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Impact of feed ionic concentration on colloidal and organic fouling of osmotically driven membrane process

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ABSTRACT

The impact of feed ionic concentration in the presence of organic and colloidal foulant on osmotically driven membrane processes (ODMPs) was demonstrated. The normalized flux of ODMPs was significantly decresed in both DI and 10 mM NaCl feed solution when the feed solution contained colloidal particles as foulants due to the deposition of colloidal particles on the membrane surface. The deposited colloidal particles strongly promoted cake-enhanced osmotic pressure near the surface of the membrane. In contrast, the normalized flux of ODMPs was slightly increased when humic acids (HA) were added as the organic foulant into the feed solution. The attachment of HA molecules changed the membrane surface conducting it more hydrophilic, and induced a stronger diffusion of water molecules into the membrane active layer. As a result, both the increased feed ionic strength and deposited colloidal fouling did not significantly alter the reversal salt selectivity of the ODMPs, while the reversal salt selectivity was significantly incresed after the addition of HA molecules to the feed solution because the HA molecules changed the properties of the membrane surface.

Keywords: Osmotically driven membrane processes; Organic matter; Colloidal particles

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1. Introduction

Osmotically driven membrane processes (ODMPs) can be simply defined as the movement of water molecules across a semipermeable membrane from a lower concentration to a higher concentration due to a difference in osmotic pressure across the membrane [1]. In ODMPs, a semipermeable membrane allows water molecules and a small amount of salt to permeate through while most of the solute or salt molecules are rejected [2,3]. There are many advantages to ODMPs in water treatment and wastewater treatment processes: they can be operated at low or no hydraulic pressures, high rejection of a wide range of contaminants in water or wastewater [3–5], and lower membrane fouling

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propensity compared to pressure-driven membrane processes [3,6–9]. Similar to other filtration systems, ODMP performance is still impeded by the persistent problem of membrane fouling, and there is a lack of a full systematic and mechanistic understanding of the fouling behavior in ODMPs [10]. It is well known that there are many determinants that can significantly affect the ODMPs performance such as the membrane surface and structural properties, feed and draw solution chemistries, and operating parameters of the ODMPs [11–14]. Bartels et al. [11] found that a salt passage through a polyamide is affected by the characteristics of the feed in the RO process and that the salt permeability increased at low feed salinities. Wong et al. [15] reported that the increase in the feed and draw solution temperature led to an increase in both the water permeability and salt passage in ODMPs. Motsa et al. [10] mentioned that the interaction between salts molecules and foulant could generate new foulants. They reported that the combined fouling with alginate and calcium ions increased the hydrophobicity of alginate (more negative free energy in the cohesion values), and further reduced the electrostatic repulsions between the alginate macromolecules and membrane surfaces. The impact of feed solution chemistries on reverse salt diffusion is one of the important factors that needs to be more considered [16]. Moreover, ODMPs have recently been used to extract water from a source of impaired water (secondary wastewater effluent) using a saline stream (seawater or brackish water concentrate as a draw solution) [3]. In this case, the feed stream may contain a high concentration of organic matter and colloids in slightly salty water. However, only a few studies have investigated the effect of the feed ionic concentration in the presence of organic molecules and particulate matters in ODMPs. Therefore, the aim of this paper was to investigate the impact of elevated feed ionic concentrations in the presence of foulants on ODMPs. The change in membrane properties after the addition of a foulant in a feed solution was shown as well as the diffusion of a solute in ODMPs.

2. Materials and methods

2.1. Membrane properties and foulant preparation

The high flux forward osmosis (FO) membrane used in this research was provided by Toray Korea. Before the experiment, the membrane was soaked in de-ionized water. The membrane was cut according to the size of the membrane cell (length, width, and channel height of 2.60, 7.75, and 0.30 cm, respectively), then, carefully put between the two chambers of the membrane unit for separating the feed solution and the draw solution. Humic acid (HA), selected as a model organic foulant in this research, was provide by Sigma–Aldrich (USA). Yellow-green fluorescent carboxylated modified latex (CML) particles (1-μm diameter; Magsphere, Pasadena, CA) were used as model colloidal particles at a concentration of 2×10^6/mL in this research.

