

Salt cleaning of EfOM-fouled MF membrane for wastewater reclamation

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ABSTRACT

A novel method to control effluent organic matters (EfOM) fouling of microfiltration (MF) membrane during the wastewater reclamation process has been investigated by applying salt cleaning. To determine the efficiency of salt cleaning, experiments were carried out using feed waters containing (i) single foulant and (ii) mixed foulants of humic acids, polysaccharides, and protein which are representative organic matters of EfOM. In addition, real wastewater obtained from the wastewater treatment plant was used to investigate the applicability of salt cleaning. Among three EfOM substances, polysaccharides in the presence of Ca^{2+} caused severe flux decline, however, the declined flux due to fouling was recovered greatly after salt cleaning. In the case of mixed foulants, flux decline accelerated when the polysaccharides portion of the mixed foulants increased. Similar to the case of single foulant, salt cleaning was quite effective to recover the declined flux due to the fouling with mixed foulants. In addition, the salt cleaning efficiency tends to be more effective for fouling caused by feed water containing more polysaccharide than the other foulants. The mechanisms of salt cleaning can be attributed to the combination of osmotic disruption and cross-transport of ions in the boundary of the fouling layer, which weakens the structure of the cross-lined gel-type fouling layer on the membrane surface and, thus, the easy detachment from the membrane by crossflow shear effect. Fluorescence excitation–emission matrix and Fourier transform infrared spectroscopy analyses of cleaning solutions obtaining after salt cleaning also confirmed that EfOM accumulated on the membrane surface during fouling detached during salt cleaning. It was also confirmed that salt cleaning was efficient for cleaning of the membrane fouled by the real wastewater. In addition, when salt cleaning was applied periodically during MF of the real wastewater, flux decline due to fouling was delayed sufficiently by periodic flux recovery. This result suggests that the clean-in-place (CIP) cycle can be extended by salt cleaning and thus, the saving of chemical cost as well as the prevention of membrane damage.

Keywords: Wastewater reclamation; Microfiltration; EfOM fouling; Salt cleaning

1. Introduction

In recent years, wastewater reclamation has been actively introduced for various purposes. Wastewater reclamation is increasingly emphasized as a strategy for the rational use of limited freshwater resources and as a way to protect the deteriorated aquatic environment from wastewater outflows.

Wastewater effluent can be discharged to rivers or the sea as long as it meets the effluent standard, but re-treatment is required for reuse. Membrane water treatment is currently the most active process for such wastewater reclamation.

The main process for wastewater reclamation using membrane technology is reverse osmosis (RO) or nanofiltration

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processes, which require proper pretreatment processes. Ultrafiltration (UF) and microfiltration (MF) processes are mainly used in the pretreatment process. It is very important to select the appropriate fouling control strategy and to identify the source of foulant, as fouling on the UF and MF membranes can be critical to the economics and efficiency of the overall process [1–3]. However, if proper cleaning methods and cycles are not followed, the membrane performance may decrease, resulting in reduced throughput. Membrane foulants include particles, colloids, proteins, polysaccharides, natural organic matter, metals and metalloids [4–6].

The main cause of the fouling of UF and MF membranes, which are pre-treatment membranes for wastewater reclamation, is EfOM, which consists of humic substance, extracellular polymeric substances (EPS), soluble microbial products (SMPs), and organic acids [7]. In particular, EPS materials are typical membrane foulant in membrane filtration processes that can degrade the quality of the final treated water [8]. Of these, soluble or colloidal metabolites below 0.45 μm are called SMP [9]. SMP is composed mainly of humic acid, fulvic acid, protein, and polysaccharide and is the main cause of irreversible membrane fouling [2]. Especially, the combination of EfOM and inorganic materials causes rapid trans-membrane pressure (TMP) rise and requires chemical cleaning of the membrane [10].

