdot 10^{-5}$ m/s).

Large “fluidized particles” have been successfully applied in *ultrafiltration* with tubular membranes: mass transfer was shown to improve when 0.7 mm and smaller glass particles were used as turbulence promoters in ultrafiltration of polyethylene glycol [22] and when 3 mm stainless steel particles were used in the separation of gelatin solutions [23]. As our results indicate, colloid-sized particles can be used to achieve improvements in flux and rejection for salt rejecting membranes as well. This opens new, perhaps counter-intuitive, possibilities for controlling the salt rejection and permeate flux by using spacers in conjunction with introducing particles with low deposition propensity into the feed.

4. Conclusions

Individual contributions of osmotic pressure and colloidal fouling to the RO permeate flux decline can be identified by determining salt permeability constant and measuring salt transport across the membrane. By using this approach, we demonstrate that the two-way coupling between salt concentration polarization and colloidal deposition is essential in determining both permeate flux and rejection. On one hand, porosity of the deposit and its resistance to the permeate flux are measured to be strong functions of the solution ionic strength. On the other hand, deposition of colloidal particles on the membrane surface influences salt transport to and across the membrane in a complex way. Formation of the stagnant colloidal deposit results in the hindrance of the back diffusion of salt away from the membrane surface. Under certain conditions, however, the presence of colloidal particles improves membrane performance. Specifically, the introduction of colloidal particles into the feed results in a short term increase in salt rejection; this increase can be sustained over the long term when feed channel spacers are used. Based on the above observations, we hypothesize that the concentrated flowing layer of colloidal particles is responsible for the local mixing of the concentration polarization layer of salt and that the overall effect of colloidal deposition on permeate flux and rejection is determined by the balance between the stagnant and flowing parts of the colloidal deposit. These findings point to the potential of using particles with low deposition propensity as “mobile mixers” to complement feed channel spacers as means of improving performance of salt-rejecting membranes.

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