



Efficiency analysis of RO fouling characteristics and forward osmotic backwashing associated with EfOM ratio in reuse of high-salinity wastewater

Junyoung Park^a, Minjin Kim^b, Kitae Park^b, Hyungsoo Kim^b,
Daesoo Park^c, Hyungsook Kim^d, Jihoon Kim^{b,*}

^aDepartment of Civil, Architectural and Environmental System Engineering, Sungkyunkwan University, Suwon, Korea

^bGraduate School of Water Resources, Sungkyunkwan University, Suwon, Korea, Tel. +82-31-290-7647;

Fax: +82-31-290-7549; email: jjtt23@skku.edu (J. Kim)

^cTechnology Development Center of Samsung Engineering Co., Ltd., Seoul, Korea

^dDepartment of Food and Nutrition, School of Human Ecology, The University of Suwon, Suwon, Korea

Received 14 November 2016; Accepted 6 January 2017

ABSTRACT

Although it is desirable to operate seawater reverse osmosis processes when reusing high-salinity wastewater, organic fouling is worsened by influent water with an organic concentration higher than that of seawater desalination processes. In particular, with regard to effluent organic matter (EfOM) included in treated wastewater, fouling is worsened by combining with calcium ion. Thus, the fouling characteristics for each organic matter ratio were confirmed by mixing humic acid (HA), sodium alginate (SA), and bovine serum albumin (BSA), representing the EfOM. As a result, the fouling index and specific cake resistance increased with increasing SA concentration and decreased with increasing BSA concentration. However, it was confirmed that the cleaning efficiency of forward osmotic backwashing was high because the fouling by SA had relatively high reversibility and the increase in the specific cake resistance was caused not only by the absorption of membrane and organic matter but also by the absorption of the organic matter layers themselves. Furthermore, changes in the properties of foulants accumulated on the membrane surface before and after forward osmotic backwashing were analyzed by liquid chromatography–organic carbon detection and organic nitrogen detection. Among the EfOM, SA showed the highest ratio of biopolymers, and HA and BSA showed a high ratio of humics and low molecular weight neutrals, respectively. The ratios of low-molecular substances and residual SA increased after forward osmotic backwashing. This made it possible to remove the organic matter that formed the large molecular structure by interaction in forward osmotic backwashing. The results showed that this tendency was particularly clear with an increase in SA concentration.

Keywords: Salinity wastewater; Forward osmotic backwashing; Organic fouling; Wastewater reuse; Effluent organic matter

1. Introduction

With the increased industrialization and urbanization, and the improvement in the quality of life, the concentration of salt contained in industrial and domestic wastewater has increased [1]. High-salinity wastewater is generated from

various environments such as coastal areas in which wastewater is generated by the production of food, drugs, chemicals, petroleum, fiber, and leather, and from the brackish water or seawater used for toilet and shipboard wastewater [1–4]. In general, such high-salinity wastewater contains salt ranging from 10,000 to 100,000 mg/L and a high concentration of organic matter. Conventional activated sludge processes, therefore, have limitations.

* Corresponding author.

Due to the effects of changes in oxygen transmission rate associated with salt concentration, salt stress of microorganisms, sludge characteristics, and operational factors, changes in operating conditions and the acclimation period of activated sludge need to respond to the high-salinity wastewater. Studies on the effect of high-salinity wastewater in activated sludge processes have been performed since 1973. Although it is possible to assess changes in the ionic strength of salt and the effect on microbial activity, a clear mechanism and typical model have not been proposed because the experimental conditions for each study differ [5].

When high-salinity wastewater inflows to general activated sludge processes, organic matter removal efficiency decreases with an increase in the salt stress of microorganisms [1,2,5–7]. However, because there are differences in experimental conditions such as salt concentration, treatment process, and operation method among previous studies on biological treatment of high-salinity wastewater, there are differences among them in the influence of high-salinity wastewater on the organic matter removal capacity. But according to most experimental results, the removal efficiency of organic matter recovered after the adaptation period of high-salinity wastewater [7–10]. In those studies, the concentration of extracellular polymeric substances (EPS) increased in order to adapt to extreme environments in the process of adaptation to high-salinity wastewater, and the number of soluble microbial products (SMP) increased because of the dead microorganisms due to failure to adapt to a high-salinity environment. In other studies, ESP and SMP decreased after the acclimation period, and this enabled us to examine the extent to which microorganisms adapt to salt [11,12].

Although the organic matter removal efficiency is recovered by microbial acclimation in high-salinity wastewater treatment, it is not possible to prevent the reverse osmosis (RO) fouling caused by effluent organic matter (EfOM) contained in treated wastewater when reusing wastewater. EfOM consists mainly of SMP and EPS released by microorganisms in the biological wastewater treatment process with natural organic matter (NOM) and synthetic organic compounds as non-biodegradable organic matter contained in raw wastewater [13]. The EfOM cause worse fouling by combining with divalent cations [14]. High-salinity treated water has a high salt concentration equal to seawater, but contains higher organic matter concentration. Its fouling becomes worse than that in conventional desalination processes. Therefore, unlike the indirect fouling control of conventional seawater reverse osmosis (SWRO) processes by enhancing pretreatment processes and using chemical cleaning [15], direct fouling control is needed that periodically removes fouling during processing [16,17].

