Effects of tannic acid on membrane fouling and membrane cleaning in forward osmosis

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ABSTRACT

The fouling behavior during forward osmosis (FO) was investigated. Tannic acid was used as a model organic foulant for natural organic matter analysis since the main characteristics are similar, and calcium ions were added at different concentrations to explore the anti-pollution capability of FO membranes. The initial permeate flux and calcium ions strength were varied in different operating conditions to describe membrane fouling with membrane cleaning methods. The observed flux decline in FO changed dramatically with the type of foulant and the type of draw solution used to provide the osmotic driving force. Calcium ions aggravated membrane fouling and decreased transmembrane flux. Membrane cleaning methods included physical and physicochemical approaches, and there was no obvious difference among the typical cleaning methods (i.e., membrane flushing with different types of cleaning fluids at various crossflow velocities and backwashing with varying osmotic driving forces) with respect to flux recovery. Ultrasonic cleaning damaged the membrane structure and decreased permeate flux, and reverse diffusion of salt from the draw solution to the feed side accelerated after cleaning.

Key words | forward osmosis, membrane cleaning, membrane fouling, tannic acid

INTRODUCTION

Inadequate access to clean water and sanitation is one of the most pervasive problems afflicting people (Shannon et al. 2008). In the past several decades, the urgent need for pure water has promoted the development of seawater desalination and groundwater purification. However, because the conventional technologies, such as reverse osmosis (RO) and multistage flash evaporation, require high pressure and energy consumption and increasing costs (Burn et al. 2015; Subramani & Jacangelo 2015), researchers are exploring novel energy-efficient technologies. The purpose of water purification in water treatment plants is to remove micro-pollutants and natural organic matter from surface water to produce water of excellent quality. Nanofiltration (NF), often combined with ultrafiltration (UF), is frequently used in waterworks with membrane processes. However, during NF and UF, as well as RO, high pressure and energy costs are required, in addition to excellent salt rejection and removal efficiency of organic foulants in feed water, and the disposal of brine concentrate is a challenging problem. It is essential that researchers develop an ideal process to achieve high retention and low energy consumption.

The forward osmosis (FO) membrane process, which is an osmotically driven process without the need for applied pressure and is thus energy saving and economically feasible, has potential as a sustainable alternative to conventional pressure-driven membrane processes (Cath et al. 2006). In FO, water molecules in the feed solution (with low concentration and osmotic pressure, i.e., high water chemical potential) move across a semipermeable membrane under the influence of the osmotic driving force across the membrane from the draw solution (high concentration of one or several draw solutes with high osmotic pressure, i.e., low water chemical potential), while the solute or salt molecules in the draw solution are rejected by the membrane. The diluted draw solution can then be re-concentrated for recycling (Cath et al. 2006).

FO is advantageous in many fields compared to pressure-driven membrane processes, such as the low level of electrical energy required (McGinnis & Elimelech 2007) (mainly for pumping feed and draw solutions (She et al. 2016)), lower fouling potential (Mi & Elimelech 2010) and higher water recovery efficiency resulting in less brine discharge.
(Kravath & Davis 1975) without the requirement of draw solution separation. With the development of draw solution recycling and draw solute synthesis technologies, the cost may be reduced in respect of product water separating from diluted draw solution (Hoover et al. 2011; Ge et al. 2013). Therefore, due to its considerable strengths, the osmotically driven process has been used in many applications, for example, seawater and brackish water desalination (McCutcheon et al. 2006; Lutchmiah et al. 2014), wastewater reclamation (Cath et al. 2005), liquid food processing (Garcia-Castello et al. 2009; Yang et al. 2009), green power production (Klayson et al. 2013), and microalgae cell separation from source water (Zou et al. 2011).

