Nano-colloidal fouling mechanisms in seawater reverse osmosis process evaluated by cake resistance simulator-modified fouling index nanofiltration

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**HIGHLIGHTS**
- The fouling mechanisms of nano-colloids in SWRO desalination were investigated.
- A novel method was developed to determine the specific cake resistance.
- Specific cake resistances were evaluated by cake resistance simulator (MFI-NFCRS).
- Flux decline in SWRO process greatly depended on the cake-enhanced osmotic pressure.

**ABSTRACT**

Fouling potentials caused by particulate matters are generally evaluated by fouling index, such as SDI and MFI, widely used in RO membrane practices. However, these fouling indices failed to predict the effect of nano-colloidal sizes on flux decline, implying that colloidal fouling is too complex to be analyzed by simple fouling index. Thus, in this study, nano-colloidal fouling mechanism in seawater reverse osmosis (SWRO) desalination was fundamentally investigated by employing new approach. Specifically, the specific cake resistance of colloidal foulants was first determined by a novel method, cake resistance simulator-modified fouling index nanofiltration (MFI-NFCRS), which was conducted under operating pressure and solute environment similar to those of real SWRO desalination. Then colloidal deposition and resulting cake-enhanced osmotic pressure (CEOP) were quantitatively assessed by fitting RO experimental data to the calculations from the CEOP model. The results clearly demonstrated that the flux decline caused colloidal deposition in the SWRO process depended greatly on the CEOP. The newly developed methodology including MFI-NFCRS is expected to contribute significantly to better understand nano-colloidal fouling mechanisms and to accurately predict their fouling potentials in the SWRO desalination.

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1. Introduction

There are various types of membrane fouling, such as colloidal deposition, organic adsorption, inorganic scaling and biofouling, which cause the gradual reduction of permeate flux and the deterioration of permeate water quality. Among these foulants, colloidal deposition appears to be one of the main causes of membrane fouling in the reverse osmosis (RO) membrane process which is becoming increasingly popular for seawater desalination [1–4]. Numerous studies have addressed the physical and chemical factors affecting colloidal deposition in pressure-driven membrane systems [5–10]. Colloids are roughly...
defined as fine particles with sizes in the range of 1 nm–1 μm [11] and those are likely to cause membrane fouling as a result of their sizes [12]. In addition, a more densely packed cake layer is formed on the membrane surface in seawater reverse osmosis (SWRO) processes, due to the reduction of electrostatic double-layer repulsive forces among colloids, which consequently causes greater resistance to permeate flux [7]. Although the removal efficiency of larger particles has been improved significantly by advanced pretreatments, such as microfiltration (MF) and ultrafiltration (UF) [13], the membrane fouling caused by smaller nano-colloids still remains as a recalcitrant problem in the SWRO desalination.

The silt density index (SDI) and/or modified fouling index (MFI) are widely used to predict the fouling potential of feed water for RO processes. These indices, however, often fail to predict the extent of colloidal fouling in real SWRO processes, primarily due to the differences in membrane pore sizes and complex fouling mechanisms. Relatively new methods, namely, MFI-UF and MFI-NF, have been proposed to predict the fouling potential caused by fine colloidal particles and organic substances, employing UF or NF membranes, respectively, in MFI measurements [14–17]. Recently, a novel fouling index determined by a set of membranes with different pore sizes was developed for more accurate estimations of feed fouling potentials [18,19]. Some researchers have suggested a new approach to incorporate crossflow hydrodynamic behavior during fouling index measurements, known as the crossflow sampler modified fouling indices (CFS-MFI) [10,20,21].

The MFI-based fouling indices are derived from cake filtration theory and have a linear relationship with specific cake resistances and particle concentrations. In addition to hydraulic resistance, the cake layer formed in the RO process causes cake-enhanced osmotic pressure (CEOP), which decreases the effective pressure across RO membrane due to increasing solute concentrations at the membrane surface [22–24]. The extent of a cake layer formation is greatly affected by solution chemistry (e.g., pH and ionic strength), membrane properties, and hydrodynamic conditions (e.g., critical flux) [25]. Despite its importance, to date, a fouling index to reflect complex mechanisms of colloidal fouling in the SWRO process has not been developed yet. Recent studies have described the significant effect of the CEOP on flux decline, but their results could not be applicable to SWRO process due to lower total dissolved solids (TDS) conditions (i.e., 10 g/L NaCl or lower) at which their RO experiments were conducted [22–24].

