Effect of cake layer structure on colloidal fouling in reverse osmosis membranes

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Abstract

A series of reverse osmosis (RO) membrane filtration experiments was performed systematically in order to investigate the effects of various hydrodynamic and physicochemical operational parameters on a cake layer formation in colloidal and particulate suspensions. Bench-scale fouling experiments with a thin-film composite RO membrane were performed at various combinations of trans-membrane pressure (TMP), cross-flow velocity (CFV), particle size, pH, and ionic strength. In this study, silica particles with two different mean diameters of 0.1 and 3.0 \( \mu \text{m} \) were used as model colloids. Membrane filtration experiments with colloidal suspensions under various hydrodynamic operating conditions resulted that more significant permeate flux decline was observed as TMP increased and CFV decreased, which was attributed to the higher accumulative mass of particles on the membrane surface. Results of fouling experiments under various physicochemical operating conditions demonstrated that the rate of flux decline decreased significantly with an increase of the ionic strength as well as particle size, while the flux decline rate did not vary when solution pH changed. The experimentally measured cake layer thickness increased with a decrease in particle size and solution ionic strength. Furthermore, the model estimation of cake layer thickness by using a cake filtration theory based on the hydraulic resistance of membrane and cake layer was performed under various ionic strength conditions. The primary model parameters including accumulated mass and specific cake resistance were calculated from the cake layer resistance. This result indicated that the formation of cake layer could be closely related with solution water chemistry. The model estimated cake layer thickness values were in good agreement with the experimentally measured values.

Keywords: Cake layer thickness; Colloidal fouling; Cake filtration theory; Reverse osmosis

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1. Introduction

Utilization of reverse osmosis (RO) is increasing exponentially in seawater desalination processes and advanced drinking water treatment [1,2]. However, like other membrane filtration processes, fouling has been a major problem in successful application and cost efficient operation of RO membrane process [3–6]. In RO separation process, RO membranes are subject to be fouled by colloidal materials (referred to as colloidal fouling) as well as by dissolved organic matters (referred to as organic fouling). Membrane fouling causes deterioration of both the quantity and the quality of treated water, and consequently results in a gradual degradation of the membrane itself which ends in a shorter membrane life [4]. Colloidal fouling presents a physical barrier to suspended particles or colloids in the feed stream, whereby all particles are retained on the feed side of the membrane [7–10]. Therefore, the retained particles accumulate on the surface of the membrane and increase the resistance to water flow across the membrane.

Permeate flux decline of colloidal suspensions is primarily governed by concentration polarization and particle accumulation in the cake layer on the membrane surface [11]. The major advantage of cross-flow filtration is that the suspension to be filtered flows parallel to the membrane surface, therefore reduces the accumulation of colloidal particles on the membrane surface [12]. This process is controlled by system hydrodynamics (TMP and CFV), physicochemical operating conditions (particle size and charge, membrane characteristics such as surface charge, roughness, and hydrophobicity), and solution chemistry (solution pH and ionic strength) [13–15]. Due to particle–membrane and particle–particle interactions, it is expected that the changes in particle size, TMP, CFV, and solution water chemistry would result in significant changes in permeate flux decline behavior and cake layer structure. Especially, in case of colloids (i.e., 0.1 μm), interparticle electrostatic repulsive forces based on colloidal interaction in the RO separation process should be considered as an important parameter, which could change the cake layer porosity and permeability.

Pretreatment processes such as coagulation/flocculation and low pressure membrane filtration (microfiltration and ultrafiltration) has been used for RO process to remove particles and large colloids, but fouling by small colloidal matters and fine suspended particles still plague RO applications [10]. Most previous studies investigating the cake layer formation on RO membranes have mainly focused on the effect of the size of colloidal or particulate matters [16–18]. However, because of the complex nature of feed water, it is important to understand and predict the change of cake layer structure under various operating conditions. Additionally, in order to accurately describe the performance of RO membranes, it is very important to develop a more quantitative understanding of the relationships among permeate flux, operational parameters, and cake layer formation.

The main objective of this study was to investigate the effect of various hydrodynamic and physicochemical operational parameters on the RO membrane performance and cake layer formation deposited on the membrane surface during the filtration of colloidal and particulate suspensions. Furthermore, the cake layer thickness was estimated by using a flux decline model under various pH and ionic strength of feed solution, and model estimated cake layer thickness values were compared with experimentally measured values by FE-SEM analysis.