Thus, in this paper, the fouling characteristics was analyzed according to the composition ratio of EfOM in SWRO processes to reuse high-salinity wastewater, and the cleaning efficiency was analyzed by performing forward osmotic backwashing as a direct fouling control method.

2. Materials and methods

2.1. Synthetic feed water

In this experiment, synthetic feed water was used to replicate the treated water in the membrane bioreactor

pretreatment process of high-salinity raw wastewater. The organic foulants chosen to represent the polysaccharides, proteins, and non-biodegradable NOM found in EfOM of wastewater effluent were sodium alginate (SA), bovine serum albumin (BSA), and humic acid (HA), respectively. Calcium ion was adjusted to 4 mM using CaCl_2 , and the total dissolved solids (TDSs) concentration was finally adjusted to TDS 20 g/L by adding NaCl. The experiment was performed by maintaining the total organic matter concentration of the synthetic feed water at 100 mg/L, and the mixing ratios of HA, SA, and BSA were adjusted to 1:1:1, 2:1:1, 1:2:1, and 1:1:2. The used HA, SA, and BSA were provided by Sigma-Aldrich (USA), and the organic matter was filtered through a 0.45 μm filter for use after stirring it in deionized water for over 12 h.

2.2. RO membrane

Commercialized 8-inch SWRO membrane made of polyamide was used in this experiment and was cut into a plate so that it could be used for a lab-scale experimental device. The cut membrane was refrigerated at 4°C by immersing in 1% sodium bisulphite solution. The SWRO membrane used in this experiment has an area of 0.0126 m², and a 34 mil (0.8636 mm) thick spacer was used for the feed water. The specifications of the used membrane are shown in Table 1.

2.3. Membrane test unit

As shown in Fig. 1, the lab-scale experimental device used in this experiment is an exclusive RO device capable of operating at constant pressure with the cross-flow method for connecting two cells with a membrane area of 0.0126 m² in series. The concentrated water line was set to repeatedly flow into the feed water tank, and the valve was set so that the permeate water could be circulated to the feed water tank. A thermostat (i.e., constant-temperature water tank) and stirrer were installed in the feed water tank and the NaCl solution tank so that the conditions of the feed water and NaCl solution could be constantly maintained.

The pipes were installed so that the NaCl solution instead of the feed water could be poured into the RO cells with forward osmotic backwashing, and the brine pipes were separated so that the NaCl solution could be circulated to the NaCl solution tank. In forward osmotic backwashing, permeate water pipes are installed for pouring water into the RO cells using an electronic scale. Considering the changes in the efficiency of forward osmotic backwashing due to the difference in the elevation head, the electronic scales were set

Table 1
Specifications of SWRO membrane

Model	SWC5
Material	Polyamide
Surface charge	Negative
Permeate flow rate (m ³ /d)	34.1
Stabilized salt rejection (%)	99.8
Maximum operating pressure (MPa)	8.27

Note: 32,000 mg/L NaCl solution at 800 psig (5.5 MPa) applied pressure, 8% recovery, 77°F (25°C), and pH between 6.5 and 7.0.

at the same height as the RO cells. The electronic scales were connected to each RO cell to measure the flux automatically, and pipes were installed to operate only a single RO cell in forward osmotic backwashing.

2.4. Experimental methods

This experiment was performed under the condition of the cross-flow method and under constant pressure filtration at a pressure of 40 bar. In addition, forward osmotic backwashing was performed until a 10% flux decline rate (FDR) was reached. Before the fouling experiments, the SWRO membrane was consolidated at an operating pressure of 40 bar using deionized water for 13 h. Conditioning was then performed for 2 h after adjusting the salt concentration using CaCl₂ and NaCl. Subsequently, fouling was caused by pouring HA, SA, and BSA for each ratio at the total organic matter concentration of 100 mg/L.

When reaching 10% FDR, the foulants were analyzed before forward osmotic backwashing by separating an RO cell after stopping the operation. In addition, after forward osmotic backwashing, the recovered flux was measured by cleaning with the feed water again for 15 min by pouring NaCl solution into the remaining RO cells. In forward osmotic backwashing, circulation was performed by pouring in NaCl solution with 35 g/L TDS to the feed water, and the forward osmotic backwashing (FOB) water was poured into the permeate water using an electronic scale and keeping its concentration at 300 mg/L TDS. In membrane filtration and forward osmotic backwashing, the shear force was constantly maintained to keep the circulation flow rate at 1 L/min. The temperature of the NaCl solution and feed water were maintained at 25°C to minimize the effect on osmotic pressure and flux associated with temperature changes.

As shown in Fig. 2, the resistance after membrane compaction using the initial deionized water was defined as the membrane resistance (R_m), and the increased resistance in the conditioned state after pouring the salt was defined as the salt resistance (R_{cp}). The sum of R_m and R_{cp} was the initial resistance and defined as R_i ; subsequently, the resistance increased by adding organic matter and was defined as fouling resistance R_f . The membrane resistance reduced by forward osmotic backwashing was defined as reversible resistance R_r , and the membrane resistance which was not removed after forward osmotic backwashing was defined as irreversible resistance R_{ir} . R_i and R_f were defined as total resistance R_t .

