Colloidal fouling in forward osmosis: Role of reverse salt diffusion

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A B S T R A C T
Colloidal fouling behavior in forward osmosis (FO) was investigated, focusing on the role of reverse salt diffusion. Two suspensions of silica nanoparticles, with average particle diameters of 24 and 139 nm, were used as model colloidal foulants. To verify the effect of reverse salt diffusion on the colloidal fouling behavior, NaCl and LaCl3 were employed as draw solutions because they exhibit different reverse diffusion rates. Our results suggest that in colloidal fouling of FO, salts diffuse from the draw to the feed solution and accumulate within the colloidal fouling layer that forms on the membrane surface. The accumulated salts result in a marked acceleration of cake-enhanced osmotic pressure (CEOP), which reduces the net osmotic driving force for permeate water flux. Fouling was not observed with the small, 24-nm particles because of the lack of substantial cake formation, but was notable for the 139-nm particles and for a feed containing a mixture of the 24 and 139 nm particles. Our findings further indicate that colloidal fouling is enhanced under solution conditions (ionic strength and pH) within the colloidal cake layer that promote aggregation or destabilization of the silica particles. Colloidal fouling reversibility was also examined by varying the cross-flow velocity during the FO fouling runs. We showed that in the absence of colloidal particle destabilization/aggregation, the permeate flux during colloidal fouling in FO recovered almost completely when the cross-flow velocity was increased from 8.5 to 25.6 cm/s. Our results suggest that reverse salt diffusion in FO is a key mechanism that controls colloidal fouling behavior as well as fouling reversibility. Therefore, minimization of reverse salt diffusion through the selection of proper draw solutes and optimization of FO membrane selectivity are important for minimizing colloidal fouling as well as enhancing FO operation efficiency.

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1. Introduction

Global water shortages and depletion of fresh water supplies place a great demand on the development of alternative water sources, such as seawater desalination and wastewater reuse [1]. Improvements in membrane technology represent one of the most viable options to meet these critical challenges. Over the past few decades, innovative membrane technologies have been developed and applied to produce cleaner and safer water, including saline water desalination and ground/surface water treatment by reverse osmosis (RO) and nanofiltration (NF) [1,2], wastewater treatment and reuse by membrane bioreactors [3,4], and replacement of conventional water treatment systems by microfiltration (MF) and ultrafiltration (UF) [5,6].

In particular, reverse osmosis (RO) technology has become the industry benchmark in membrane-based desalination and wastewater reuse because of its competitive cost and superior product water quality compared to conventional thermal and biological processes. Although RO technology has been vastly improved over the last few decades, its efficiency and sustainable operation are hampered by membrane fouling and by the considerable energy consumption for seawater desalination [1,7–13]. Due to these limitations of RO technology, there is a demand for sustainable alternatives to conventional pressure-driven membrane processes.

For efficient and eco-friendly operation, future water treatment technologies should overcome the following limitations of conventional pressure-driven membrane processes: high energy consumption, demand for chemical cleaning agents to mitigate fouling, and considerable environmental impacts due to brine discharge. One technology that has the potential to become a sustainable alternative is forward osmosis (FO) [14–18]. In lieu of hydraulic pressure, FO utilizes a highly concentrated draw solution to induce the driving force for separation. The absence of hydraulic pressure in FO is expected to not only minimize the system energy consumption, but also to lower membrane fouling and the associated deleterious effects to the quality and quantity of the product water [19,20].

In the FO process, a highly concentrated draw solution is placed opposite to the feed solution, which is separated by a semi-permeable membrane. The difference in the chemical potential...
across the membrane induces water flow from the feed to the draw solution side. However, this desired water flow is also accompanied by a concomitant transport of draw solutes to the feed side. This phenomenon of reverse diffusion of draw solutes to the feed solution is unavoidable in the current stage of FO technology. Recently, several attempts have been made to understand this mechanism and to quantify the amount of reverse diffusion of draw solutes [20–23].