Most of the studies of FO use an asymmetric semipermeable membrane with a dense active layer and a porous support layer (Cath et al. 2006). The presence of the internal concentration polarization (ICP) caused by foulants in the porous structure results in severe membrane fouling and flux decline (Tang et al. 2010), especially at high flux levels when the membrane process is performed under active-layer-facing-feed-solution mode, which is caused by internal clogging and the enhanced ICP effect in the support layer. Membrane fouling is influenced by chemical and physical aspects, such as permeation drag, shear forces and Ca$^{2+}$ binding effects (Mi & Elimelech 2008). Investigators have shown that the severe fouling at the active-layer-facing-draw-solution is related to the greater concentration of organic foulants and the Ca$^{2+}$ binding effect (McCutcheon & Elimelech 2006). Researchers have focused on membrane fouling and water flux decline during the FO membrane process to demonstrate the contamination mechanism, but research on membrane cleaning and flux recovery to describe the membrane fouling by dissolved organic matter (DOM) is limited.

Membrane fouling is often caused by inorganic and organic matter and biomass (Cath et al. 2006). In the studies of membrane fouling in FO, humic and nonhumic substances are often used as model DOM components to explore membrane contamination. To obtain sustainable treatment results in membrane-based systems, investigators have explored physical and chemical methods to achieve flux recovery (Li & Elimelech 2004; Mi & Elimelech 2010). The popular membrane processes, such as RO, UF and NF, use various chemical methods to achieve flux recovery, including acids, alkalis, metal chelating agents, surfactants and enzymes, and physical methods, including normal flushing, osmotic backwash and high-flow osmotic flushing (Achilli et al. 2009).

This study used commercial FO flat sheet membranes made of cellulose triacetate (CTA), which cannot be cleaned with strong acid, alkali or other aggressive chemicals. The objective of this study was to evaluate the effectiveness of several physical membrane cleaning methods in FO. In our previous studies (Wang et al. 2014, 2016), we chose tannic acid (TA) as a surrogate for DOM foulants and investigated the physical and chemical factors influencing the water flux and retention behavior in FO filtration. Fouling experiments were conducted at different concentrations of TA and draw solution. Flow flushing at normal and high rates, osmotic backwashing under different transmembrane pressures and ultrasonic washing were investigated to achieve flux recovery of fouled FO membranes.

### MATERIALS AND METHODS

#### FO membrane

A commercial FO membrane obtained from Hydration Technology, Inc. (HTI, USA) was used in a benchscale FO setup. This flat sheet FO membrane is composed of CTA. The membrane has an asymmetric structure with an active layer, which is mechanically supported by embedded polyester mesh and a porous support layer. The thickness of the membrane is approximately 30–50 μm according to the relative location between the dense surface and the embedded polyester mesh side; the other membrane characteristics have been reported elsewhere (Wang et al. 2014). Membrane samples were soaked in deionized (DI) water at 4 °C for at least 24 hours to remove organic solvent from the membrane surface and to become hydrated before each experiment. A new piece of FO membrane was used for each fouling test.

#### Feed and draw solutions

DI water, with an electrical resistivity of 15 MΩ-cm, was used to prepare all working solutions except the TA stock solution. TA was used as a model foulant to prepare the feed solution. TA is a polyphenolic compound with a molecular weight (MW) distribution of 500–3,000 g·mol$^{-1}$ and strong biological and pharmacological activities that is representative of a low molecular mass. The average molecular mass of TA is 1,701 g·mol$^{-1}$ with the chemical formula C$_{76}$H$_{52}$O$_{46}$ provided by the supplier (Sinopharm Chemical Reagent Co., Ltd, China). TA stock solution 1 g C·L$^{-1}$ was prepared more than 12 hours before the experiment, and was stored in the dark at 4 °C and had a maximum shelf-life of a month. The feed solutions were...
diluted from the stored bulk with DI water. Calcium chloride (CaCl₂, purchased from Sinopharm Chemical Reagent Co., Ltd, China) was used as a metal ion contaminant in the feed solution. Sodium chloride (NaCl, purchased from Sinopharm Chemical Reagent Co., Ltd, China) acted as a draw solute to provide higher osmotic pressure than that of the other side of the membrane.