The coefficient of viscosity in the fouling evaluation was determined using Eqs. (1)–(4) proposed by Sharqawy et al. [18] because it was affected by the water temperature and salinity:

$$\mu_{sw} = \mu_w(1 + A \cdot S + B \cdot S^2) \tag{1}$$

$$\mu_{sw} = 4.2844 \times 10^{-5} + (0.157(t + 64.993)^2 - 91.296)^{-1} \tag{2}$$

$$A = 1.541 + 1.998 \times 10^{-2}t - 9.51 \times 10^{-5}t^2 \tag{3}$$

$$B = 7.974 - 7.561 \times 10^{-2}t + 4.724 \times 10^{-4}t^2 \tag{4}$$

where μ_w is the viscosity coefficient of pure water, S is the salinity (kg/kg), and t is the water temperature (°C). The flux reduction rate associated with the constant pressure operation was calculated from Eq. (5):

$$\text{FDR (flux decline rate)} = \left(1 - \frac{J}{J_0}\right) \times 100 \tag{5}$$

where FDR is the flux decline rate (%), J is the reduced flux (LMH), and J_0 is the initial flux (LMH). After reaching 10% FDR, the cleaning efficiency was calculated from the flux recovered by forward osmotic backwashing as follows:

$$\text{Cleaning efficiency} = \frac{(J_c - J_f)}{(J_i - J_f)} \tag{6}$$

where J_i is the initial flux (LMH), J_f is the reduced flux (LMH), and J_c is the recovered flux after cleaning (LHM).

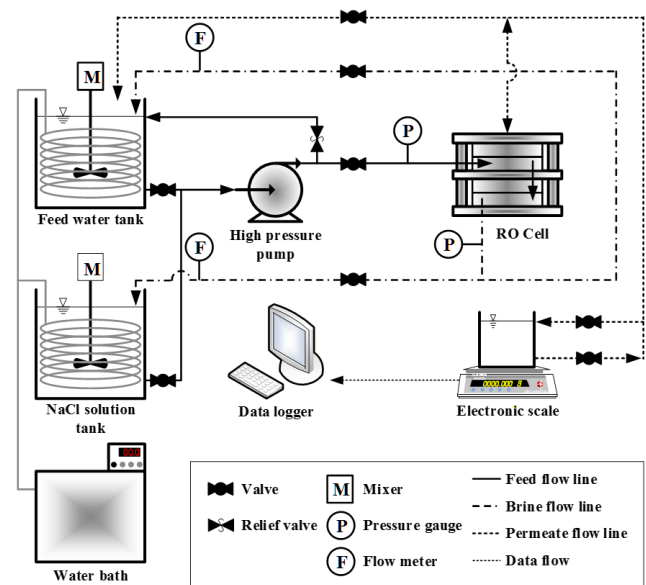


Fig. 1. Schematic diagram of experimental device for lab-scale continuous RO membrane.

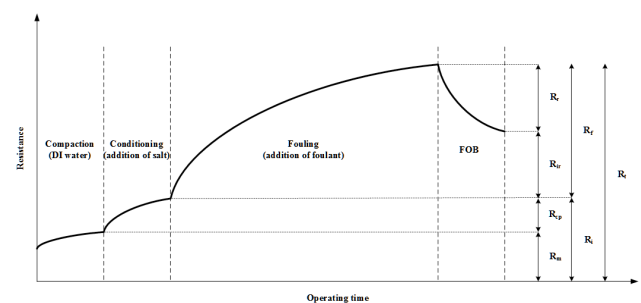


Fig. 2. Resistance classification according to experimental procedures.

2.5. Extraction and analysis methods of fouling

In this experiment, organic matter was extracted by neutralizing the pH using HCl after cleaning using an ultrasonic bath at 25°C for 1 h by immersing the fouled membrane in 0.05 M NaOH solution. It is considered possible to perform an almost perfect quantitative analysis of the organic matter on the membrane surface because the cleaning efficiency was more than $99.8\% \pm 0.3\%$ under these conditions derived by preliminary experiments in FDR 10%. The concentration of the eluted organic matter was 0.013 mg/L in the sampling experiment using virgin RO membranes and was excluded from the following experimental results. Total organic carbon (TOC) was measured using the Shimadzu TOC analyzer (TOC-L CPH), and the mean value analyzed three times using the calibration curve of 0–15 mg/L was used.

2.6. LC–OCD–OND analysis

Liquid chromatography–organic carbon detection and organic nitrogen detection (LC–OCD–OND) was used for quantitative analysis of the organic matter accumulated on the membrane surface. LC–OCD–OND is an analytical method that exploits the phenomenon whereby the transfer rate inside the column varies according to molecular weight. High-molecular weight substances pass through the pores rapidly because they cannot enter the deeper parts of the pores of the column filling, while the small-molecular weight substances enter into the pores, and their retention time increases until they move outside the pores. Accordingly, organic substances can be separated into biopolymers, humic substances, building blocks, and low molecular weight (LMW) neutrals according to the retention time. Subhi et al. [19] analyzed LC–OCD–OND on HA, SA, and BSA, and demonstrated that SA showed the highest ratio in the biopolymers, and HA and BSA showed a high ratio in the humics and LMW neutrals, respectively. In the current experiment, LC–OCD–OND was analyzed using DOC-LABOR system model 8 (DOC-LABOR, Germany).