Since reverse transport of draw solutes is a mechanism unique to FO compared to conventional pressure-driven membrane processes, several phenomena that could be influenced by the transported draw solutes should be investigated. In particular, reverse salt diffusion may affect fouling behavior in FO, and therefore, have a significant impact on the efficiency of the process. While several recent studies investigated fouling of FO [24–26], very few studies addressed the effects of reverse solute diffusion on FO fouling [20,26].

In this study, we investigate the impact of reverse draw solute diffusion on colloidal fouling behavior in the FO process. To better understand the role of reverse salt diffusion in FO fouling by colloidal silica particles, draw solutions which exhibit vastly different reverse diffusion rates, namely NaCl and LaCl₃, were used. In addition to colloidal fouling rate, FO fouling reversibility was also investigated by employing different feed cross-flow velocities during the fouling runs, which is a common approach for fouling control in NF and RO. Based on the results, important mechanisms and factors that control colloidal fouling in FO are delineated and discussed.

2. Materials and methods

2.1. Colloidal particle foulants

Two types of commercial silica particles were used as model foulants for the fouling experiments. The manufacturer (Nissan Chemical Industries, Ltd.) reports that these particles, denoted as ST-30 and ST-ZL, have diameters ranging from 10 to 20 nm and 70 to 140 nm, respectively. Our dynamic light scattering (ALV-5000, Langen, Germany) measurements, however, revealed that the intensity averaged diameters of the ST-30 and ST-ZL suspensions are 24 ± 5 and 139 ± 5 nm, respectively. According to the manufacturer, the densities of the 24 and 139 nm nanoparticles are 2.1 and 2.3 g/cm³, respectively. The particles were prepared as a concentrated, monodisperse aqueous suspension at an alkaline pH in the range of 8.5–9.5. The particle concentration of the stock suspension was determined by gravimetric analysis, yielding particle concentrations of 30 and 40% (w/v) for ST-30 and ST-ZL, respectively. Nanoparticle suspensions at the desired concentration were prepared by dispersing aliquots from the stock suspension in deionized (DI) water. Prior to use, the stock suspensions were first hand shaken and then sonicated for 10 min to ensure complete dispersion of the colloidal particles. The electrophoretic mobilities of the two silica suspensions were measured as a function of solution pH in the presence of 50 mM NaCl as a background electrolyte to characterize the charge properties of the colloidal suspensions (ZetaPlus, Brookhaven Instruments Corp., Holtsville, NY).

2.2. FO membrane

The FO membrane used in this study was provided by Hydration Technology Innovations (HTI, Albany, OR). HTI manufactures several types of commercial-grade FO membranes that exhibit different water and salt permeabilities. The membrane used for this study exhibited relatively low water permeability and high salt rejection compared to other HTI FO membranes used in other studies [20,25,27]. While the exact chemical composition of the membrane is proprietary, it is likely to be cellulose-based with an embedded polyester mesh for mechanical support. The total thickness of the membrane is approximately 50 µm [28]. To better understand the interaction of the silica particles with the FO membrane, the zeta potential of the FO membrane was measured by a streaming current electrokinetic analyzer (SurPASS, Anteon Paar GmbH, Australia), following the procedure described by Luxbacher [29].

2.3. Fouling tests

Accelerated fouling tests were conducted for 10 h with different concentrations (1.0 and 2.0 g/L) and combinations (monodisperse and polydisperse) of the colloidal silica. Two liters of both feed and draw solutions were recycled during the course of fouling runs. The feed water chemistry was fixed at a total ionic strength of 50 mM NaCl and the temperature was maintained at 21.0 ± 1.0 °C. Most fouling experiments were carried out at ambient pH (pH 6–7 for feed solution and 7–8 for draw solution), except for the experiments examining the impact of solution pH, which were carried out at feed solution pH of 4 or 9. Two draw solutions (NaCl and LaCl₃) that exhibit different reverse diffusion rates were employed. Permeate water flux was continuously monitored using a digital balance and recorded on a PC every 3 min for the entire 10-h duration of each fouling experiment. No feed spacers were used in the feed or draw solution channels of the FO cell.