2.2. Operating conditions of the ODMPs

A gear pump (Longer Pump, China) was applied to control the flow of the solution. Both the feed and draw solutions flowed in counter directions with a cross-flow velocity of 15.0 cm/s. The permeate flux was continuously monitored from the draw solution by a digital weighing scale (AND GF-400, USA), and an increase in the permeate volume was automatically transmitted to a computer every five minutes. The conductivity of the feed solution was monitored and recorded by the data logger (LabPro, Vernier) connected to the computer. Each experiment was continuously run for 8 h including the stable flux stage. The experimental protocol of the FO process has been previously described elsewhere [17].

2.3. Contact angle and FT-IR

Contact angle measurement was applied to determine the hydrophobicity of the membrane surface [13]. Membrane samples were carefully removed from the membrane unit, air-dried, and kept in storage. Virgin and fouled membranes were measured with a contact angle goniometer (Phenix-300, USA). Thus, 50 μL of de-ionized water was used to monitor the contact angle of the membrane. To measure of membrane surface properties, FT-IR was done with the Spectum One System (Perkin-Elmer, USA) at ranges from 450 to 4,000 cm^{-1}.

3. Results and discussion

3.1. Impact of the feed ionic concentration on water and salt flux in ODMPs

To investigate the impact of the feed ionic concentration on the ODMP performance, the water flux and the reverse solute flux of the virgin membrane were investigated. In this section, the draw solution concentration was fixed at 2.0 M NaCl, and the feed ionic concentration was varied (0.0, 3.16, 10.0, 31.6 mM NaCl). Fig. 1 shows the water flux and the reverse salt flux of the virgin membrane under different feed ionic concentrations. The water flux of the ODMPs after

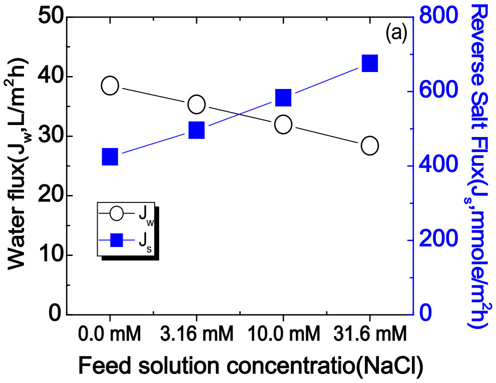

Fig. 1. Water flux of the ODPM with different feed ionic concentrations and 2 M NaCl as the draw solution at pH of 6.5, and a temperature of 21 ± 0.5°C.

increasing the feed ionic concentration was slightly decreased due to a decreased osmotic pressure gradient as the net driving force of the FO process [18,19]. Moreover, instead of a decrease in the reverse salt flux, a slight increase was clearly observed when the feed ionic concentration was increased. Two possible factors that can explain the findings are the membrane properties and the salt passage. In this study, the main component of the membrane active layer was a polyamide (PA). Salt passage through a polyamide membrane is affected by increased NaCl concentrations in the feed solution [11]. The diffused solute was significantly increased when the feed ionic concentration was increased due to an increase in the salt passage. A high feed ionic concentration is most pronounced when treating a strong negatively charged membrane with a sodium chloride solution.