3. Results and discussion

The fouling was evaluated when reaching 10% FDR by dividing the ratios of HA, SA, and BSA into 1:1:1, 2:1:1, 1:2:1, and 1:1:2 after maintaining the feed water salt concentration at 20 g/L, operating pressure at 40 bar, and organic matter concentration at 100 mg/L. Fig. 3 shows a graph of the changes in the flux according to the EfOM ratio based on FDR. It took 8, 7, 5.5, and 7.5 h to reach 10% FDR when the ratios of HA, SA, and BSA were 1:1:1, 2:1:1, 1:2:1, and 1:1:2, respectively. Rapid fouling occurred when the SA ratio was high. Herzberg et al. [20] studied the fouling characteristics by EPS of RO membrane using SA and BSA and then confirmed that fouling by SA occurred rapidly. They also reported that the fouling was worsened by divalent cations. Moreover, Lin et al. [21] reported that hydrophilic organic matter worsened fouling more than hydrophobic organic matter. Ba [22] conducted experiments on nano filtration membrane fouling after mixing 100 mg/L HA, SA, and BSA with 2 g/L NaCl solution. As a result, rapid fouling was caused during the first 2 h, and it was reported that the fouling of SA, HA, and BSA worsened in that order.

Fig. 4 shows a graph of the changes in the salt removal efficiency for each ratio of organic matter. The lowest salt removal efficiency was found when the ratio of HA was high, and the highest salt removal efficiency was found when the ratio of SA was high. These results were the same as those reported by Kim et al. [23], in which the SA fouling layer was relatively denser than the HA fouling layer and that the salt removal efficiency increased in the experiment compared with HA and SA fouling.

Fig. 5 shows the measurement results of the organic matter concentration on the membrane surface after operating when reaching 10% FDR for each EfOM ratio. The organic matter was 911.67, 764.05, 677.22, and 801.35 mg/m² when HA, SA, and BSA were in the ratio of 1:1:1, 2:1:1, 1:2:1, and

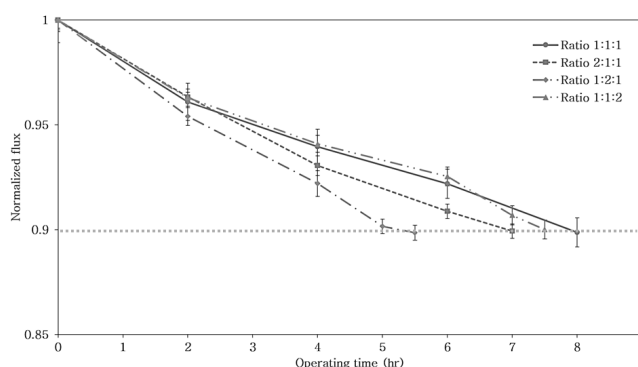


Fig. 3. Changes in flux according to EfOM ratio.

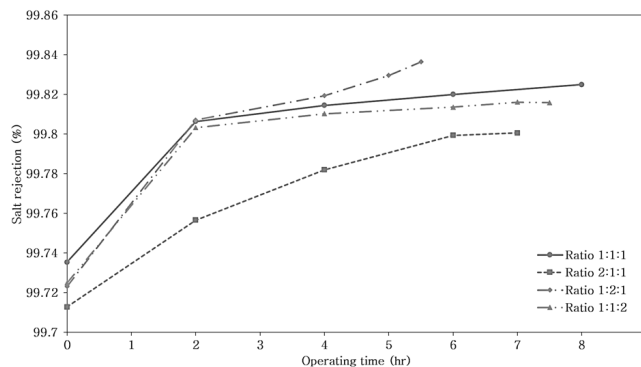


Fig. 4. Changes in salt removal efficiency according to EfOM ratio.

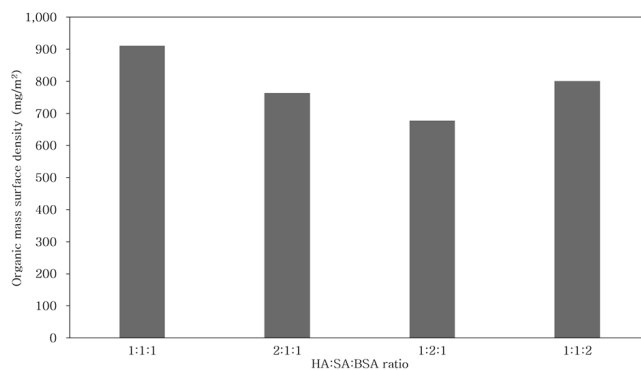


Fig. 5. Changes in organic matter concentration on membrane surface according to EfOM ratio.

1:1:2, respectively. It was confirmed that the organic matter concentration accumulated on the membrane surface was low when the SA ratio was high.

The cleaning efficiency of forward osmotic backwashing performed when reaching 10% FDR according to the EfOM ratio in feed water is shown in Table 2. The cleaning efficiencies were 28%, 24.6%, 34.6%, and 27.4% when HA, SA, and BSA were in the ratios of 1:1:1, 2:1:1, 1:2:1, and 1:1:2, respectively. In addition, the highest cleaning efficiency was found when the SA ratio was high. The organic matter removal efficiency was 67.6%, 49.4%, 77.5%, and 66.8% when HA, SA, and BSA were in the ratios of 1:1:1, 2:1:1, 1:2:1, and 1:1:2, respectively.