During the FO runs, water permeates from the feed to the draw solution side; consequently, the feed solution gradually becomes more concentrated while the draw solution becomes diluted. To account for these effects, baseline tests were performed with foulant-free feed solution for all draw solution types and concentrations. The water flux curves obtained from the baseline tests were used to correct the water flux obtained during the fouling runs. More details on the protocols for FO fouling tests have been described in our previous study [20].

2.4. Evaluation of colloidal stability of silica nanoparticles

Time-resolved dynamic light scattering (DLS) measurements were conducted to determine the aggregation behavior of the silica particles. A multi-detector light scattering unit (ALV-5000, Langen, Germany), which employs an Nd:vanadate laser (Verdi V2, Coherent Inc., Santa Clara, CA) at a wavelength of 532 nm, was used to carry out the measurements. The sonicated nanoparticle stock suspension was diluted 60 times with deionized water for the DLS experiments. A pre-measured amount of electrolyte stock solution was added into a clean vial to induce aggregation of the nanoparticles. The vial was briefly vortexed (Mini Vortexer, Fisher Scientific) before being inserted into the light scattering unit, and the DLS measurements were started immediately. The scattered light was detected by a photodetector positioned at a scattering angle of 90°. Each autocorrelation function was accumulated for 15 s, and the intensity-weighted hydrodynamic radius of the aggregates was derived through second-order cumulant analysis (ALV software). The silica nanoparticles were left to aggregate for between 10 min and 4 h. All DLS measurements were conducted at 23 °C.

2.5. Measuring membrane water and salt (NaCl) permeabilities

The pure water permeability coefficient, A, of the HTI-CTA membrane was evaluated in a laboratory-scale cross-flow reverse osmosis test unit. The effective membrane area was 20.02 cm² and the cross-flow velocity was fixed at 25.6 cm/s. During the experiments, the temperature was kept constant at 21.0 ± 1.0 °C. Initially, the membrane was equilibrated with DI water at an applied
pressure, \( \Delta P \), of 17.2 bar (250 psi), until the permeate flux reached a steady value. After equilibration, the volumetric permeate flux was measured by a digital scale at applied pressures ranging from 3.5 to 17.2 bar (50–250 psi) in increments of 3.5 bar (50 psi). The water permeability coefficient, \( A \), was obtained from the slope of water flux plotted versus applied pressure.

Observed NaCl rejection, \( R \), for the membrane was determined from a cross-flow reverse osmosis test, with 10 mM NaCl feed solution. The salt (NaCl) permeability coefficient, \( B \), was calculated from [22]

\[
B = J_w \left( 1 - \frac{R}{R_m} \right) \exp \left( \frac{J_w}{k} \right)
\]

\[
k = \frac{S_h D}{d_h}
\]

Here, \( J_w \) is the water flux, \( k \) is the cross-flow cell mass transfer coefficient for the FO cell, \( S_h \) is the Sherwood number, and \( D \) is the salt (NaCl) diffusion coefficient [22]. A \( k \) value of \( 3.70 \times 10^{-5} \) m/s for the cross-flow channel was used in our calculations.

2.6. Determining the resistance of the colloidal fouling layer

Comparing the resistance of the fouling layer \( (R_f) \) to the intrinsic resistance of the membrane \( (R_m) \) can be used to assess the contribution of the fouling layer to overall water flux decline [30]. The fouling layer resistance \( (R_f) \) was determined by measuring the deposited mass of silica nanoparticles on the membrane surface, assuming the particles to be monodisperse. The intrinsic membrane resistance \( (R_m) \), determined from the measured water permeability coefficient, \( A \), was 3.525 \( \times \) \( 10^{14} \) m \(^{-1} \).