In this study, the colloidal fouling mechanism that significantly affects the permeate flux in the SWRO process was systematically investigated through fouling index measurements and lab-scale RO experiments using nano-colloids with different sizes. Specifically, the fouling potentials of colloidal foultants were first evaluated through SDI, MFI-MF, and MFI-UF. The discrepancy between the fouling potentials measured by fouling indices and the actual flux decline of SWRO experiments was identified with respect to colloidal size, leading to a more fundamental investigation on nanocolloidal fouling mechanism in the SWRO process. The specific cake resistance of nano-colloids was first determined by a novel method, cake resistance simulator-modified fouling index nano-filtration (MFI-NF_CRS). More specifically, NF dead-end filtrations were conducted under the same operating pressures and solute conditions as the practical SWRO process to obtain values similar to the specific resistances of the cake layer formed in the real SWRO process. Then, colloidal fouling mechanisms were fundamentally elucidated by performing systematic theoretical and experimental analysis based on cake enhanced osmotic pressure (CEOP) model and MFI-NF_CRS. Finally, the contributions of cake resistance and CEOP to the flux decline under seawater conditions were compared and delineated. Our observations from experiments as well as modeling provide new insights into nano-colloidal fouling mechanisms in the SWRO process and strategies for the prediction of their fouling potentials.

2. Materials and methods

2.1. Colloidal particle foulants

Commercial silica (SiO₂) particles with different sizes were used as model foulants to evaluate fouling potential with respect to particle size. The sizes of model particles were 3 μm (SILOS-3 M, ABC Nano-tech, Korea), 70–100 nm, 40–60 nm and 10–15 nm (ST-ZL, ST-XL and ST-30, Nissan Chemical Industries, Japan). The 3 μm particles were obtained in a powdered form, and the other nano-colloidal particles were supplied in a dissolved form at 40% (ST-ZL, ST-XL) or 30% (ST-30) concentrations (w/w). The feed water samples containing different concentrations of these particles were prepared by adding them to deionized (DI) water (SHUVQ-90ST, Sinhan Science Tech.) or pretreated seawater. Gravimetric analysis revealed the density of 70–100 nm, 40–60 nm and 10–15 nm particles to be 2.3, 2.1 and 2.1 g/cm³, respectively. The size distributions of these silica particles were measured using a particle size analyzer (Zetasizer Nano ZS, Malvern Instrument Ltd.) in DI water and 35 g/L NaCl solution.

To elucidate the effect of particle size on flux decline in the SWRO process, the sizes of nano-colloidal suspensions at the seawater-level solute conditions were measured accurately, as shown in Fig. 1. The average sizes of 10–15 nm, 40–60 nm and 70–100 nm colloidal particles increased to 28 nm, 91 nm and 164 nm, respectively, due to the aggregation of colloids in the 35 g/L NaCl solution. The average particle size of 3 μm, however, did not show any changes (i.e., 2.90 μm in DI water and 2.92 μm in the 35 g/L NaCl solution). These observations are in good agreement with the results of a previous study [10]. The high ionic strength leads to a reduction of the electrostatic double layer (EDL) repulsion among the colloids, causing particle size increase due to particle aggregation. Because the main goal of this study is to elucidate the colloidal fouling mechanism in the SWRO process, colloidal sizes of 28 nm, 91 nm and 164 nm were used to evaluate the effect of particle size on nano-colloidal fouling in the following sections.

2.2. Feed water

Two types of feed water were used to investigate the mechanism of colloidal fouling in SWRO process. One was a pretreated seawater taken from the sea near Changwon, Korea. The pretreated seawater sample was collected from the feed tank of an RO pilot plant (50 m³/day) equipped with a microfiltration membrane (i.e., pore size 0.1 μm), which served as a pretreatment process. The pretreated seawater sample was carefully delivered to the laboratory and stored in a refrigerator. The basic water quality of the sample was analyzed, and the results are listed in Table 1.