Table 2 shows the changes in FOB water volume of forward osmotic backwashing according to the EfOM ratio. The FOB water volumes were 23.9, 20.6, 27.9, and 23.4 mL when HA, SA, and BSA were in the ratios of 1:1:1, 2:1:1, 1:2:1, and 1:1:2, respectively. These changes in FOB water volume occur because SA has a low interaction with the membrane surface but has a high interaction with organic matter. Thus, fouling with a high ratio of SA shows the characteristics of reversible fouling, and it is easy to pour in backwashing water in forward osmotic backwashing. Therefore, it is considered that the cleaning efficiency is high. Katsoufidou et al. [24] studied the fouling and backwashing characteristics of SA and HA using ultra filtration membranes. They reported that SA caused rapid fouling but showed a very high cleaning efficiency in backwashing, and that HA caused gradual fouling but showed a low cleaning efficiency. In addition, they confirmed that the cleaning efficiency of SA increased with increasing calcium ion, but that of HA decreased in inverse proportion to calcium ion concentration.

The flux of in membrane processes can be expressed by the resistance in the series model based on Darcy's law [25].

$$J = \frac{\Delta P - \Delta \pi}{\mu(R_i + R_f)} \tag{7}$$

As shown in Eq. (8), R_f can be expressed by α (specific cake resistance) and I (fouling index):

$$R_f = \frac{\alpha C_b V}{A} = \frac{IV}{A} \tag{8}$$

where C_b is the organic matter concentration, V is the accumulated permeate volume, and A is the effective membrane surface area. Based on the above description, fouling resistance can be expressed by the specific cake resistance and M

(amount of organic matter accumulated on the membrane surface) as shown in Eq. (9).

$$R_f = \alpha \cdot M \tag{9}$$

The specific cake resistance shows the mass density of the fouling layer by dividing the fouling filtration resistance by the amount of organic matter accumulated on the membrane surface. This makes it possible to examine how the fouling layer is compacted. The fouling index is represented by the specific cake resistance and the organic matter concentration of the feed water, and the organic matter contained in the feed water permeated by turbulence flow due to cross-flow. The spacer on the feed water side is not accumulated on the membrane surface. Thus, as shown in Eq. (10), the fouling index was determined by deriving the relative organic matter concentration based on the amount of surface organic matter after reaching 10% FDR.

$$I = \alpha \times \frac{MA}{V} \tag{10}$$

Table 2 shows the fouling resistance changed in forward osmotic backwashing according to the EfOM ratio as reversible and irreversible resistances. The resistances were $2.57 \times 10^{13} \text{ m}^{-1}$, $2.48 \times 10^{13} \text{ m}^{-1}$, $2.45 \times 10^{13} \text{ m}^{-1}$, and $2.33 \times 10^{13} \text{ m}^{-1}$ when HA, SA, and BSA were in the ratios of 1:1:1, 2:1:1, 1:2:1, and 1:1:2, respectively. The highest resistance was found in the ratio of 1:1:1, and the lowest resistance was confirmed when the ratio of BSA was high. The ratio of reversible and irreversible resistances according to the EfOM ratio was 30:70, 27:73, 36:61, and 32:68 when HA, SA, and BSA were in the ratios of 1:1:1, 2:1:1, 1:2:1, and 1:1:2, respectively. The reversible resistance was high when the ratio of SA was high.

Fig. 6 shows a graph of the changes in the fouling index before and after forward osmotic backwashing according to the EfOM ratio. Before forward osmotic backwashing, the fouling indexes were $8.3 \times 10^{13} \text{ m}^{-2}$, $9.17 \times 10^{13} \text{ m}^{-2}$, $1.15 \times 10^{13} \text{ m}^{-2}$, and $7.98 \times 10^{13} \text{ m}^{-2}$ when HA, SA, and BSA were in the ratios of 1:1:1, 2:1:1, 1:2:1, and 1:1:2, respectively. The highest fouling index was confirmed when the ratio of SA was high. The results demonstrated that SA showed a rapid decrease in the flux and that the fouling tendency varied according to the ratio of SA. After forward osmotic backwashing, the fouling indexes were $5.82 \times 10^{13} \text{ m}^{-2}$, $6.66 \times 10^{13} \text{ m}^{-2}$, $7.05 \times 10^{13} \text{ m}^{-2}$, and $5.45 \times 10^{13} \text{ m}^{-2}$ when HA, SA, and BSA were in the ratios of 1:1:1, 2:1:1, 1:2:1, and 1:1:2, respectively. Overall, the values were lower than those before forward osmotic backwashing, but the highest fouling index was confirmed when the ratio of SA was high.