2. Materials and methods

2.1. Colloidal suspensions and reagents

Two types of silica (SiO₂) colloids used in this study as model colloidal particles were ST-XL (Nissan Chemicals, Houston, TX) and SILNOS-3M (ABCNanoTech, Seoul, South Korea). The
ST-XL was received as a stable concentrated (40.7% by weight) aqueous suspension at an alkaline pH. The required suspension of SILNOS-3M particles was prepared by diluting the powder with deionized (DI) water (Milli-Q® Ultrapure Water Purification System, Millipore Corp., Billerica, MA). Gravimetric analysis revealed that the density of the particles was 2.36 and 2.25 g/cm³ for ST-XL and SILNOS-3M, respectively. Both colloids were spherical in shape and the mean diameter was 0.10 ± 0.03 and 3.0 ± 0.25 μm for ST-XL and SILNOS-3M, respectively. The size (uniformity) and shape of these model colloids were further verified by an analysis of field emission scanning electron microscope (FE-SEM, S-4100, HITACHI High-Tech Science Systems Corp., Japan). Concentrated stock suspensions of both silica colloids were stored at 4°C. Before and during each experiment, the colloidal suspension was mechanically mixed in order to agitate all visible precipitate and the concentration of the stock suspension was routinely monitored. Throughout all experiments, feed particle concentration was 200 mg/L.

In order to obtain the desired feed ionic strength and pH for the fouling experiments, all solutions were prepared by dissolving ACS grade KCl, NaOH, and H₂SO₄ (Fisher Scientific, Pittsburgh, PA) in DI water having a conductivity less than 0.8 μS/cm when in equilibrium with atmosphere.

2.2. Membrane characterization

RO polyamide thin film composite (TFC) membrane (FE, Saehan Inc., Seoul, South Korea) was used in all fouling experiments and the observed salt rejection of this membrane was 98.7–99.6% (determined at an applied pressure of 225 psi and 2000 mg/L NaCl concentration). Membrane samples were received as 1.8 in spiral-wound type and stored in DI water at 4°C. All membrane samples were cut and rinsed thoroughly with DI water prior to use.

<table>
<thead>
<tr>
<th>Code</th>
<th>Characterization of RO membrane used in this study</th>
</tr>
</thead>
<tbody>
<tr>
<td>Type</td>
<td>Polyamide TFC (thin film composite)</td>
</tr>
<tr>
<td>Manufacturer</td>
<td>Saehan, South Korea</td>
</tr>
<tr>
<td>Roughness</td>
<td>87.62 nm</td>
</tr>
<tr>
<td>Zeta potential</td>
<td>–8.77 mV (pH 6.0)</td>
</tr>
<tr>
<td>Contact angle</td>
<td>36.5°</td>
</tr>
<tr>
<td>Specific water flux ($K_w$)</td>
<td>$6.2 \times 10^{-5}$ m/s-kgf/cm²</td>
</tr>
<tr>
<td>Mass transfer coefficient ($K_s$)</td>
<td>$2.8 \times 10^{-5}$ m/s</td>
</tr>
<tr>
<td>Membrane resistance</td>
<td>$(10.23 \pm 0.2) \times 10^{13}$ m⁻¹</td>
</tr>
<tr>
<td>Max. operating temperature</td>
<td>45°C</td>
</tr>
<tr>
<td>Max. operating pressure</td>
<td>4136 kPa (600 psi)</td>
</tr>
<tr>
<td>Operating pH range</td>
<td>3–10</td>
</tr>
</tbody>
</table>

The primary membrane characteristics such as roughness, zeta potential, and hydrophobicity are summarized in Table 1. The surface roughness was characterized by atomic force microscopy (AFM, XE-100, PSIA, Seoul, South Korea) in tapping mode operation. Membrane surface charge was evaluated by the zeta potential at the shear plane and was calculated from streaming potential measurements (ELS 8000, Otsuka Electronic, Japan). The pH of the electrolyte was adjusted in order to obtain zeta potential measurements between pH 2 and 10, as shown in Fig. 1. The...
hydrophobicity of the membrane was determined by a contact angle measurement using a goniometer (TanTec, IL). The sessile drop method was used to determine contact angle by passing bubbles in aqueous conditions. The surface of fouled membranes was analyzed by using field emission scanning electron microscope (FE-SEM, S-4100, HITACHI High-Tech Science Systems Corp., Japan).