The feed and draw solutions were prepared 12 hours before each test at room temperature. All the chemical agents mentioned above were analytically pure.

**Bench-scale FO setup**

The FO fouling and cleaning tests were conducted with a bench-scale cross flow FO membrane cell (C10-T, Nitto Denko, Japan). The membrane unit had symmetric, double channels and plastic mesh on both sides of the FO membrane to support the membrane, improve fluid turbulence and enable simultaneous flow of the feed and draw solutions. The channel dimensions of the cell were 180 mm × 46 mm × 1.25 mm (length × width × thickness), providing an effective membrane coupon area of 60 cm². Figure 1 shows a schematic diagram of the bench-scale FO system used in the tests. Two variable-speed gear pumps (Micropump Inc., USA) and a constant-speed peristaltic pump (KPP-B, Kamoer (Shanghai) Fluid Technology Co., China) were used to pump particular flows. The two gear pumps provided concurrent crossflow of the feed and draw solutions at 1,000 mL·min⁻¹ (29.2 cm·s⁻¹) in the fouling tests and 1,000 mL·min⁻¹ (29.2 cm·s⁻¹) or 2,000 mL·min⁻¹ (58.4 cm·s⁻¹) in the cleaning tests. The peristaltic pump, under intermittent operation, maintained the concentration of the draw solution. All three pumps were driven by a control system using a programmable logic controller (PLC) to set the operating parameters.

The feed solution tank was placed on a digital balance (UW8200s, Shimadzu, Japan), and the weight change was recorded by a computer logging system at regular time intervals to reveal the permeate flux across the membrane. A mechanical stirrer was placed on the feed side to mix the solution evenly, and the draw solution tank was set on a magnetic stirrer. Salt reverse diffusion was evaluated based on conductivity changes in the feed solution using a conductivity meter. The temperature of the entire system was maintained at 22 ± 0.2 °C by a water bath (SC100-A10, Thermal Scientific Haake, USA) with plastic heat exchanger coils submerged in the bath.

**FO membrane fouling tests**

The FO membrane fouling tests included the following steps. The feed and draw solutions (FW and DS for short) were prepared ∼12 hours before each test. A new membrane piece was placed in the membrane cell with two plastic meshes sandwiched on both sides and a rubber ring to fix them. Next, the new membrane piece was equilibrated with feed solution of the background electrolyte and non-foulant and the draw solution (NaCl, 2 M or 4 M for the purification and cleaning tests) for 20–30 min until the water flux was stable prior to the membrane fouling process in the active layer facing draw solution (AL-facing-DS) orientation. In the previous studies (Zhao et al. 2014; Wang et al. 2014) of AL-facing-FW and AL-facing-DS orientations, the membrane flux under AL-facing-DS orientation was significantly higher than under AL-facing-FW orientation. The process with higher water flux and lower solute reverse diffusion, which indicates that the membrane has a better selectivity and effectiveness, is most likely to be chosen. In this paper, we chose AL-facing-DS orientation for FO filtration tests with the higher water flux value. At this stage, feed solution with 10 mg·L⁻¹ TA (at 10 mM ionic strength adjusted using NaCl and pH 5.8 ± 0.1) was introduced to the feed tank, and the following fouling test was conducted for 5 hours at 22 ± 0.2 °C. The PLC system regulated and controlled two gear pumps to run the filtration process and the peristaltic pump to maintain the DS concentration, while a computer recorded the permeate flux according to weight measurements.
During the FO filtration process, the osmotic driving force for permeate flux continuously decreased due to the concentration of the feed solution and the ICP. Thus, the flux decline during the fouling tests was caused not only by foulant deposition but by changing the osmotic driving force.