3.2. *Impact of the feed ionic concentration on organic and colloidal fouling*

To investigate the impact of the feed ionic concentration in the presence of foulants, the ODMP was continuously operated, and its performance was observed. Fig. 2 shows the normalized flux of the ODMP with HA molecules and colloidal particles as foulants. The finding clearly shows that the normalized flux of the ODMP is slightly increased when HA molecules were used as a foulant for both 0.00 and 10.0 mM NaCl feed ionic concentrations (Fig. 2). To further understand HA phenomenon on ODMP as reported by Valladares Linares et al. [9], the change in membrane properties from the interactions between the HA molecules and the membrane surface was investigated. During the FO process operations, HA molecules were successively obstructed by the sieving mechanism of the FO membrane. The HA molecules accumulated on the membrane surface, and the negatively charged functional groups of HA directly dominated the membrane surface properties. Then, the membrane surface became more hydrophilic and negatively charged. Therefore, the slight enhancement in the flux in the presence of a feed solution containing HA is attributed to the change in the membrane surface properties becoming more hydrophilic. Hong and Elimelech [20] also mentioned that the accreted HA molecules on the active layer can lead to a more negatively charged membrane surface and that the more negatively charged membrane surface greatly promotes the diffusion of water molecules. Furthermore, Xie et al. [21] reported that the formation of a humic acid fouling layer on the membrane surface did not result in significantly decreasing the membrane pure water permeability coefficient, and the external and internal concentration polarizations were negligible. Further analysis of the membrane surface properties were studied by measurement of the contact angles and FT-IR. Ang and Elimelech [13] stated that a decreased contact angle was directly attributed to an increase in hydrophilicity on the membrane surface, which would favor an increase in water flux. Fig. 3 shows that the membrane fouled with HA molecules had a smaller contact angle compared to that of the virgin membrane. Consequently, the attachment of HA molecules during operation altered the membrane surface to become more hydrophilic, and water molecules could easily access the membrane surface.

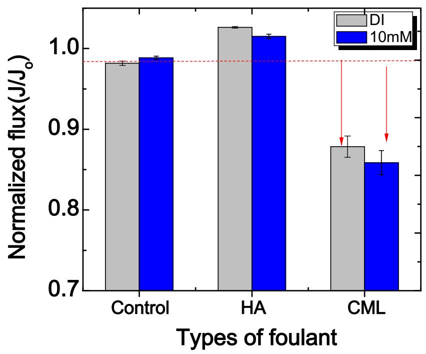

Fig. 2. Normalized flux (J/J_o) after 420 min of operation.

Furthermore, FT-IR was also done to show the changes in functional groups on the membrane surface and hence its properties [22]. The wave ranges used in this experiment were 400–4,000 cm^{-1}. Fig. 4 shows the FT-IR of a membrane surface containing HA molecules and colloidal particles as foulants. Because significant differences between the virgin and fouled membranes appeared only at less than 1,800 cm^{-1} of

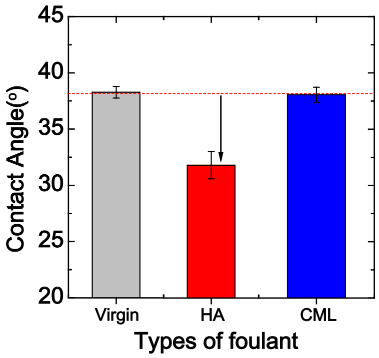

Fig. 3. Water contact angle of the virgin and fouled membrane surfaces.

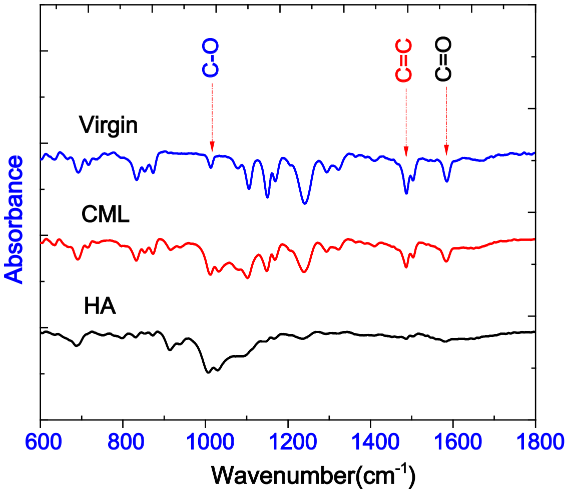

Fig. 4. FT-IR spectra of the virgin and fouled membranes.