To calculate the resistance of the fouling layer, the deposited particle mass on the membrane surface was determined using [30]:

\[
M_{d, final} = C_{F, initial} V_0 - C_{F, final} (V_0 - V_{cum, final})
\]

By measuring both the concentrations of colloidal particles in the feed water at the initial \( (C_{F, initial}) \) and final \( (C_{F, final}) \) stages and the corresponding cumulative permeate volume increase \( (V_{cum, final}) \) in the draw solution during the course of the fouling experiment, the deposited mass of colloidal particles was determined. Note that the colloidal particles were completely retained by the FO membrane. After determining the value of deposited particle mass \( (M_{d, final}) \), the fouling layer resistance was calculated using the Carman–Kozeny equation [31–33]:

\[
R_c = \frac{l_c}{l_c}
\]

\[
R_c = \frac{M_d}{\rho_p (1 - \varepsilon) A_s}
\]

\[
r_c = 180 \left( 1 - \varepsilon \right)^2 \frac{d_p^3}{\rho_p}
\]

Here, \( r_c \) is the specific fouling layer resistance (per unit length of fouling layer thickness), \( l_c \) is the fouling layer thickness, \( M_d \) is the deposited colloid mass per unit membrane area, \( \rho_p \) is the density of the colloidal particles (2.3 g/cm\(^3\) for the 139 nm particles), \( \varepsilon \) is the porosity of the colloidal fouling layer (assumed to be 0.36, i.e., the porosity corresponding to maximum random packing of 0.64 for rigid spherical particles), \( A_s \) is the membrane surface area (20.02 cm\(^2\)), and \( d_p \) is the diameter of the colloidal particles. We note that the silica particles are rigid and do not deform, such that compaction of the fouling layer is negligible.

3. Results and discussion

3.1. Characteristics of membrane and colloidal particles

The membrane water and salt (NaCl) permeability coefficients \( A \) and \( B \) were determined to be 2.81 \( \times \) \( 10^{-12} \) m/(s Pa) and 4.66 \( \times \) \( 10^{-8} \) m/s, respectively. The water permeability coefficient was lower than that reported for other cellulose-based membranes from HTI [25,27]. The salt permeability coefficient was lower by more than a factor of two than that reported for FO membranes from HTI [27].

A transmission electron microscopy (TEM) image of the polydisperse silica suspension (i.e., a mixture of the small and large particles) is shown in Fig. 1a. The silica particles are mostly spherical, with intensity averaged hydrodynamic diameters (determined by dynamic light scattering) of 24 and 139 nm for the small and large particles, respectively. The zeta potentials of the silica particle suspensions as a function of solution pH in the presence of 50 mM NaCl as a background electrolyte were also determined (Fig. 1b). As expected, the zeta potentials became more negative with increasing solution pH. Also presented in Fig. 1b is the zeta potential of the FO membrane. The FO membrane exhibited relatively less negative zeta potential compared to the silica particles. The results in Fig. 1b indicate that repulsive electrostatic interactions would develop between the particles and the membrane and among the particles themselves when the solution pH is greater than 4. These interactions are expected to influence the deposition of particles on the membrane surface and the cohesion of the colloidal cake layer.
3.2. Flux decline is governed by cake-enhanced osmotic pressure

For salt-rejecting membranes, such as those used in RO and NF, cake-enhanced osmotic pressure (CEOP) is the major contributor to overall flux decline in colloidal fouling [34]. With this phenomenon, the deposited cake layer hinders the back diffusion of salt into the bulk feed solution, thereby resulting in elevated osmotic pressure near the membrane surface. The elevated osmotic pressure near the membrane surface leads to a substantial drop in the net driving force and, thus, results in a significant decline in permeate flux. Hoek et al. [35] elucidated the CEOP mechanism in RO, and Lee et al. [30] proved the dominant role of CEOP in overall flux decline in colloidal fouling of NF membranes by calculating the colloidal cake resistance \((R_c)\) and comparing it to the membrane resistance \((R_m)\).

In the FO process, salt can diffuse across the membrane from the highly concentrated draw solution to the feed solution side. Because of this reverse salt diffusion, there would be a greater salt build-up near the membrane surface, thereby accelerating CEOP in FO colloidal fouling. Our recent study proposed this accelerated CEOP mechanism and the corresponding significant flux decline in organic matter fouling of FO by direct comparison to the fouling behavior observed in RO [20].