MF membranes in wastewater reclamation processes have large pores but fouling occurs for various reasons. Membrane fouling is aggravated by the combined effects of various physical, chemical, and biological agents as well as by the operating conditions such as flux and crossflow velocity. It has been reported that materials accumulated on a membrane surface, which cannot be removed by cross-flow, backflushing, or backpulsing, can lead to irreversible adhesion, resulting in permanent permeability loss or membrane fouling [11,12]. Physical, chemical, and biochemical cleaning methods are generally used to improve the performance of fouled membranes. Physical cleaning includes backwashing and air scrubbing. Chemical cleaning uses acids, bases, oxidants, and adsorbents as cleaning agents. Biochemical methods using enzymes are applied to remove foulant from the membrane surface or inside the membrane matrix [13–15]. However, if the membrane performance is not restored even after cleaning in these manners, CIP is essential. In this case, membrane damage is accompanied. In general, membrane damage includes the ultimate tensile strength, elongation, and elasticity [16,17]. NaOCl, the most commonly used chemical cleaner, can modify membrane structure and shorten its lifespan, but membrane manufacturers do not offer clear alternatives. In addition, reprocessing is essential because cleaning wastes after chemical cleaning cause high COD [10,18].

Recently, there have been several researches on salt cleaning as an alternative to chemical cleaning [19,20]. In the case of salt cleaning, the NaCl solution is used as the cleaning solution, which minimizes the effect on the membrane and the cost of cleaning waste solution. According to a previous paper, membrane fouling control mechanisms for salt cleaning are osmotic swelling and ion exchange [19,20]. The basic principle is that divalent cations bind between adjacent organic foulant molecules to form a cross-linked fouling layer. These divalent cations such as Ca^{2+} undergo ion exchange with Na^+ in NaCl solution to break

or loosen them, reducing structural integrity. As a result, it is easier to control membrane fouling. Previous studies have confirmed the effect of salt cleaning on RO membrane fouling [19]. The effect of salt cleaning on the UF membrane by Mn^{2+} binding has also been studied [20]. However, until recently, there has been no study applying salt cleaning to membrane processes for wastewater reclamation. In addition, the exact mechanisms of salt cleaning have not been suggested yet until recently. This study is to quantitatively and qualitatively investigate whether salt cleaning is effective for membrane fouling of MF membranes by EfOM using three representative organic foulants such as humic acids, polysaccharides, and proteins. These three foulants were used to identify the effects of salt cleaning when membrane fouling occurred with each foulant or with mixed foulants. Furthermore, the cleaning efficiency was verified by applying the periodic cleaning method that is performed in the actual treatment plant using real secondary wastewater effluent. In addition to presenting the flux recovery results after salt cleaning in various cases, fluorescence excitation–emission matrix (FEEM) and Fourier transform infrared spectroscopy (FTIR) analyses were used to determine how much EfOM foulants were eluted from the membrane surface after salt cleaning. Based on these investigations, a more detailed description of the mechanisms of salt cleaning has been made.

2. Materials and methods

2.1. MF membrane and EfOM foulants

The MF membrane used in the experiments is a flat-sheet type membrane of C-PVC from Pure Envitech Co., Ltd., Siheung-si, Gyeonggi-do, South Korea, with a mean pore size of 0.15 μm and a maximum pore size of 0.4 μm . The filtration cell used for the fouling and cleaning experiments is a plate and frame type (ENVIS[®]) with a novel modification allowing continuous filtration and cleaning without disrupting the fouling layer formed on the membrane surface. Details about the novel modification and operation method are described in section 2.2. The membrane surface area is 20.28 cm^2 , in width 7.8 cm and in length 2.6 cm. The detailed membrane specification is listed in Table 1. The concentration of EfOM in the feed water was set at a concentration of 10 mg/L, whether the three EfOM representatives were used alone or in combination. EfOM concentration in feed water is listed in Table 2. Humic acid (Humic acid sodium

Table 1
MF membrane specifications

Manufacture	Pure Envitech Co., Ltd.
Material	Chlorinated polyvinylchloride (C-PVC)
Type	Flat sheet
Mean pore size	0.15 μm
Surface area	20.28 cm^2 (7.8 \times 2.6)
Allowable temperature	2°C–38°C
Allowable pH	2–10

Table 2
EfOM composition in synthetic feed water

EfOM composition	Humic acid (mg/L)	Sodium alginate (mg/L)	Bovine serum albumin (mg/L)	Total (mg/L)
Single EfOM	10	–	–	10.0
Single EfOM	–	10	–	10.0
Single EfOM	–	–	10	10.0
Mixed EfOM (1:1:1) ^a	3.33	3.33	3.33	10.0
Mixed EfOM (1:1.5:1)	2.86	4.28	2.86	10.0
Mixed EfOM (1:2:1)	2.5	5	2.5	10.0
Mixed EfOM (1:4:1)	1.67	6.66	1.67	10.0