Another feed water was DI water in which the TDS was adjusted to be 35 g/L (i.e., similar to seawater TDS) by adding NaCl, and the pH was fixed at 7.0 ± 0.5 using 0.1 N NaOH or 0.1 N HCl stock solutions. Aldrich humic acid (HA) was also added to the solution to produce an organic concentration similar to seawater. The stock solution was prepared by dissolving HA in DI water, followed by stirring for 2 days. The stock solution (2000 mg/L) was filtered through a UF membrane with an MWCO of 30 kDa to remove colloidal organics, and then, the dissolved organic carbon (DOC) was determined using a TOC analyzer (TOC-V, Shimadzu Corp.). The DOC value of this feed water was adjusted to 0.5 mg/L by adding the HA stock solution.

2.3. SDI and MFI measurements

SDI measurement was performed by the standard test method (ASTM 4189-07). The SDI equipment consisted of a membrane holder, a high pressure pump controlled by pressure control system, feed water reservoir, and data acquisition system. During SDI tests, the applied pressure was kept at 2.07 ± 0.07 bar and the feed water temperature was controlled at 20 ± 1 °C through a cooling coil submerged...
in the reservoir. The MFI-MF and MFI-UF were also evaluated using the same equipment used for the SDI, except that MFI-UF was measured at the pressure of 12.4 bar. The volume of permeate flow during the MFI measurements was recorded every second for 20 min in the MFI-MF and for 1 h in the MFI-UF. The detailed methods of the MFI measurements have been presented in our previous work [19] and are summarized in Table 2 including the information about the membranes used for SDI and MFI measurements.

2.4. NF and RO membranes

A commercial thin film composite RO membrane (ESPA 2-4040, Hydranautics, CA) with an average salt rejection of 99.6% (determined at an applied pressure of 10.3 bar and 1500 mg/L NaCl concentration) was used for the fouling experiments. An NF membrane (NE 4040-70, Woongjin Chem. Inc.) with an observed salt rejection of 40–70% (determined at an applied pressure of 5.17 bar and 2000 mg/L NaCl concentration) was used in the dead-end filtration to determine the specific cake resistance of colloidal particles in the absence of the CEP effect. All the membranes were stored in deionized (DI) water at 4 °C and rinsed regularly prior to use.

2.5. Lab-scale RO crossflow fouling experiments

A schematic diagram of the lab-scale test unit for the crossflow RO experiments is presented in Fig. 2. The configuration of a plate-and-frame type membrane cell was 146 × 95 × 1.85 mm, and the effective membrane area was 0.0139 m². During crossflow filtration, the permeate was collected in a reservoir (300 mL) and returned to the feed tank (5 L), and the system was operated for another 24–48 h.

2.6. Evaluation of the MFI-NF

The specific cake resistance of the colloidal fouling layer formed under SWRO conditions was experimentally measured by a novel method, cake resistance simulator-modified fouling index nanofiltration (MFI-NFCS). This experimental system using dead-end NF filtration was similar to typical crossflow NF/RO test unit, but all feed water supplied to the membrane cell permeated through NF membrane by closing valve 1, as shown in Fig. 2. The permeate was collected in a reservoir (3 L), and the flow rate was monitored using a digital balance. The operating pressure (50 bar) and temperature (21 ± 1 °C) were the same as those employed in the SWRO experiments.

3. Results and discussion

3.1. Colloidal fouling assessed by various fouling indices

The fouling potentials of various particles were evaluated through three different fouling indices (SDI, MFI-MF and MFI-UF) using four model particles of which the sizes were 3 μm, 164 nm, 91 nm, and 28 nm. Then, the correlations between fouling index measurements and actual flux reduction in the SWRO experiments were investigated using pretreated real seawater.

3.1.1. Evaluation of particle fouling potential by fouling indices

The effect of particle size on the SDI, MFI-MF and MFI-UF measurements was investigated systematically using pretreated seawater with particles of various sizes, and the results are presented in Fig. 3. The

<table>
<thead>
<tr>
<th>Region</th>
<th>Conductivity (mS/cm)</th>
<th>Turbidity (NTU)</th>
<th>DOC (mg/L)</th>
<th>SUVA (mL/mg m)</th>
<th>UVa254 (mL/mg m)</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>Changwon</td>
<td>51.7</td>
<td>0.19</td>
<td>1.25</td>
<td>0.015</td>
<td>1.2</td>
<td>7.56</td>
</tr>
</tbody>
</table>

*pH was adjusted to be 7.0 ± 0.5 using 0.1 N HCl solutions before fouling experiments.
SDI and MFI-MF of pretreated seawater containing 3 μm particles increased significantly, while those of pretreated seawater containing nano-colloids of 164, 91 and 28 nm did not show any significant changes compared to the values of pretreated seawater without any particles (Fig. 3(a) and (b)). Thus, it was confirmed that the SDI and MFI-MF measurements responded sensitively to larger particles, but failed to predict the fouling potential of nano-colloids smaller than the pore size (0.45 μm) of the MF membrane used to evaluate these fouling indices.