In the present study, to verify the accelerated CEOP mechanism in FO colloidal fouling, we used two suspensions of silica particles of different sizes, because these suspensions would form cake layers at different extents due to their differing transport characteristics. As shown in Fig. 2a, no significant flux decline was observed with the 24 nm colloidal suspension, regardless of the particle concentration used, because the small particles that are transported to the membrane surface by the permeate flow readily diffuse back into the bulk solution. On the other hand, much greater flux decline was observed with the 139 nm colloidal suspensions, particularly when higher particle concentration was used (Fig. 2b), because of their much lower back transport rate compared to the 24 nm particles. This observation indicates that only the thicker fouling layer, composed of large particles, induced observable flux decline, which we attribute to the predominant effect of CEOP.

In the following analysis, we confirm that CEOP is the major cause of flux decline in colloidal fouling of FO. The calculated cake layer thickness and the colloidal fouling layer resistance, as normalized by the membrane resistance \((R_c/R_m)\) for the 139-nm-sized silica particles, are shown in Fig. 3. Even though we assume a minimum porosity value of 0.36, the cake layer resistance normalized by the membrane intrinsic resistance was at most 0.1 (for the 2 g/L particles). For the actual case, the cake porosity is likely greater than 0.36 [31], which will yield an even lower cake resistance. This result implies that cake layer resistance does not contribute significantly to the overall flux decline; the flux decline in FO colloidal fouling is mainly due to the accelerated cake-enhanced osmotic pressure.

3.3. Effect of solution pH on colloidal fouling

Solution chemistry has a marked effect on the electrokinetic properties of colloidal particles, and hence, on the rate of fouling in membrane separation [31,36–39]. However, previous colloidal fouling studies were performed with pressure-driven membrane processes. In the FO process, the reverse permeation of draw solution can significantly affect the feed solution chemistry near the membrane surface on the feed side. In order to elucidate the potential fouling mechanisms that may be present in FO, feed silica suspensions with different solution pH values were employed.

3.3.1. Fouling with a monodisperse colloidal suspension

Our first set of experiments was designed to investigate the effect of solution pH on colloidal fouling with a monodisperse
Fig. 4. Flux-decline curves obtained during the FO colloidal fouling runs with silica particles at pH 4 and 9: (a) 1 g/L of 24 nm silica colloids, (b) 2 g/L of 24 nm silica colloids, (c) 1 g/L of 139 nm silica colloids, and (d) 2 g/L of 139 nm silica colloids. Feed solution ionic strength (50 mM NaCl) and the draw solution concentration (5.0 M NaCl) were identical for all fouling runs. Other experimental conditions: initial flux of 5.3 μm/s (19.1 L/(m² h)), cross-flow velocity of 8.5 cm/s, and temperature of 21.0 ± 1.0°C.

colloidal suspension. Feed suspensions with two different solution pH (4 and 9) and particle concentrations of 1 and 2 g/L were tested. Identical mass particle concentrations were used with both the small (24 nm) and large (139 nm) colloidal particles. As shown in Fig. 4, solution pH had very little effect on the colloidal fouling behavior with the two silica suspensions. Interestingly, for the 139-nm particle suspension at a concentration of 2 g/L, a slightly greater flux decline was observed at pH 9, where the particles are more negatively charged (Fig. 1b), which will be discussed later in the paper.

3.3.2. Fouling with a polydisperse colloidal suspension

The effect of solution pH on colloidal fouling with a polydisperse colloidal suspension was also studied by using a suspension containing both small (24 nm) and large (139 nm) particles, each at 1 g/L. In Fig. 5, the flux decline curves at different pH values are compared to those obtained from summing the flux decline at each point of time from the individual fouling curves for the 24 nm and 139 nm particles shown in Fig. 4. The results indicate that the influence of particle polydispersity on flux decline is negligible at low pH (pH 4), but significant at high pH (pH 9).