2.3. Cross-flow membrane filtration systems

The cross-flow membrane unit used in this study is schematically shown in Fig. 2. A rectangular flat sheet RO membrane was housed in a stainless steel cell, through which the feed water was circulated by a diaphragm pump from a high-density polyethylene 20 L (5.3 gal) feed reservoir. The dimension of the cell was 15.0 cm length, 10.0 cm width, and 0.25 cm channel height, providing an effective membrane area of 150 cm$^2$.

The temperature of feed suspension was maintained at 20°C (68 F) using a refrigerated recirculator (DH Water Master, Donghwa Cooling System, South Korea) which circulated the coolant through a stainless steel coil submerged in the feed solution. Initial operating conditions (e.g. permeate flux and CFV) were set and maintained through the careful manipulation of feed, concentrate, and bypass needle valves. Concentrate and filtrate flows were measured both by an in-line flow meter (Blue-White Industries, Westminster, CA) and by the timed collection of filtrate in a graduated cylinder, respectively.

3. Results and discussion

3.1. Effect of trans-membrane pressure (TMP)

Flux decline experiments were conducted using 0.1 and 3.0 μm silica particles and feed particle concentrations were 200 mg/L at pH 7.0. The effect of initial permeate flux on flux decline and cake layer structure was investigated by varying TMP. For filtering suspensions with both 0.1 and 3.0 μm silica particles, permeate flux decline was faster at higher TMP as shown in Fig. 3 (a) and (b). Initial flux of selected RO membrane was 54.9 LMH. The extent of flux decline was 35%, 48%, 61% for 0.1 μm colloidal suspension and 8%, 17%, 25% for 3.0 μm particulate suspension under the TMP of 588, 784, and 980 kPa, respectively. This observation was attributed to the higher accumulative mass of particles on the membrane surface at higher TMP and to the

Fig. 2. Schematic diagram of a bench-scale cross-flow RO membrane filtration system.
dependence of the cake layer porosity on the TMP [11]. Hence, as the TMP increases, the higher permeation drag and compressive forces exerted on the cake layer favor a thicker. In comparison with 3.0 μm particulates, 0.1 μm colloids resulted in more significant permeate flux decrease as TMP increased under the same feed particle concentration. This result suggests that smaller particles could provide larger hydraulic resistance to permeate flow than larger particles and therefore results in a faster flux decline.

3.2. Effect of cross-flow velocity (CFV)

The influence of CFV on the flux decline behavior was investigated with 200 mg/L particles in suspension containing different size of particles (0.1 and 3.0 μm) at pH 7.0. In a cross-flow membrane filtration system, higher CFV resulting in an increase of shear rate reduces the particle accumulation on the membrane surface [12]. As expected, Fig. 4 (a) and (b) present that the observed extent of flux decline for 0.1 and 3.0 μm particles was 48%, 25%, 7% and 17%, 13%, 6% under the CFV of 0.067, 0.111, and 0.256 m/s, respectively. This observation demonstrated that permeate flux decline with 0.1 μm colloidal suspension decreased significantly with increasing the CFV, while there was no significant difference in the flux decline with 3.0 μm particulate suspension. Thus, for the RO filtration of colloidal suspensions, the CFV should be considered as one of the key operational parameters like TMP as described in above section.
3.3. Effect of solution pH

The effect of solution pH on the flux decline behavior of 0.1 and 3.0 μm particles in suspension is shown in Fig. 5 (a) and (b). At an initial filtration experiment, variation of normalized flux was observed under various pH conditions. In case of 0.1 μm colloids, the initial permeate flux decline at pH 4.0 was faster than those under pH 7.1 and 10.1 conditions, because membrane surface charge retained the positive value (+18.2 mV) at pH 4.0 (see Fig. 1). The rate of initial flux decline was 22.0, 15.6, and 9.1 LMH/h at pH 4.0, 7.1, and 10.1, respectively. At pH 7.1 and 10.1, much slower initial flux decline was observed due to negatively charged (−16.8 and −27.1 mV, respectively) membrane surface. Feed suspension with 200 mg/L silica particles was negatively charged (−20.9 to −38.8 mV) under all tested pH conditions. Thus, repulsive double layer interactions developed between the silica colloids and the membrane surface at pH 7.1 and 10.1. Despite differences in the initial flux decline behavior, the permeate flux decline behavior for 0.1 μm colloidal suspension during the later part of filtration period from 48 h to the end of run, where cake layer resistance dominated membrane resistance to permeate flow, was almost identical under all pH conditions. Unlikely, for 3.0 μm particulate suspension, there was no significant effect of solution pH on the flux decline behavior. This is mainly due to the fact that the number of particles on the membrane surface was significantly lower than 0.1 μm colloids. In conclusion, the influence of solution pH on permeate flux behavior should not be seriously considered for the RO filtration system when mainly containing the large particulates (not colloids) in feed water.