However, as shown in Fig. 3(c), the MFI-UF values of pretreated seawater containing nano-colloids increased significantly, particularly in the case of the smallest colloids (i.e., 28 nm). Another interesting point is that the MFI-UF of the pretreated seawater containing 3 μm particles slightly decreased. This could be explained by small foulants, such as nano-colloids and organic matter, which are filtered by the cake layer of larger particles formed on the membrane surface during the MFI measurements, preventing the small foulants from clogging the membranes pores. Similar observations were reported previously by Park et al. [26].

The SDI and/or MFI-MF are commonly used as a guideline for the selection of proper pretreatment to successfully operate the SWRO desalination process. The fouling potential of colloidal foulants smaller than the pore size of the MF membrane (0.45 μm), however, could not be precisely predicted by the SDI and/or MFI-MF. Therefore, it is expected that the flux decline caused by the nano-colloidal foulants could be predicted better by MFI-UF than by the SDI and/or MFI-MF.

### 3.1.2. Correlation between fouling indices and RO flux decline rate with respect to the size of nano-colloids

The fouling potentials evaluated by the SDI, MFI-MF and MFI-UF (see Fig. 3) and the flux decline rate \((1 - J/J_0)\) obtained after 1000 min of RO fouling runs were correlated with respect to the size of colloidal foulants, as presented in Fig. 4. It was clearly demonstrated that SDI and MFI-MF were not suitable to predict membrane fouling caused by nano-colloidal foulants because they did not show any correlations to reflect the variation of nano-colloidal sizes.

The MFI is defined by the slope of \(t/V\) vs. \(V\) under constant pressure filtration as follows [27]:

\[
MFI = \frac{\mu l}{2 \Delta P A t^2}
\]

(1)

where \(\mu\) is the solution viscosity, \(I\) is the fouling index, \(\Delta P\) is the applied pressure, and \(A\) is the membrane surface area. The fouling index, \(I\), is the product of specific cake resistance (\(\alpha\)) and colloidal concentration (\(C_c\)).

\[I = \alpha \times C_c\]

(2)

The specific cake resistance (\(\alpha\)) can be further related to the particle radius (\(a_p\)) via Kozeny–Carman equation:

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

(3)

Therefore, the MFI is inversely proportional to the square of particle size according to Eqs. (1)–(3). As the size of colloidal foulants increased, the MFI-UF values decreased, as shown in Fig. 4(c), although they were not exactly inversely related to the square of particle size.

However, the fouling potentials predicted by the MFI-UF did not correlate well with actual flux decline rates observed in the RO experiments. The more severe fouling was observed with increasing nano-colloidal size from 28 nm to 164 nm, which was opposite to MFI-UF measurements. This discrepancy existed since RO fouling experiments were conducted in the crossflow mode, while the MFI-UF measurements were performed in the dead-end mode. The amount of colloidal particles deposited on the membrane surface during crossflow filtration was affected by hydrodynamic shear force as well as Brownian diffusion [12,28]. The flux reduction was lesser as the size of nano-colloids

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**Table 2**

<table>
<thead>
<tr>
<th>Fouling indices</th>
<th>Membrane characteristics</th>
<th>Operating conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>SDI &amp; MFI-MF</td>
<td>0.45 μm, HAWP, millipore</td>
<td>2.07 bar, 20 ± 1 °C</td>
</tr>
<tr>
<td>MFI-UF</td>
<td>100 kDa, PLHK, millipore</td>
<td>12.4 bar, 20 ± 1 °C</td>
</tr>
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**Fig. 2.** Schematic diagram of a lab-scale RO membrane filtration and MFI-NFCRS measurement system. In crossflow RO experiments, the retentate water was recycled back to the feed tank after passing through the membrane cell by opening valve 1. In MFI-NFCRS, the measurements were performed at dead-end filtration by closing valve 1 using nanofiltration membranes.
decreased due to Brownian diffusion, while the flux declined less for larger particles as their size increased due to hydrodynamic effects [29]. Therefore, in order to elucidate complex colloidal fouling mechanisms, a more systematic theoretical and experimental approach was developed for SWRO desalination in the following sections. As a first step, a novel method, based on new MFI measurement technique, was developed to experimentally determine the specific cake resistance of colloidal foulants without any corrections.