Table 2
Results of forward osmotic backwashing according to EfOM ratio

EfOM ratio HA:SA:BSA	Cleaning efficiency (%)	Organic matter removal efficiency (%)	FOB water volume (mL)	Reversible resistance (m^{-1})	Irreversible resistance (m^{-1})
1:1:1	28.0	67.6	23.9	7.76×10^{12}	1.79×10^{13}
2:1:1	24.6	49.4	20.6	6.77×10^{12}	1.80×10^{13}
1:2:1	34.6	77.5	27.9	9.49×10^{12}	1.50×10^{13}
1:1:2	27.4	66.8	23.4	7.41×10^{12}	1.59×10^{13}

Fig. 7 shows a graph of the changes in specific cake resistance before and after forward osmotic backwashing according to the EfOM ratio. The specific cake resistances were 2.82×10^{16} m/kg, 3.25×10^{16} m/kg, 3.62×10^{16} m/kg, and 2.91×10^{16} m/kg when HA, SA, and BSA were in the ratios of 1:1:1, 2:1:1, 1:2:1, and 1:1:2, respectively. The highest value of the specific cake resistance was confirmed when the ratio of SA was high. Ang et al. [14] reported that SA formed a gel by the binding of calcium ions and that the fouling changed more denser when other organic substances were contained. Sioutopoulos et al. [26] reported that SA had the highest fouling index when experimenting with fouling for each organic matter concentration at the same salt concentration, and that the specific cake resistance increased with an increasing ratio of SA in feed water because SA had a higher compressibility than HA.

After forward osmotic backwashing, the specific cake resistance increased to 6.09×10^{16} m/kg, 4.67×10^{16} m/kg,

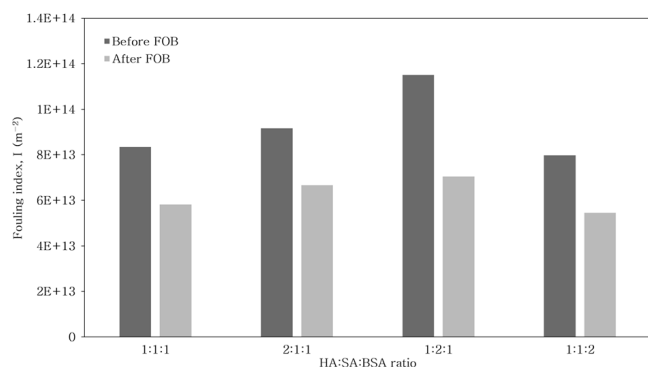


Fig. 6. Changes in fouling index before and after forward osmotic backwashing according to EfOM ratio.

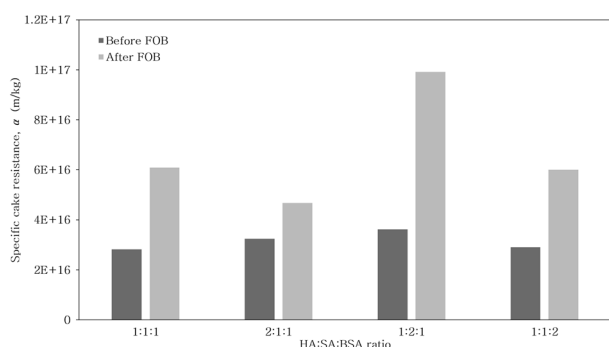


Fig. 7. Changes in specific cake resistance before and after forward osmotic backwashing according to EfOM ratio.

9.91×10^{16} m/kg, and 6.0×10^{16} m/kg overall when HA, SA, and BSA were in the ratios of 1:1:1, 2:1:1, 1:2:1, and 1:1:2, respectively. The largest increase was found in the ratio of 1:2:1 with high cleaning efficiency, and the smallest increase was found in the ratio of 2:1:1 with low cleaning efficiency. This was because the organic matter removed due to an increase in the amount of HA was relatively small but had a high irreversible resistance. This shows that irreversible fouling with a high ratio of HA is worse than SA, but relatively loosely structured fouling is formed.

Jermann et al. [27] reported that the irreversible fouling of HA was worsened by hydrophobic interactions with membranes, but that of SA worsened not only by the interactions with membranes but also by the electrostatic effect between SA molecules. Additionally, when mixing HA and SA, SA was not separately attached, but HA was bound to SA after HA was attached to the membrane first by hydrophobic binding. Ang et al. [14] conducted experiments on the interactions among SA–SA, SA–HA, and SA–BSA and then confirmed that the SA–SA interaction was the maximum and interactions decreased in the order of SA–BSA and SA–HA. According to these results, the cleaning efficiency was high because the interaction between HA and SA was small when the ratio of SA was high, and irreversible fouling was worsened by the effect of the hydrophobic interactions between the membrane and HA when the ratio of HA was high.

Although the increase in salt removal efficiency in fouling for each organic matter ratio is considered to be caused by the reduction of the salt concentration on the membrane surface with a decrease in the concentration polarization before pouring organic matter, the effect on the cake reduced concentration polarization (CRCP) could not be reflected in this study because it was not able to be quantitatively analyzed. It is thought that fouling filtration resistance increases in accordance with the CRCP, and that the fouling index and specific cake resistance will then increase. However, it is estimated that the tendency shown in the results in this study will be similar to that in accordance with the CRCP.