The sudden drop in water flux for the polydisperse suspension in Fig. 5b after ~230 min is noteworthy. To better understand the cause for this behavior, we carried out fouling runs under similar conditions but with different combinations of small and large particles (Fig. 6). As the concentration of the small (24 nm) particles in the feed suspension is increased, the sudden drop in the water flux appears at an earlier time. We propose that the abrupt drop in water flux takes place when a cohesive cake is formed with small particles incorporated in the cake with the large particles. Such a cake layer will have a much lower porosity than the case with only large particles, and thus will significantly enhance CEOP due to a much reduced back diffusion of salts. As the concentration of the small particles increases, such low-porosity cakes form earlier, which results in an abrupt drop in water flux.

To isolate the mechanism responsible for inducing different flux decline behavior with polydisperse suspensions at the two solution pH tested, lanthanum chloride (LaCl₃) was used as an alternative draw solution. The reverse diffusion of LaCl₃ was expected to be much lower than NaCl because the hydrated size of the trivalent lanthanum cation is much greater than the sodium ion, subsequently less accelerated CEOP was expected. Also, when using LaCl₃ as draw a solution, reverse diffusion of protons may occur because the solution pH of LaCl₃ is low due to the hydrolysis of lanthanum. To compare fouling behavior with the different draw solutions, 3 M of NaCl and 2.5 M of LaCl₃ were used in order to obtain an identical osmotic driving force and initial water flux.

Similar to the results obtained when using a draw solution of 5 M NaCl (Fig. 5), notable flux decline was observed with the 3 M NaCl draw solution at high feed solution pH (Fig. 7a). However, almost identical flux decline behavior was observed when LaCl₃ was used as a draw solution at both high and low pH. This observation suggests that fouling behavior with silica colloids depends on the draw solution and its reverse diffusion rate. The much lower reverse diffusion of LaCl₃ did not result in enhanced CEOP and thus the flux decline was low (Fig. 7b). However, because of the much higher NaCl reverse diffusion, the enhanced accumulation of salt within the cake layer, caused significant flux decline for the run at pH 9 (Fig. 7a). Further discussion on this observation and the role of solution pH is given in the following subsection.

3.4. Draw solution reverse diffusion and particle destabilization enhance fouling

To further demonstrate the reverse diffusion of draw solution to the feed side, we monitored the change in feed water salt concentration and pH. Fig. 8a presents the cumulative amount of salt
leaking to the feed side when using DI water as a feed solution and either 3 M NaCl or 3 M LaCl₃ as draw solution. The observed reverse salt diffusion is in agreement with our expectation, namely that a much lower reverse diffusion of LaCl₃ occurred compared to that of NaCl. The variation in feed solution pH (Fig. 8b), measured using DI water as the feed and 2.5 M LaCl₃ as the draw solution, is due to the reverse diffusion of protons generated by the hydrolysis of LaCl₃.

It is generally accepted that colloid cake layer thickness and porosity are governed by the size and polydispersity of the colloidal suspension, respectively. As described in the previous section, the reverse diffusion of salts from the draw solution results in their accumulation on the feed side of the membrane. The back diffusive transport is hindered by the cake layer, thereby resulting in changes to the solution composition within the cake layer and thus affecting the interactions between the particles in the cake layer. Such changes become important for thick and less porous (or more compact) cake layers that effectively hinder the back diffusion of accumulated salts and protons. A schematic description of this phenomenon for salinity-rich and low-pH environments near the membrane surface is presented in Fig. 9.

To further explain the significant flux decline observed at high feed solution pH with the polydisperse silica suspension, we evaluated the colloidal stability of the 139 nm silica particles by dynamic light scattering (DLS). Our DLS results (data not shown) indicated that the hydrodynamic radius of the 139-nm particles significantly

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**Fig. 5.** Flux decline curves for FO fouling experiments with the polydisperse silica suspension (1 g/L of 24 nm particles plus 1 g/L of the 139 nm particles) at: (a) pH 4 and (b) pH 9. Also presented (open circles) are the “additive” flux decline curves obtained by summing the flux decline data of the separate fouling runs with the 24 nm and 139 nm particles (shown in Fig. 2). Feed solution ionic strength (50 mM NaCl) and the draw solution concentration (5.0 M NaCl) were identical for all fouling runs. Other experimental conditions during the fouling runs: initial flux of 5.3 µm/s (19.1 L/(m² h)), cross-flow velocity of 8.5 cm/s, and temperature of 21.0 ± 1.0 °C.