3.2. Development of cake resistance simulator-modified fouling index nanofiltration

The precise appraisal of colloidal fouling potentials in SWRO desalination begins with accurate determination of specific cake resistance. In this study, the specific cake resistance of colloidal fouling layer was experimentally measured by cake resistance simulator-modified fouling index nanofiltration (MFI-NFCRS) which did not require any adjustments for the differences in applied pressure and solution environments of SWRO process.

3.2.1. Concept of MFI-NFCRS

The cake resistances ($\alpha$) applied to RO process were determined by MFI measurements conducted at low pressure (0–3 bar) using MF, UF, and NF membranes in previous studies [21,23,24]. However, the cake layers formed during the MFI measurements are different from those formed in SWRO process due to the differences in operation conditions such as operating pressure and salt concentration. Therefore, the correction factors were used to obtain $\alpha$ values for SWRO process from MFI measurements. In this study, the specific cake resistance ($\alpha_{\text{ro}}$) was determined by MFI-NFCRS which was measured by NF dead-end filtration....

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**Fig. 3.** Effect of particle sizes on fouling indices using pretreated seawater spiked with various colloids: (a) SDI, (b) MFI-MF and (c) MFI-UF. Concentration of spiked particles and nano-colloids was 7.5 mg/L.

**Fig. 4.** The correlations between fouling indices and RO flux decline rate with respect to particle size: (a) SDI, (b) MFI-MF and (c) MFI-UF.
under the same operating pressure and salt concentration as those in SWRO experiments.

In the early stage of NF dead-end filtration, the permeate salt concentration ($C_p$) is lower than the salt concentration of feed solution ($C_f$) as shown in Fig. 5. Due to salt retention by NF membrane, the retained salt concentration at the membrane surface ($C_m$) continues to increase and thus, as a result, the permeate salt concentration ($C_p$) also increases, until the equilibrium is established at which $C_p$ becomes the same as $C_f$. As discussed, the observed salt rejection of the NF dead-end experiments became almost zero after the permeate volume was more than 500 mL (Fig. 6), when the salt concentration of permeate ($C_p$) increased up to be equal or similar to that of feed water ($C_f$). After the equilibrium was reached, it could be assumed that the osmotic pressure on the membrane did not continue to increase further. The difference of salt concentration ($C_m - C_f$) calculated from the osmotic pressure ($\Delta \pi = 21.4$ bar) was about 0.5 M and thus, $C_m$ was about 1–1.1 M which was similar to the $C_m$ calculated from CEOP (39–42 bar) in SWRO experiments. $C_m$ can be controlled by choosing the NF membrane with suitable salt rejection because $C_m$ depends on the salt rejection of the NF membrane. It could be assumed that the resistances of the cake layer formed on the NF membrane were similar to those of the cake layer formed in SWRO desalination, because the MFI-NFCRS were measured under the similar conditions (i.e., operating pressure and TDS conditions).

### 3.2.2. Specific cake resistance ($\alpha$) measured by MFI-NFCRS

A cake layer formed on the membrane surface during SWRO desalination provides an additional trans-cake hydraulic pressure ($\Delta P_{cc}$) and an enhanced osmotic pressure drop ($\Delta \pi^*$), and thus the pressure drop across the membrane ($\Delta P_m$) can be described by the following equation [22]:

$$\Delta P_m = \Delta P - \Delta \pi^* - \Delta P_{cc}$$

(4)

where $\Delta P$ is the applied pressure. The pressure drop in the cake layer is related to the specific cake resistance ($\alpha_{ro}$), where the subscript $ro$ refers to the RO desalination process.

$$\Delta P_{cc} = J \mu R_{cc} = J M_{cc}$$

(5)

Here, $J$ is the permeate flux, $R_{cc}$ is the cake layer resistance, and $m_{cc}$ is the cake mass accumulated on the membrane per unit membrane area.