Baseline tests were conducted to eliminate the impact of decreasing the transmembrane drag force on the flux decline. The feed solution of each baseline test was identical to the corresponding fouling test, which in each baseline test, the DS was same as the corresponding fouling test and the FW did have the same properties except for the foulant. These parameters are presented in Table 1. The flux decline curve observed from the baseline test was normalized by the flux decline in the fouling experiment. The normalization flux was the ratio of the real fouling flux ($J_{\text{fouling}}$) to its corresponding baseline flux ($J_{\text{baseline}}$).

Membrane cleaning tests

After the fouling procedure, the system was thoroughly rinsed with DI water for at least 3 min. Then, the clean step of the FO membrane system was performed at different crossflow velocities (29.2 cm·s$^{-1}$ or 58.4 cm·s$^{-1}$), transmembrane osmotic pressures (provided by 2 M or 4 M NaCl solution), rinsing times (15 min or 2 hours), and membrane orientations (AL-facing-FW or AL-facing-DS). These parameters are presented in Table 1. The flux recovery test was conducted immediately after membrane cleaning for at least 30 min with DI water as the feed solution and the corresponding operating condition of the draw solution as the concentrated NaCl solution.

### ANALYTICAL METHODS

**Determination of foulant removal, retention and adsorption**

For both fouling and cleaning tests, the removal, retention and adsorption were measured based on the total organic carbon (TOC) value of samples from the feed and draw solutions at specific time intervals.

The actual permeate foulant concentration ($C_{p(t)}$) and the foulant removal rate were calculated as in our previous study (Wang et al. 2014):

$$C_{p(t)} = \frac{C_{d(t)}V_{d(t)} - C_{d(t-1)}V_{d(t-1)}}{V_{p(t)}}$$

$$R_m = \left(1 - \frac{C_{p(t)}}{C_{f(t)}}\right) \times 100\%$$

where $R_m$ is removal for short; $C_{d(t)}$ and $C_{d(t-1)}$ are the concentrations of the foulant in the draw solution at time points $t$ and $(t-1)$, respectively; $C_{f(t)}$ is the concentration of the foulant in the feed solution; and $V_{d(t)}$ and $V_{d(t-1)}$ are the volumes of the draw solution at time $t$ and $(t-1)$, respectively.

$$R_t = \frac{C_{f(t)}V_{f(t)}}{C_{f(0)}V_{f(0)}} \times 100\%$$

where $R_t$ is retention for short, $C_{f(0)}$ is the initial foulant concentration in the feed solution, $V_{f(0)}$ is the initial volume of the feed solution and $V_{f(t)}$ is the volume at time $t$.

$$A_d = \frac{C_{f(0)}V_{f(0)} - C_{f(t)}V_{f(t)} - (C_{d(t)}V_{d(t)} - C_{d(t-1)}V_{d(t-1)})}{M}$$

### Table 1 | Parameters in three different tests: baseline tests, fouling tests, and cleaning tests

<table>
<thead>
<tr>
<th>Parameters in three different tests: baseline tests, fouling tests, and cleaning tests</th>
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<tr>
<td><strong>Baseline tests</strong></td>
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<tr>
<td>Feed solution (FW)</td>
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<td>Draw solution (DS)</td>
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<td>Osmosis pressure (bar)</td>
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<td>Membrane orientation</td>
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<td>pH</td>
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<td>Crossflow velocity</td>
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<td><strong>Fouling tests</strong></td>
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<td>Feed solution (FW)</td>
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where Ad is adsorption for short, and M is the effective area of FO membrane.

**Other analysis**

The concentration of TA was determined using a TOC analyzer (TOC-L CSH, Shimadzu, Japan) and an ultraviolet (UV) spectrophotometer (DR5000, Hach, USA) for UV absorbance measurement. SUVA is the ratio of UV254 to DOC (dissolved organic carbon) and reflects the content of unsaturated carbon–carbon bonds of the foulant in the DOC.