Table 3 shows the analysis results of LC–OCD–OND of the feed water according to the EfOM ratio. Hydrophobic organic carbon (HOC), a hydrophobic dissolved organic carbon (DOC) among the total DOCs, is a hydrocarbon or particulate matter and is excluded from the analysis. The compositions of chromatographable DOC (CDOC) by organic matter excluding HOC were analyzed. According to the results, the ratio of humics increased with increasing HA, that of biopolymers increased with increasing SA, and that of biopolymers and LMW neutrals increased with increasing BSA. In general, biopolymers, humics, and building blocks are represented by EPS such as carbohydrate and protein, HAs, and hydrolysates of HAs, respectively. In addition,

Table 3
Concentration of organic matter fractions of feed water according to EfOM ratio

EfOM ratio HA:SA:BSA	DOC (mg/L)	HOC (mg/L)	CDOC (mg/L)	Biopolymer (mg/L)	Humics (mg/L)	Building block (mg/L)	LMW neutrals (mg/L)
1:1:1	29.68	2.75	26.93	14.2	8.24	1.77	2.72
2:1:1	27.51	3.24	24.27	8.13	12.75	1.24	2.15
1:2:1	28.11	2.81	25.3	16.21	5.68	1.92	1.49
1:1:2	31.52	2.44	29.08	15.72	5.14	1.06	7.16

Table 4

Concentration of organic matter fractions on membrane surface before and after forward osmotic backwashing according to EfOM ratio

FOB	EfOM ratio HA:SA:BSA	DOC (mg/L)	HOC (mg/L)	CDOC (mg/L)	Biopolymer (mg/L)	Humics (mg/L)	Building block (mg/L)	LMW neutrals (mg/L)
Before	1:1:1	11.5	1.519	9.981	4.521	2.215	1.131	2.114
After	1:1:1	3.721	0.617	3.104	1.1234	0.5846	0.317	1.079
Before	2:1:1	9.64	1.617	8.023	3.003	2.444	0.924	1.652
After	2:1:1	4.878	0.126	4.752	1.404	0.325	0.417	2.606
Before	1:2:1	8.546	0.9	7.646	5.192	1.447	0.326	0.681
After	1:2:1	1.923	0.164	1.759	0.452	0.196	0.258	0.853
Before	1:1:2	10.11	1.6	8.51	3.865	1.322	0.502	2.821
After	1:1:2	3.354	0.7375	2.6165	0.462	0.211	0.204	1.7395

LMW neutrals are represented by low-molecular weight substances such as amino acids, alcohols, and aldehydes.

Table 4 shows the analytical results of the organic matter composition on the membrane surface before and after forward osmotic backwashing according to the EfOM ratio. The results show that the ratio of the LMW neutrals increases before and after forward osmotic backwashing, and it is believed that the organic materials that form a relatively large molecular structure by the binding of SA and calcium ion as well as HA and BSA are removed through forward osmotic backwashing. Moreover, it is believed that SA is more easily removed because the changes in biopolymers are relatively larger than those in humics.

4. Conclusions

The fouling characteristics of EfOM for each mixing ratio were analyzed when treating high-salinity wastewater. The results showed that fouling was worst with a high ratio of SA and the fouling index increased due to the rapid occurrence of fouling. In addition, it was confirmed that the specific cake resistance increased resulting from the formation of a gel layer due to the binding of SA and calcium ions and the formation of a more consolidated layer due to the binding of SA and other organic matter. However, with regard to the fouling by SA, it was confirmed that the fouling layer was easily removed in forward osmotic backwashing because of its relatively high reversibility. The results showed that the increase in specific cake resistance caused by SA was caused not only by the adsorption of membrane and organic matter but also by the increase in the interaction of the organic matter layer itself. Moreover, the results showed that the organic matter forms a polymeric structure due to the mutual interactions in forward osmotic backwashing; in particular, this tendency became clear with increasing SA concentration. Thus, the consolidation of the fouling layer was strong because the organic matter that formed an irreversible fouling layer after forward osmotic backwashing showed relatively high ratios of low-molecular substances and residual SA.

Acknowledgements

This research was supported by a grant (code 16IFIP-C088924-03) from Industrial Facilities and Infrastructure Research Program funded by Ministry of

Land, Infrastructure and Transport (MOLIT) of the Korea government and the Korea Agency for Infrastructure Technology Advancement (KAIA).