In general, the specific cake resistance can be determined through the following empirical relationship [21]:

$$\alpha = \alpha_0 \times \Delta P^\omega$$

(6)

where $\omega$ is the compressibility of the cake, and $\alpha_0$ is a constant. Eq. (6) then becomes

$$\frac{\alpha_{ro}}{\alpha_{MFI-UF}} = \left( \frac{\Delta P_{ro}}{\Delta P_{MFI-UF}} \right)^\omega$$

(7)

where $\Delta P_{ro}$ is the operating pressure of the MFI-UF measurements, $\Delta P_{MFI-UF}$ is the operating pressure of the SWRO desalination process, and $\alpha_{MFI-UF}$ is calculated from the MFI-UF measurements using Eq. (2).

In this study, the specific cake resistance ($\alpha_{ro}$) was determined using Eq. (2) and the MFI-NFCRS evaluated by NF dead-end filtration. The cake porosity ($\varepsilon$) was also calculated from specific cake resistance ($\alpha$) via Kozeny–Carman equation. The results are summarized in Table 3. As shown, specific cake resistance increased with decreasing the size of nano-colloids from 28 to 164 nm. The cake porosity, on the other hand, increased as nano-colloids became smaller. Lastly, the compressibility coefficients calculated using Eq. (7) were small (i.e., 0.14) compared to the values reported (0.5–1) in the previous studies [21].

### 3.3. Elucidation of nano-colloidal fouling mechanisms in SWRO desalination

The flux decline caused by colloidal fouling at the low TDS conditions is mainly attributed to the cake resistance of a colloidal layer. The formation of colloidal fouling layer in SWRO process (i.e., high TDS condition), on the other hand, results in not only additional hydraulic resistance but also cake enhanced osmotic pressure (CEOP), which often causes more severe flux decline compared to low TDS conditions [2,4,6]. In addition,
the crossflow operation in SWRO desalination could affect the deposition of nano-colloids on the membrane surface and, consequently, CEOP as well as cake resistance. To quantitatively evaluate colloidal fouling mechanisms, theoretical framework was developed and utilized to determine colloidal deposition and consequent CEOP, based on experimental data including MFI-NFCRS.

### 3.3.1. Theoretical framework for investigating colloidal fouling mechanisms

The flux decline caused by colloidal fouling in SWRO desalination is heavily dependent on the cake-enhanced osmotic pressure ($\Delta \pi^c$), which can be calculated using the CEOP fouling model [22]:

$$\Delta \pi^c = 2RT\epsilon \frac{R_m C_b}{\epsilon^c} \exp \left[ \frac{J_0}{k} \right] = 2RT\epsilon \frac{C_b}{\epsilon^c} CP^*$$  \hspace{1cm} (8)

where $R$ is the universal gas constant, $T$ is the absolute temperature, $\phi$ is the molar osmotic coefficient [30], $R_m$ is the observed salt rejection, $C_b$ is the bulk molar salt concentration, $J_0$ is the initial permeate flux, $CP^*$ is the cake-enhanced concentration polarization, and $k^*$ is the cake-hindered mass transfer coefficient described by:

$$k^* = \left[ \sqrt{\frac{f}{D^*}} - 1 \right] + \frac{1}{k^*}$$  \hspace{1cm} (9)

where $D$ is the bulk diffusion coefficient [31] and $D^*$ is the hindered diffusion coefficient [22], given by:

$$D^* = D_{ct} = \frac{4D_e}{1 - \ln \epsilon^2}$$  \hspace{1cm} (10)

where $\epsilon$ is the cake porosity, and $\tau$ is the tortuosity of the cake. The variable $k$ in Eq. (9) refers to mass transfer coefficient of the solute in bulk solution, and for laminar flow in a thin rectangular channel, $k$ is obtained by:

$$k = 1.47 \left( \frac{QD^2}{WL(H - \delta_c)^2} \right)^{1/3}$$  \hspace{1cm} (11)

where $Q$ is the volumetric feed flow rate, $W$ is the channel width, $L$ is the channel length, and $H$ is the channel height [22]. The cake layer thickness ($\delta_c$) is $m_c/p_0(1 - \epsilon)$ by definition. With Eqs. (9)-(11), Eq. (8) can be rewritten as Eq. (12):

$$\Delta \pi^c = 2RT\epsilon \frac{R_m C_b}{\epsilon^c} \exp \left[ J_0 \delta_c \left( \frac{1 - \ln \epsilon^2}{D_e} - \frac{1}{D} \right) + J_0 \delta_c \frac{1}{1.47 \left( \frac{QD^2}{WL(H - \delta_c)^2} \right)^{1/3}} \right]$$  \hspace{1cm} (12)