The MW distribution of the foulants was analyzed by a high-performance size exclusion chromatography (HPSEC, Waters Corporation, USA) with ultraviolet absorbance (UVA, Waters Corporation, USA) and on-line total organic carbon (TOC, GE Corporation, USA).

**RESULTS AND DISCUSSION**

The fraction characteristics of TA were analyzed in our previous studies (Wang et al. 2014, 2016), which proved that TA has a similar MW distribution and percentage of hydrophilic/hydrophobic substances as natural dissolved organic matter (natural DOM), so the former is approximately representative of the latter.

**TA purification tests**

Fouling experiments with TA were performed to elucidate the FO fouling behavior under different conditions. The concentration of the draw solute was kept constant to maintain the osmotic pressure. The initial ionic strength of the feed solution was adjusted using NaCl to simulate the background value of feed water. The ionic strength and concentration were held constant to maintain the initial flux in each purification test to compare the effect of varying cleaning methods. The fouling time was 5 hours, and the basic foulant concentration used to observe the fouling and flux recovery behavior was 10 mg·L⁻¹.

**Effects of the initial flux on membrane fouling**

The effect of the DS concentration on TA purification was studied using the same initial feed solution and different osmotic pressures of DS in the AL-facing-DS orientation. The osmotic pressure is related to the draw solute concentration. Figure 2(a) shows the flux decline for the same foulant (TA: 10 mg/L) and two draw solution concentrations: 2 M and 4 M. The higher draw solution concentration provided higher osmotic pressure, leading to more severe water flux decline during filtration (Cath et al. 2014, 2016).
2005; McCutcheon & Elimelech 2006; Yang et al. 2009; Subramani & Jacangelo 2015), which showed similar effect trends with our previous study at higher crossflow velocity (Wang et al. 2014). As the osmotic pressure increased, the initial flux of the baseline increased from 33.6 L/(m²·hour) to 46 L/(m²·hour), higher flux loss was observed and the 4 M baseline curve dropped dramatically. During the fouling process, the increasing DS concentration resulted in more severe membrane fouling owing to ICP within the membrane support layer (Cath et al. 2005; Yang et al. 2009). The ICP also affected the solute flux by reducing its driving force, which is called the effective concentration difference across the dense rejection layer (Yang et al. 2009). The decrease in baseline flux during the filtration process at 4 M was more severe for the higher initial flux level. A higher osmotic pressure across the membrane led to transmembrane flux, as shown in Figure 2(a). Figure 2(b) shows that the normalized flux (Fouling/Baseline) decreased slightly at constant DS osmotic pressure. Additionally, there was no significant difference between the 2 M and 4 M normalized curves. The trend of normalized water flux at the two DS concentrations indicated that the FO membrane fouling by TA produced no additional flux loss compared with the corresponding baseline tests. The constant DS osmotic pressure largely offset the effect of DS dilution and ICP on the additional flux loss during fouling when comparing the fouling curve to the corresponding baseline and compared with previous studies (Mi & Elimelech 2008; Wang et al. 2014). At DS concentrations of 2 M/4 M, the ICP effect on the water flux decline was almost excluded, in other words, ICP was the main cause of the flux decline during low TA concentration membrane fouling in the AL-facing-DS orientation.

According to the retention and adsorption curves in Figure 2(c), the DS retention was always greater than 90%, as expected, similar to the observations of several previous investigators (McCutcheon & Elimelech 2006; Garciaicastello et al. 2009; Tang et al. 2010; Subramani & Jacangelo 2015). The FO membrane could effectively reject TA because the rejection of TA by the FO process was not influenced by the DS concentration in the AL-facing-DS orientation. The adsorption values of TA increased with decreased retention values during FO filtration, but the changes occurred within a small range compared with the bulk concentration of TA in the feed solution. The FO membrane exhibited good performance, with high foulant rejection and low adsorption. The membrane adsorption values increased with increasing initial flux. The contamination during FO filtration of TA was related to hydrodynamic interactions. The hydrodynamic forces between the membrane and foulant include the permeation drag force caused by convective flow toward the membrane and shear force caused by crossflow parallel to the membrane (Garciaicastello et al. 2009). A higher transmembrane differential osmotic pressure leads to higher permeation drag force due to the higher concentration of the DS solution. In the AL-facing-DS mode, TA molecules were adsorbed within the porous support layer where the shear force was precluded by the vanished crossflow to drive the foulant away from the membrane. So, the foulant was more likely adsorbed by the FO membrane at 4 M DS that at 2 M DS and the retention values were slightly reduced. Based on the removal efficiency of the FO membrane and the negligible foulant loss in the loop system, the vast majority of TA loss in the feed solution was due to absorption on the membrane surface or in the porous support layer of the FO membrane.