^a This indicates the mixing ratio of three EfOM (humic:polysaccharides:protein).

salt, Sigma-Aldrich, USA), sodium alginate (alginic acid sodium salt, Sigma-Aldrich, USA), and serum albumin (Sigma-Aldrich, New Zealand) were used as representative EfOM foulants. The compositional ratios of the three EfOM foulants were changed by varying the sodium alginate inclusion rate as shown in Tables 2 and 3. The tables show the characteristics of the real secondary wastewater effluent used in periodic fouling and salt cleaning experiments. The salt cleaning solution was prepared using NaCl and DI water to the desired concentration. For most salt cleaning, 300 mM NaCl solution was used and 300, 600, and 900 mM NaCl solutions were used to determine the effect of salt concentration during salt cleaning on the cleaning efficiency.

2.2. Filtration set-up and operation conditions

The filtration set-up for fouling and cleaning experiments consists of a pressure vessel and a filtration system as shown in Fig. 1. The pressure vessel is composed of an integrated electronic pressure gauge and vessel capable of measuring

pressure. The filtration cell is a flat and frame type cell with a novel modification allowing the fouling and cleaning experiments continuously without disrupting the fouling layer (Figs. 1 and 3 for filtration and cleaning, respectively). The feed water injected from the pressure vessel enters through the inlet at the top of the device and passes through the separation membrane in a total filtration method, and the treated water comes out to the outlet port of the lower part. The filtration pressure was fixed by adjusting the nitrogen gas pressure to be 1 kg f/cm². The amount of treated water was automatically recorded through a computer connected to the scale by placing the treated water in a beaker placed on the scale.

Operational steps for fouling and cleaning experiments are shown in Fig. 2. In step 1, DI water was permeated to confirm the intrinsic permeability of the membrane, and in step 2, the change of membrane fouling was confirmed by permeating raw water. In step 3, as shown in Fig. 3, the cleaning solution was introduced into one hole in the upper part of the filtering device by blocking the outlet part of the

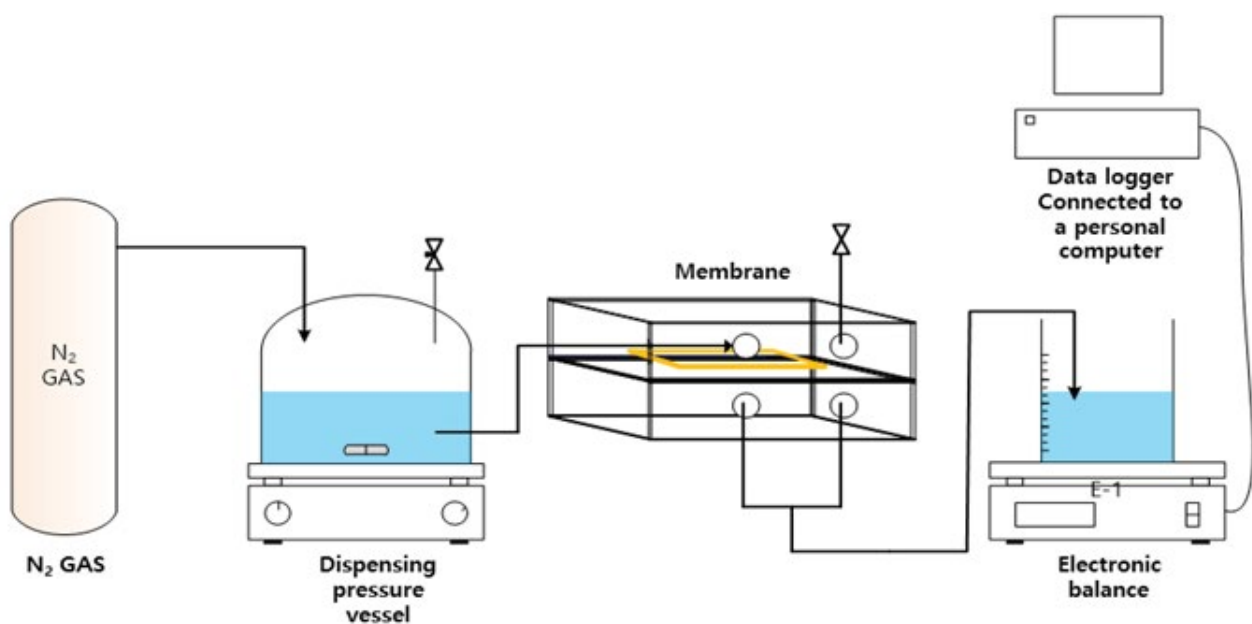


Fig. 1. Filtration set-up for fouling experiments.