the wave number, the FT-IR spectra only showed the range of 600–1,800 cm^{-1} of the wave number. Generally, the active layer of the membrane surface is polyamide (PA). The FT-IR peaks of the PA layer were observed at 1,609 cm^{-1} (C=O) and 1,541 cm^{-1} (C=C) as shown in Fig. 4. After the adsorption of the HA molecules onto the active layer of membrane surface, the FT-IR peaks of the PA layer from the HA-fouled membrane did not appear because the membrane surface properties were changed by the adsorption of the HA molecules. In addition, carboxylated functional groups (C–O, 1,040 cm^{-1}) appeared strong on the spectrum of the HA-fouled membrane. Draževič et al. [23] reported that functional groups of C–O (1,040 cm^{-1}) were a characteristic property for hydrophilic organic matter. This confirms the hypothesis that the membrane surface is more hydrophilic after the adsorption of HA molecules.

On the other hand, the normalized flux of the ODMP was much more significantly decreased when the feed solution contained colloidal particles used as the foulant (Fig. 2). The findings also showed that around a 12 and 15% decline in flux was obtained with the DI and 10 mM NaCl feed solutions, respectively, within 7 h. The phenomena between the colloidal particles and the membrane surface need to be further elucidated. In the previous results, the remodeled membrane properties due to the adsorption of HA molecules induced more hydrophilicity. In contrast, the deposition of colloidal particles on the membrane surface did not affect the properties of the membrane surface measured by the contact angle (Fig. 3). The FT-IR peaks of colloids-fouled membrane were quite similar to the virgin membrane (Fig. 4) because the deposition of the colloidal particles did not change the properties of the membrane surface. The carboxylated functional groups (C–O, 1,040 cm^{-1}) appeared on the spectrum of the colloidal-fouled membrane surface were due to the colloidal particles used in this study containing the carboxylated functional groups. Thus, the flux decline of feed solution in the presence of colloidal particles of feed solution was related to the cake-enhanced osmotic pressure (CEOP) as what have been observed by Boo et al. [24]. During the continuous operation of the ODMPs, the colloidal particles were also obstructed by the sieving phenomena of membrane. The elevated osmotic pressure due to the confined salt molecules near the membrane surface leads to a substantial drop in the net driving force, and thus, results in a significant decline in the permeate flux. Lee et al. [5] also mentioned that the cake-enhanced osmotic pressure (CEOP) was the major contributor in overall flux decline in colloidal fouling in which the deposited colloid layer hinders the back diffusion of salt into the bulk solution.

3.3. Reversal salt selectivity

Salt passage is one of the important factors in the ODMPs because it is directly related to the efficiency of the system. In the previous section, we observed that the increased feed ionic concentration directly reduced the ODMPs performance as well as the increased diffusion of salt molecules from the draw solution to the feed solution. In this section, there are two important factors that were investigated: the reverse solute flux and the reversal salt selectivity under different feed ionic concentrations in the presence of foulants (Colloidal particles and HA molecules). Fig. 5 illustrates the reverse solute flux with different foulant types. Interestingly, the reverse solute flux of the feed solution in the presence of HA molecules significantly decreased in both DI and 10 mM NaCl clearly seen in Fig. 5. Possible explanations for the observed results are the changed properties of the HA molecules and the interaction of the HA molecules and with the membrane properties. As discussed in Section 3.2, the formation of HA fouling layer induced the more negatively charged and more hydrophilicity on the membrane surface. In addition, the increased negative charge of membrane surface reduced the transport of feed and draw solution ions in the forward and reverse directions [19,25]. Moreover, the reverse flux of Cl^- was hindered by an enhanced electrostatic interaction with the more negatively charged humic acid fouling layer. Furthermore, Hancock and Cath [26] also showed that the increase in HA deposition on the membrane surface led to a substantial decrease in the membrane salt (NaCl) permeability coefficient but did not result in a significant decrease in the membrane pure water permeability coefficient. Therefore, the reverse solute flux was significantly decreased when the feed solution contained the HA molecules. However, the reverse solute flux of feed solution in the presence of colloidal particles did not show any significant difference because the properties of the membrane did not change (as seen by the contact angle and FT-IR spectra).