Effects of calcium ions

To investigate the effect of calcium ions (Ca²⁺) on FO membrane fouling, Ca²⁺ was added to the feed solution. Compared with the membrane fouling curves with only TA, the water flux rapidly declined when Ca²⁺ was added, as shown in Figure 3(a). In the baseline tests, calcium ions had no obvious effect on the flux decline when isolated from the mix. The flux decline curve with Ca²⁺ showed slightly lower levels of initial flux and water flux across the membrane during FO filtration. In the fouling tests, the difference was apparent throughout the FO process.

Figure 3(b) shows the normalized flux of Ca²⁺ added to FW, revealing more serious membrane fouling. In the presence of Ca²⁺, the fouling became more severe, and the flux reduction dropped from 85% to 70%.

As the previous results showed, the effect of Ca²⁺ on the removal of TA during FO was minor. However, the level of adsorption of foulant with Ca²⁺ added to the FO membrane was lower than that without Ca²⁺, and the retention values were higher, as shown in Figure 3(c).

The effect of calcium ions on membrane fouling has been extensively studied in RO and NF membranes, demonstrating that calcium ions can bind with organic matter through their acidic functional groups via complex formation (Hong & Elimelech 1997; Garciaicastello et al. 2009; Zou et al. 2011), consequently resulting in charge loss of the foulants and increased levels of foulant adsorption onto the membrane. The charge loss (or charge neutralization) and intermolecular binding forces of TA by Ca²⁺ were conducive to membrane adsorption of foulants. In Figure 3(c), the more severe the initial water flux decline,
the lower the permeation force drag, which was most likely to hinder the amount of TA adsorbed onto the FO membrane in our study. Additionally, the calcium bonding with TA might be attributed to the formation of a dense fouling layer of small coiled TA macromolecules in or on the porous support layer of the FO membrane, causing more severe flux decline but less foulant retention and adsorption.

**Membrane cleaning tests**

Both physical and chemical methods are used to clean membranes. The FO membrane is composed of CTA and is unable to withstand strong acid or alkali treatment. Therefore, gentle membrane cleaning methods with mild detergents are the prime option. Physical membrane cleaning methods have been used to restore fouling membrane permeation flux in osmotically driven membrane processes (Arkhangelsky et al. 2012; Subramani & Jacangelo 2015). Physical membrane cleaning methods include membrane surface flushing and backwashing at varying crossflow rates and osmotic transmembrane pressures. Three types of membrane cleaning methods were performed to wash the FO membranes after the fouling tests in the presence and absence of calcium ions with TA (10 mg/L). The system temperature of each process was controlled at 22 ± 0.2°C, and the ionic strength of the FW was adjusted to 10 mM using NaCl. The DS was 2 M NaCl solution controlled by the feedback system of the PLC. The cleaning tests were conducted for 15 min or 2 hour after a 5 hour fouling process. The cleaned membrane was subjected to the membrane flux recovery procedure, which used DI water as the FW and NaCl solution (2 M/4 M, the same concentration as the corresponding fouling test) as the DS in AL-facing-DS orientation for at least 30 min, to determine the pure water permeability of the membrane after cleaning (shown in Figure 4). The water flux recovery of each method revealed the extent of foulant deposition on the FO membrane.