**Fig. 6.** Flux decline curves for FO fouling experiments with polydisperse silica suspensions with different mixtures of large (139 nm) and small (24 nm) particles as indicated in the figure. Feed solution ionic strength (50 mM NaCl) and the draw solution concentration (5.0 M NaCl) were fixed for all fouling runs. Other experimental conditions during the fouling runs: initial flux of 5.3 µm/s (19.1 L/(m² h)), cross-flow velocity of 8.5 cm/s, and temperature of 21.0 ± 1.0 °C.

**Fig. 7.** Effect of reverse salt diffusion on FO fouling with the polydisperse silica suspension (1 g/L of 24 nm particles plus 1 g/L of the 139 nm particles) using the following draw solutions: (a) NaCl and (b) LaCl₃. In order to achieve the same initial flux, 2.5 M LaCl₃ and 3.0 M NaCl were used for draw solutions. Experimental conditions during the fouling runs: feed solution ionic strength of 50 mM NaCl, initial flux of 4.3 µm/s (15.48 L/(m² h)), cross-flow velocity of 8.5 cm/s, and temperature of 21.0 ± 1.0 °C.
increased for high pH (pH 9) and high ionic strength (1 M of NaCl) solutions. However, no change in the hydrodynamic radius of the silica particles was observed at pH 4, even at very high salt concentrations. The observed increase in the hydrodynamic radius implies that the colloidal silica particles are destabilized under these solution conditions (i.e., pH 9 and high ionic strength). The unusual stability of silica particles at low pH compared to higher pH, contrary to the behavior of typical colloidal suspensions and the zeta potential of the particles (Fig. 1b), is well documented in the literature [40,41]. This behavior is attributed to short-range strong repulsive hydration forces that exist at low pH and prevent silica particle aggregation [42]. We therefore propose that the thicker (2 g/L of 139 nm) or less porous (or more compact) (1 g/L of 24 nm plus 1 g/L of 139 nm) cake layers generate salinity-rich environments near the membrane surface on the feed side which, in turn, induce destabilization/aggregation of colloidal particles and the formation of a cohesive cake layer.

3.5. Impact of reverse diffusion of draw solutes on reversibility of colloidal fouling

While reverse salt diffusion has been shown to impact colloidal fouling behavior, it is of practical interest to study whether it has an impact on fouling reversibility. To evaluate the colloidal fouling reversibility in FO, physical cleaning, achieved by increasing the cross-flow rate, was applied after a 10-h accelerated colloidal fouling test. As shown in Fig. 10, in most cases, the initial flux recovered to nearly 100%, indicating that FO colloidal fouling is reversible. However, when the particles aggregated under conditions of high salt concentration due to reverse salt diffusion and high feed...
solution pH (specifically, the 3 M NaCl draw solution at pH 9), the flux was not recovered. Therefore, we can conclude that in the absence of particle destabilization, the colloidal fouling layer is reversible when subjected to simple physical cleaning, achieved by increasing the cross-flow rate.

4. Conclusion

This study demonstrates the importance of reverse salt diffusion in colloidal fouling and fouling reversibility in the FO process. Significant flux decline rates were observed with thick or less porous fouling layers composed of large (139 nm) particles or a mixture of particles (24 and 139 nm), respectively. The back diffusion of salts that permeated from the draw solution was hindered by the colloidal fouling layer and, consequently, the salt concentration near the membrane surface dramatically increased. Colloidal fouling was enhanced under solution conditions that favor particle destabilization and aggregation. Reverse salt diffusion and the resulting particle destabilization within the cake layer also determine the fouling reversibility and cleaning behavior. In the absence of particle aggregation, the colloidal fouling layer is reversible when subjected to simple physical cleaning (by increasing cross-flow rate). Our results imply that minimizing reverse salt diffusion by improving membrane selectivity and selecting proper draw solutions that do not induce particle destabilization and colloidal fouling are important to efficient operation of the FO process.

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