References

- [1] O. Lefebvre, R. Moletta, Treatment of organic pollution in industrial saline wastewater: a literature review, *Water Res.*, 40 (2006) 3671–3682.
- [2] C. Sun, T. Leiknes, J. Weitzenböck, B. Thorstensen, Development of an integrated shipboard wastewater treatment system using biofilm-MBR, *Sep. Purif. Technol.*, 75 (2010) 22–31.
- [3] J.P. Bassin, R. Kleerebezem, G. Muyzer, A.S. Rosado, M.C. van Loosdrecht, M. Dezotti, Effect of different salt adaptation strategies on the microbial diversity, activity, and settling of nitrifying sludge in sequencing batch reactors, *Appl. Microbiol. Biotechnol.*, 93 (2012) 1281–1294.
- [4] J. Hong, W. Li, B. Lin, M. Zhan, C. Liu, B.-Y. Chen, Deciphering the effect of salinity on the performance of submerged membrane bioreactor for aquaculture of bacterial community, *Desalination*, 316 (2013) 23–30.
- [5] M. Perneti, L. Di Palma, Experimental evaluation of inhibition effects of saline wastewater on activated sludge, *Environ. Technol.*, 26 (2005) 695–703.
- [6] E. Reid, X. Liu, S.J. Judd, Effect of high salinity on activated sludge characteristics and membrane permeability in an immersed membrane bioreactor, *J. Membr. Sci.*, 283 (2006) 164–171.
- [7] W.C.L. Lay, Y. Liu, A.G. Fane, Impacts of salinity on the performance of high retention membrane bioreactors for water reclamation: a review, *Water Res.*, 44 (2010) 21–40.
- [8] A. Oren, Diversity of halophilic microorganisms: environments, phylogeny, physiology, and applications, *J. Ind. Microbiol. Biotechnol.*, 28 (2002) 56–63.
- [9] F. Kargi, A.R. Dinçer, Saline wastewater treatment by halophile-supplemented activated sludge culture in an aerated rotating biodisc contactor, *Enzyme Microb. Technol.*, 22 (1998) 427–433.
- [10] A. Uygur, Specific nutrient removal rates in saline wastewater treatment using sequencing batch reactor, *Process Biochem.*, 41 (2006) 61–66.
- [11] P. Artiga, G. García-Toriello, R. Méndez, J.M. Garrido, Use of a hybrid membrane bioreactor for the treatment of saline wastewater from a fish canning factory, *Desalination*, 221 (2008) 518–525.
- [12] D. Jang, Y. Hwang, H. Shin, W. Lee, Effects of salinity on the characteristics of biomass and membrane fouling in membrane bioreactors, *Bioresour. Technol.*, 141 (2013) 50–56.
- [13] H.K. Shon, S. Vigneswaran, S.A. Snyder, Effluent organic matter (EfOM) in wastewater: constituents, effects, and treatment, *Crit. Rev. Environ. Sci. Technol.*, 36 (2006) 327–374.
- [14] W.S. Ang, A. Tiraferri, K.L. Chen, M. Elimelech, Fouling and cleaning of RO membranes fouled by mixtures of organic foulants simulating wastewater effluent, *J. Membr. Sci.*, 376 (2011) 196–206.

- [15] J.-W. Nam, S.-H. Hong, J.-Y. Park, H.-S. Park, H.-S. Kim, A. Jang, Evaluation of chemical cleaning efficiency of organic-fouled SWRO membrane by analyzing filtration resistance, *Desal. Wat. Treat.*, 51 (2013) 6172–6178.
- [16] J.W. Nam, J.Y. Park, J.H. Kim, Y.S. Lee, E.J. Lee, M.J. Jeon, H.S. Kim, A. Jang, Effect on backwash cleaning efficiency with TDS concentrations of circulated water and backwashing water in SWRO membrane, *Desal. Wat. Treat.*, 43 (2012) 124–130.
- [17] J. Park, W. Jeong, J. Nam, J. Kim, J. Kim, K. Chon, E. Lee, H. Kim, A. Jang, An analysis of the effects of osmotic backwashing on the seawater reverse osmosis process, *Environ. Technol.*, 35 (2014) 1455–1461.
- [18] M.H. Sharqawy, J.H. Lienhard, S.M. Zubair, Thermophysical properties of seawater: a review of existing correlations and data, *Desal. Wat. Treat.*, 16 (2010) 354–380.
- [19] N. Subhi, G. Leslie, V. Chen, P. Le-Clech, Organic fouling of ultrafiltration membrane: detailed characterization by liquid chromatography with organic carbon detector (LC-OCD), *Sep. Sci. Technol.*, 48 (2012) 199–207.
- [20] M. Herzberg, S. Kang, M. Elimelech, Role of extracellular polymeric substances (EPS) in biofouling of reverse osmosis membranes, *Environ. Sci. Technol.*, 43 (2009) 4393–4398.
- [21] H. Lin, M. Zhang, F. Wang, F. Meng, B.-Q. Liao, H. Hong, J. Chen, W. Gao, A critical review of extracellular polymeric substances (EPSs) in membrane bioreactors: characteristics, roles in membrane fouling and control strategies, *J. Membr. Sci.*, 460 (2014) 110–125.
- [22] C. Ba, Design of Advanced Reverse Osmosis and Nanofiltration Membranes for Water Purification, Ph.D. Thesis, University of Illinois at Urbana-Champaign, Champaign, IL, USA, 2010.
- [23] S. Kim, S. Lee, E. Lee, S. Sarper, C.-H. Kim, J. Cho, Enhanced or reduced concentration polarization by membrane fouling in seawater reverse osmosis (SWRO) processes, *Desalination*, 247 (2009) 162–168.
- [24] K. Katsoufidou, S. Yiantsios, A. Karabelas, An experimental study of UF membrane fouling by humic acid and sodium alginate solutions: the effect of backwashing on flux recovery, *Desalination*, 220 (2008) 214–227.
- [25] G. Belfort, R.H. Davis, A.L. Zydney, The behavior of suspensions and macromolecular solutions in crossflow microfiltration, *J. Membr. Sci.*, 96 (1994) 1–58.
- [26] D. Sioutopoulos, A. Karabelas, S. Yiantsios, Organic fouling of RO membranes: investigating the correlation of RO and UF fouling resistances for predictive purposes, *Desalination*, 261 (2010) 272–283.
- [27] D. Jermann, W. Pronk, S. Meylan, M. Boller, Interplay of different NOM fouling mechanisms during ultrafiltration for drinking water production, *Water Res.*, 41 (2007) 1713–1722.