The cake mass per membrane area ($m_c$) in crossflow filtration can be defined as the product of the cake mass per area deposited on the membrane in dead-end filtration and the deposition factor ($\Omega$). Therefore, $m_c$ is described as:

$$m_c = \frac{VC_c}{A} \Delta \Omega = \sum J_c \Delta \Omega$$  \hspace{1cm} (13)

where $V$ is the permeate volume, $A$ is the membrane area, and $\Delta t$ is the filtration time. Using Eqs. (4), (5) and (12), the flux can be calculated from

$$J = \frac{\Delta P_m}{\mu R_m} = \frac{\Delta P - \Delta P_c - \Delta \pi^c}{\mu R_m}$$  \hspace{1cm} (14)

The trans-cake hydraulic pressure ($\Delta P_c$) and cake-enhanced osmotic pressure ($\Delta \pi^c$) depend on the cake mass per membrane area ($m_c$) as indicated in Eqs. (5) and (12). The $m_c$ could be calculated by fitting the slopes of the flux over time to allow experimental data to be identical to the calculations from the model (Eq. (14)). The deposition factor ($\Omega$) could be also determined from the Eq. (13).

### 3.3.2. Significance of CEOP in SWRO desalination

Fig. 7 shows the initial flux decline rates of 28, 91 and 164 nm colloidal suspensions containing 0.5 mg/L of HA at 35 g/L NaCl. The flux decline of feed solution containing 164 nm colloids was the most severe, while only a slight flux decline was found with 28 nm colloids. These fouling trends were consistent with those of the RO experiments with pretreated seawater containing the same colloids as discussed in the previous sections.

The deposition factors ($\Omega$) was first calculated by fitting the results of these RO experiments after 500 min of filtration to the calculations from the CEOP model. The deposition factors of 28, 91 and 164 nm colloids were 0.016, 0.099 and 0.167, respectively, when the cake porosities ($\epsilon$) calculated from MFI-NFCRS in Table 3 were used. Therefore, 16.8% of the 164 nm colloids was accumulated on the membrane surface in crossflow filtration compared with dead-end filtration, while only 1% of the 28 nm colloids deposited because fine colloids can easily diffuse back to the bulk solution due to Brownian diffusion.

Besides deposition factors, various model parameters, such as cake mass per membrane area, cake thickness, and cake-hindered mass transfer coefficient, were evaluated following the procedures described in the previous section, and are summarized in Table 4.
calculations, both pressure drop ($\Delta P_c$) caused by the hydraulic cake resistance and the cake-enhanced osmotic pressure ($\Delta \pi^*$) were estimated to elucidate colloidal fouling mechanism. Surprisingly, the hydraulic pressure drop by colloidal cake layer was very small compared to the CEOP. The hydraulic pressure drop by hydraulic cake resistance after 500 min was only 0.013 bar, while the CEOP ($\Delta \pi^*$) increased up to 2.89 bar. Thus, it could be concluded that the trans-membrane pressure drop resulting from colloidal fouling layer formation was mainly caused by the CEOP increase. This phenomenon was supported by a previous study that the contribution of CEOP to flux decline was more than 95% at TDS 35,000 ppm for particle size > 100 nm [29].

The significance of CEOP in SWRO desalination was further verified by comparing the flux decline between NF dead-end filtration and RO crossflow filtration using a 35 g/L NaCl solution with 164 nm colloids, as shown in Fig. 8. It should be noted that the effect of CEOP by colloidal deposition became negligible when NF dead-end filtration was operated at equilibrium as explained in Section 3.2.1. There was no significant flux decline in NF dead-end filtration even when higher colloidal concentration (i.e., 200 mg/L) was used. The flux decline in crossflow RO filtration, however, was much more pronounced, although only 16.7% of the colloids were deposited on the membrane surface. Therefore, it was demonstrated that the flux decline caused by the hydraulic cake resistance was almost negligible, as observed in the NF dead-end filtration, implying that the CEOP is the key mechanism for nanocolloidal fouling in the SWRO process.