3.4. Effect of ionic strength

The effect of solution ionic strength on the rate and extent of membrane fouling is presented in Fig. 6 (a) and (b). The fouling tests were carried out at three KCl concentrations: 10^{-4}, 10^{-3}, and 10^{-2} M. According to colloidal interactions theory [18–21], the magnitude of the electrostatic double layer (EDL) repulsion is proportional to the debye screening length (κ⁻¹) which related in ionic strength of the solution. The debye screening length is a calculation for the range of the EDL repulsive force between colloidal particles (<1.0 μm), however, they could be not used when filtering suspensions with the particulate matters. In colloidal suspensions, the debye screening length (in SI units) was calculated by using following equation (for a 1:1 electrolyte).
where $e$ is the elementary charge, $N_A$ is Avogadro’s number, $I$ is the ionic strength (M), $\varepsilon_r$ is the dielectric permittivity of water, $\varepsilon_0$ is the permittivity of free space, $\kappa$ is the Boltzmann constant, and $T$ is the absolute temperature.

According to above equation, the debye screening length decreases as the ionic strength concentration increases, and then EDL repulsive force decreases. The reduction in repulsive forces results in the formation of a more densely packed cake layer on the membrane surface, which consequently causes a greater resistance to permeate flow [22–24]. Therefore, higher ionic strength in feed solution resulted in lower permeate flux.

Fig. 6 (a) shows that initial flux decline for 0.1 μm colloidal suspension at an ionic strength of $10^{-2}$ M was fastest due to most significant membrane fouling. At the end of filtration runs, the permeate flux at an ionic strength of $10^{-2}$ M about 22% and 47% lower than those at $10^{-3}$ and $10^{-4}$ M, respectively. These fouling results are consistent with the colloidal interactions theory and previously reports [3,11,23,25]. Fig. 6 (b) is showing that for 3.0 μm particulate suspension, the ionic strength did not significantly affect the permeate flux decline because the EDL repulsive force for the large particles is not significant. Overall, for RO filtration of colloidal suspension, the effect of EDL repulsive forces on the permeate flux is quite significant, and therefore solution ionic strength should be considered as an important operational parameter.

3.5. Model estimation of cake layer thickness

For pressure-driven membrane processes, the permeate flux can be evaluated from Darcy’s law which relates the total resistance to permeate flow:

$$J = \frac{\Delta P}{\mu (R_m + R_c)}$$  \hspace{1cm} (2)

where $\Delta P$ is the TMP, $\mu$ is the solution viscosity, $R_m$ is the membrane resistance, and $R_c$ is the resistance imparted by the cake layer deposited over the membrane surface. For all experiments in this study, $\mu$ and $R_m$ are constant values, and the latter may be expressed in terms of $R_c$.

$$R_c = \frac{\Delta P}{J \cdot \mu} - R_m$$  \hspace{1cm} (3)

The cake layer resistance ($R_c$) calculated from Darcy’s law equation can be expressed in terms of the specific cake resistance ($\alpha$) as $R_c = \alpha M_d$. 

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**Fig. 6.** Effect of ionic strength on normalized flux decline. The filtration conditions employed were particle size 0.1 (a) and 3.0 μm (b), pH 7.0, TMP 784 kPa, CFV 0.067 m/s, and temp. 20°C.

M can be calculated from the accumulated particle mass per unit area on the membrane surface. Thus, \( a \) can be calculated from the \( R_c/M_d \) equation. \( a \) can be further related to the cake porosity (\( \varepsilon \)) via following Kozeny-Carman equation.

\[
\alpha = \frac{45(1 - \varepsilon)^2}{\rho a_p^2 \varepsilon^3}
\]

where \( \rho \) is the particle density and \( a_p \) is the particle radius. Finally, cake layer thickness (\( \delta_c \)) can be calculated from the deposited mass using a mass balance on the cake layer [17].

\[
\delta_c = \left( \frac{4/3}{1 - \varepsilon} \right) \frac{M_c}{M_d}
\]

where \( M_c \) is the total number of particles (per unit area) accumulated in the cake layer, as calculated from the accumulated mass and particle density, and \( \varepsilon \) is the cake porosity obtained from Kozeny-Carman equation.