The reverse solute flux is one of important phenomenon in the ODMPs as well as the relationship between the diffused water and the solute. Phillip et al. [19] stated that the reversal salt selectivity was the ratio of the volume of water produced per moles of draw solute lost. The reversal salt selectivity did not show any significance change even when the feed ionic concentration was increased (Fig. 6). The reversal salt selectivity is significantly increased when the feed solution contained the HA as foulant due to the changed properties of membrane surface. As discussed above, the adsorption of HA molecules caused the membrane surface to become more hydrophilic.

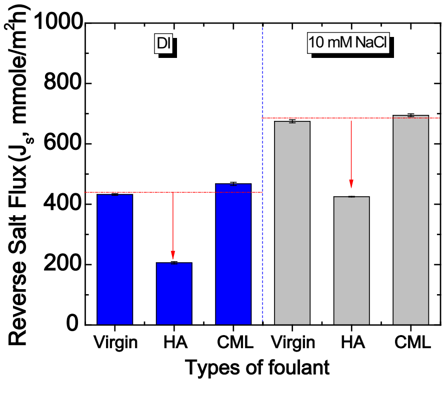

Fig. 5. Revere solute flux (mmol/m^2 h) of the membranes at various feed salt concentrations and foulants. The temperature was 21 ± 0.5°C.

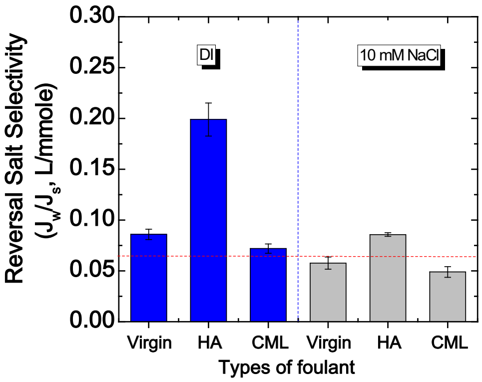

Fig. 6. Reversal salt selectivity of the membranes with various feed concentration and foulants.

The diffusion of water molecules was increased, while the reverse solute flux was decreased thereby resulting in the increased reversal salt selectivity. On the other hand, the reversal salt selectivity of the feed solution containing colloidal particles did not show the significance change in resulting due to the properties of the membrane surface were not affected by the colloidal particles, and the CEOP only affected the osmotic pressure gradient as the net driving force of the ODMP.

4. Conclusions

This study showed the impact of elevated feed ionic concentrations in the presence of HA molecules and colloidal particles as foulants in the ODMPs. The findings showed that the normalized flux of ODMPs was significantly decreased when the feed solution contained colloidal particles because the deposition of colloids strongly promoted the CEOP of the ODMPs. On the other hand, the feed solution containing HA molecules increased the normalized flux due to the changed properties of the membrane surface. The coverage of the membrane surfaces by HA molecules induced a more hydrophilic membrane surfaces. In addition, an increase in the feed ionic concentration from DI to 10 mM NaCl did not alter the reversal salt selectivity of the ODMPs. Interestingly, the reversal salt selectivity was significantly increased when the feed solution contained the HA molecules because of the change in the membrane surface properties including its hydrophilicity and functional groups. The deposition of colloidal particles on the membrane surface did not show any significant change in the reversal salt selectivity.

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