**Effect of membrane surface flushing on flux recovery**

Membrane surface flushing tests were performed at two crossflow velocities (29.2 cm/s or 1,000 mL/min and 58.4 cm/s or 2,000 mL/min) and with two washing liquids (DI and NaCl solution at 15 mM). In the membrane fouling tests with TA (initial concentration: 10 mg/L) in the feed solution, the water flux decreased approximately 40% compared with baseline test, as shown in Figure 4. The membrane surface flushing duration with only DI had no significant effect on the flux recovery but restored the water flux from 40% to 80%. When the flushing rate increased to 58 cm/s (i.e., 2,000 mL/min), the water recovery was almost the same as the flux recovery at the lower crossflow velocity. The crossflow rate and duration had no

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**Figure 3** | Effects of calcium ions on membrane fouling: (a) flux decline in fouling test (water flux versus filtration time); (b) normalized flux $J_{	ext{fouling}}/J_{	ext{baseline}}$ decline (normalized flux versus filtration time); (c) membrane retention and adsorption (retention and adsorption values versus filtration time).
obvious effect on the fouling reversibility of FO membranes in the AL-facing-DS orientation with DI flushing. When NaCl was added to the washing liquid, the flux recovery was slightly less than the flux recovery of the former flushing procedure with DI. Consequently, both pure DI and diluted salt solutions resulted in approximately 80% flux recovery, indicating that the solution chemistry or ionic strength did not significantly affect the membrane cleaning efficiency.

The four lefthand columns in Figure 5 show the membrane fouling and flux recovery after membrane surface flushing with TA (10 mg/L) and Ca\(^{2+}\) (1 mM) in the feed solution. The changes in crossflow rates and cleaning liquid produced no significant differences between the four conditions, and the normalized flux was restored to approximately 72%. Bearing in mind the calcium binding between calcium ions and the acidic functional groups of the organic foulant molecules, surface flushing provided the sheer force for foulant removal. However, the flux recovery (80% or 72%) in AL-facing-DS mode was less than the FO cleaning efficiency (up to 98%) in AL-facing-FW mode (Subramani & Jacangelo 2015), which suggested that a certain proportion of the flux decline was attributed to internal fouling caused by TA (Li & Elimelech 2004). In the PRO operation (i.e., AL-facing-DS mode), the sheer force decreased within the porous support layer and the surface flush became ineffective against internal fouling (Yip & Elimelech 2013).

**Effect of backwashing on flux recovery**

Osmotic backwashing is a common fouled membrane cleaning method in FO that was originally developed by the desalination industry for RO to remove membrane fouling (Sagiv & Semiat 2005; Sagiv et al. 2008; Kim 2014). During osmotic backwashing, the cleaning liquid creates a negative water flux that breaks up the foulant layer on the membrane surface, flushing out the internal foulants in the porous support layer of the fouled membrane. A 2 M NaCl solution provided the optimal osmotic pressure for membrane backwashing after fouling tests with feed solution that included only TA, and the flux recovery increased to 90%, higher than that after membrane flushing with DI water and diluted NaCl solution, as shown in Figure 5. A transmembrane osmotic drag force similar to that in the corresponding operation conditions of the fouling test favored flux recovery during the backwashing procedure. In contrast, as the transmembrane osmotic pressure increased, the flux recovery values showed no significant difference with TA and Ca\(^{2+}\) in the feed solution (up to 76%, shown in Figure 6, lower than the efficiency of the membrane flux recovery after backwashing fouled by only TA). The lower efficiency of osmotic backwashing at 4 M for water flux recovery could be due to the accumulation of salt within the foulant layer during cleaning, which decreased the effective osmotic driving force (Linares et al. 2015). Compared to the osmotic backwashing process of 58 cm/s-15 min-2 M-FO mode, the process of
29 cm/s-15 min-4 M-FO mode showed higher flux recovery, which may be caused by the higher crossflow rate increasing the sheer force and decreasing the accumulation of salt and foulant layer.