The cake layer thickness on the RO membrane surface under various solution pH and ionic strength conditions was estimated according to the above equations. Because the significant membrane fouling was only occurred during the filtration of colloidal suspensions, the filtration studies with 0.1 \( \mu \)m colloids were only considered. Table 2 summarizes the parameter values (\( R_c \), \( \alpha \), and \( M_d \)), model estimated and experimentally measured cake layer thickness. Based on the estimated cake layer thickness values in Table 2, the cake layer thickness was almost identical under various pH conditions, which indicated the effect of solution pH on the cake layer formation was not significant. However, the model estimated cake layer thickness as well as the cake layer resistance and the accumulated mass on the membrane surface increased significantly as the solution ionic strength increased. This result suggests that an ionic strength of feed solution is an important operational parameter for the cake layer formation in the application of RO filtration system. As it is clear from Table 2, the measured cake layer thickness by FE-SEM analysis resulted in good agreement with the model estimated values, which further confirms the applicability of the cake filtration theory based on the hydraulic resistance of membrane for the RO filtration of colloidal suspensions.

### Table 2
Model estimated and measured cake layer thickness (\( \delta_c \)) under various solution pH and ionic strength conditions

<table>
<thead>
<tr>
<th>Conditions</th>
<th>( R_c \times 10^{13} \text{ m}^{-1} )</th>
<th>( M_d ) (g/m²)</th>
<th>( \alpha \times 10^{15} \text{ m/kg} )</th>
<th>Estimated ( \delta_c )</th>
<th>Measured ( \delta_c )</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4.0</td>
<td>2.32 ± 0.20</td>
<td>10.54</td>
<td>2.20</td>
<td>22</td>
<td>20</td>
</tr>
<tr>
<td>7.1</td>
<td>2.32 ± 0.19</td>
<td>8.56</td>
<td>2.71</td>
<td>20</td>
<td>20</td>
</tr>
<tr>
<td>10.1</td>
<td>2.30 ± 0.15</td>
<td>6.91</td>
<td>3.32</td>
<td>20</td>
<td>–</td>
</tr>
<tr>
<td>Ionic strength</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( 10^{-4} \text{ M} )</td>
<td>2.61 ± 1.25</td>
<td>5.20</td>
<td>5.02</td>
<td>22</td>
<td>–</td>
</tr>
<tr>
<td>( 10^{-3} \text{ M} )</td>
<td>2.68 ± 1.30</td>
<td>21.74</td>
<td>1.23</td>
<td>27</td>
<td>25</td>
</tr>
<tr>
<td>( 10^{-2} \text{ M} )</td>
<td>2.81 ± 1.44</td>
<td>36.76</td>
<td>0.76</td>
<td>35</td>
<td>30</td>
</tr>
</tbody>
</table>

*Data from FE-SEM analysis.*

4. Conclusions

The hydrodynamic operational parameters had significant effects on the RO membrane fouling by colloidal particles. The role of TMP and CFV in membrane fouling was investigated systematically. Membrane filtration experiments of colloidal suspensions with 0.1 \( \mu \)m colloids resulted that more severe permeate flux decline was observed as TMP increased and CFV decreased.
These results were due to the higher accumulative mass of colloidal particles on the membrane surface under higher TMP and lower CFV conditions. Therefore, for the RO filtration of colloidal suspensions, both TMP and CFV should be considered as key operational parameters.

Results of fouling experiments under various physicochemical operating conditions demonstrated that the rate and extent of permeate flux decline significantly increased as particle size decreased under identical feed particle concentration. At an initial filtration experiment, the initial flux decline rate at pH 4.0 was much faster than those at pH 7.1 and 10.1, which was due to the repulsive double layer interactions developed between the tested silica colloids and the membrane surface at pH 7.1 and 10.1. The effect of solution ionic strength was more significant and higher initial rate and extent of flux decline in colloidal suspension filtrations was observed with an increase of the ionic strength. This result was mainly due to the reduction in EDL repulsive force, which resulted in the formation of a more densely packed cake layer on the membrane surface and consequently caused a more resistance to permeate flow under higher solution ionic strength conditions.

Cake layer thickness was estimated by using a cake filtration theory based on the hydraulic resistance of membrane and cake layer under various pH and ionic strength conditions. Model estimated and experimentally measured cake layer thickness was almost identical under various pH conditions. However, both estimated and measured cake layer thickness values increased significantly as the solution ionic strength increased. These results were in good agreement with those of flux decline experiments.

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References