4. Conclusions

Based on systematic understanding of the nano-colloidal fouling mechanisms in the SWRO process, the factors to be considered for a more accurate prediction of the fouling potential were investigated in this study. First, it was demonstrated that fouling indices such as SDI, MFI-MF and MFI-UF, widely employed in RO practices, were not adequate to reflect the complexity of colloidal fouling phenomenon (e.g., failure to predict the effect of particle size), requiring a more fundamental investigation on fouling mechanism of nano-colloids for SWRO process. The specific cake resistances of colloidal fouling layer formed on the SWRO membrane surfaces were evaluated experimentally through a novel method, cake resistance simulator-modified fouling index nanofiltration (MFI-NFCRS), which allowed measurements under the operating pressure and TDS condition similar to those employed in the practical SWRO process. Next, the colloidal deposition and resulting cake enhanced osmotic pressure (CEOP) were quantitatively estimated by fitting the RO experimental data to the calculations from the CEOP model. The results clearly revealed that flux decline observed in SWRO desalination was primarily contributed by the CEOP resulting from the formation of colloidal fouling layer. The methodology newly developed in this study including MFI-NFCRS provides more systematic experimental and theoretical approaches to achieve accurate evaluation of colloidal fouling potentials in the SWRO process.

**Nomenclature**

A  membrane area (m²)

$\alpha_p$  particle radius (m)

$C_{hi}$  bulk molar salt concentration (mol/L)

$C_c$  colloidal bulk concentration (kg/m³)

$C_m$  salt concentration at the membrane surface

CEOP  Cake-enhanced osmotic pressure (bar)

CP*  Cake-enhanced concentration polarization

$D$  diffusion coefficient (m²/s)

$D^*$  hindered diffusion coefficient (m²/s)

EDL  electrostatic double layer

H  channel height (m)

HA  Humic acid

$J$  Permeate flux (L m⁻² h⁻¹)

$J_0$  initial permeate flux (L m⁻² h⁻¹)

$k$  mass transfer coefficient (m/s)

$k^*$  cake-hindered mass transfer coefficient (m/s)

$L$  channel length (m)

$m_c$  cake mass per membrane area (kg/m²)

MFI-MF  Modified Fouling Index-Microfiltration (slL⁻²)

MFI-NF  Modified Fouling Index-Nanofiltration (slL⁻²)

MFI-NFCRS  Cake Resistance Simulator-Modified Fouling Index Nanofiltration (slL⁻²)

MFI-UF  Modified Fouling Index-Ultrafiltration (slL⁻²)

$\Delta P$  applied pressure (bar)

$\Delta P_c$  trans-cake hydraulic pressure (bar)

$\Delta P_{eff}$  effective pressure of the NF-MFI

$\Delta P_m$  pressure drop across the membrane (bar)

$\Delta P_{MFI-UF}$  operating pressure of the MFI-UF (bar)

$\Delta P_{RO}$  operating pressure in the RO experiments (bar)

$Q$  volumetric flowrate (m³/s)

$R$  gas constant (= 8.314 m³ Pa K⁻¹ mol⁻¹)

$R_c$  cake layer resistance (m⁻¹)

RO  reverse osmosis

$R_{obs}$  observed salt rejection

SDI  Silt Density Index

SWRO  seawater reverse osmosis

$t$  time (s)

$V$  permeate volume (m³)

$W$  channel width (m)

![Fig. 8. Comparison of flux decline rates between NF dead-end filtration and RO crossflow filtration using 164 nm colloids in 35 g/L NaCl solution.](image-url)
Greek letters
- \( \alpha \) specific cake resistance \((\text{m/kg})\)
- \( \alpha_{\text{MFI-UF}} \) specific cake resistance calculated from the MFI-UF \((\text{m/kg})\)
- \( \alpha_{\text{RO}} \) specific cake resistance calculated from the RO experiments \((\text{m/kg})\)
- \( \delta_c \) cake layer thickness \((\text{m})\)
- \( \varepsilon \) cake porosity
- \( \Delta \pi \) osmotic pressure
- \( \Delta \pi^* \) enhanced osmotic pressure drop \((\text{bar})\)
- \( \mu \) solution viscosity \((\text{bar} \cdot \text{s})\)
- \( \rho_p \) density of particles \((\text{kg/m}^3)\)
- \( \tau \) tortuosity of the cake
- \( \phi \) molar compressibility coefficient
- \( \omega \) compresibility factor
- \( \Omega \) deposition factor

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