**Effect of the ultrasonic cleaning method on flux recovery**

The normalized flux after ultrasonic processing shown in Figures 5 and 6 was decreased, which revealed the ineffectiveness of this cleaning approach. Considering the physical and chemical ultrasound reactions and that the salt rejection of the FO membrane declined rapidly, as observed in the membrane flux recovery process after cleaning, the FO membrane structure may be damaged, especially the dense active layer (Cath et al. 2006; McCutcheon & Elimelech 2006; Garcia-Castello et al. 2009).

**Membrane fouling during FO in AL-facing-DS orientation**

FO membranes can purify TA and achieve flux recovery through physical cleaning. The FO membrane flux declined to 60% (50% when fouled by a mixture of TA and calcium ions) when fouled by TA at low concentration and recovered to 70-90% by various cleaning methods. Differences among the decreased flux decline and the recovery indicated that TA (alone or together with calcium ions) may be found at different locations during the FO membrane fouling process in the AL-facing-DS orientation. Figure 7 illustrates the possible locations of foulants during membrane fouling and after cleaning. In the fouling tests with only TA, molecules or molecular clusters of relatively large size that can hardly
enter the porous structure deposited onto the outer surface of the support layer, which can be described as external fouling. The foulant layer on the outer surface of the support layer was loose and was easily flushed out by physical scrubbing (shown in Figure 7(a) and 7(c)). In contrast, the molecules of relatively small size can enter the porous support layer by the osmotic drag force, which can be described as internal fouling. The small foulants were adsorbed in the porous structure (i.e., on the pore walls of the support layer or the back side of the active layer), and those that were loosely retained could be flushed out by the reverse osmotic drag force (Figure 5). However, increasing the osmotic drag force or crossflow rate had no significant effect on the flux recovery for these fouling conditions. It may be caused by some of the foulants being adsorbed in the support layer and retained by the porous structure and by the more severe ICP caused by the higher concentration of draw solution, which weakened solute diffusion (McCutcheon & Elimelech 2006; Thorsen & Holt 2009; Tang et al. 2010).

The flux decreased more severely in fouling tests with a mixture of TA and calcium ions than when only organic foulant was used (shown in Figure 3). Additionally, the calcium bonding interactions caused mixtures of foulants, including both large and small molecular clusters. Calcium bonding with TA, which could lead to larger clusters, may be attributed to the foulant layer on the outer surface of the membrane. The bonding of smaller organic molecules with calcium ions absorbed into the support layer may result in more severe fouling due to the more serious flux decline and minimal flux recovery after cleaning compared with a membrane fouled with only TA (Figures 5 and 6). Larger foulants that could not be adsorbed into the porous structure formed a loose fouling layer on the membrane surface and were easily removed by water flushing, similar to the results of membrane fouling with only TA. The difference in the flux recovery results after the cleaning method of 29 cm/s-15 min-2 M-FO mode indicated that the foulant mixture was more tightly linked to the porous structure than the single foulants under the same reverse osmotic drag force. Additionally, as shown in Figure 6, the linkage was so strong that the reverse osmotic drag force barely improved flux recovery during membrane cleaning.

**CONCLUSIONS**

This study investigated the effects of TA and mixed foulants of TA and calcium ions on membrane fouling using membrane fouling tests and physical cleaning methods for foulant removal and flux recovery after membrane cleaning. The experimental results demonstrated the effectiveness of purification during FO for TA removal. In addition, the flux recovery after physical cleaning could exceed 75% in AL-facing-DS mode (i.e., PRO mode). The physical cleaning method provided sheer force on the surface and osmotic drag force across the membrane. Furthermore, the fouling and cleaning mechanism shifted from external fouling with foulant accumulation on the membrane surface to internal fouling with foulant trapped in the porous support layer.

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