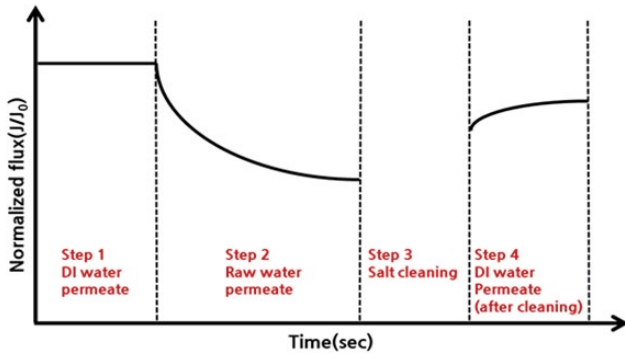


Fig. 2. Operational steps for fouling and cleaning experiments.

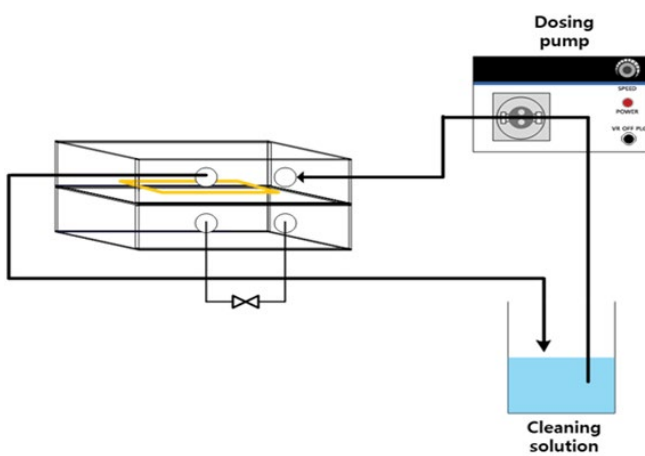


Fig. 3. Flows in the cell during a cleaning procedure.

lower part of the filtering device, and the cleaning solution was discharged through the other hole to contact the surface of the separation membrane. During the cleaning, the flowrate of 40 mL/min was applied in all cases as this flowrate does not allow permeation and, thus only surface cleaning takes place. In all cases, DI solution cleaning was also performed and compared with salt cleaning. In step 4, DI water was permeated again to confirm the recovery rate after cleaning.

2.3. Calculation of cleaning efficiency and filtration resistance

In this study, cleaning efficiency was estimated by flux recovery as well as the reduction of filtration resistance. The formula for indicating the cleaning efficiency is as follows. The permeate flux (J) is calculated as the permeate flux per unit time of the membrane per unit area. The permeate flux can be derived by Darcy's law.

$$J = \frac{\Delta P}{\mu R_t} = \frac{\Delta P}{\mu (R_m + R_f)} \quad (1)$$

$$J = \frac{\Delta P}{\mu R_t} = \frac{\Delta P}{\mu (R_m + R_{rev} + R_{irr})} \quad (2)$$

P is the TMP difference, μ is the viscous coefficient of the fluid, and R_m (clean membrane resistance) is the clean membrane resistance, which can be derived from the initial pure permeation flux and R_t is the total resistance. R_t can be derived from the sum of R_m and R_f (fouling resistance). The fouling resistance is the sum of the reversible resistance (R_{rev}) disappeared after cleaning and the irreversible resistance (R_{irr}) remaining after cleaning. Therefore, at a given condition, R_{rev} and R_{irr} correspond to the reversible and irreversible fouling, respectively. Flux recovery (FR) was calculated by Eq. (6) with data obtained from flux decline and recovery experiments shown in Fig. 4, where J_{wi} , J_{ww} and J_{wc} represents virgin membrane flux, fouled membrane flux, and cleaned membrane flux, respectively [21].

$$R_m = \frac{\Delta P}{\mu J_{wi}} \quad (3)$$

$$R_f = \frac{\Delta P}{\mu J_{ww}} \quad (4)$$

$$R_c = \frac{\Delta P}{\mu J_{wc}} \quad (5)$$

$$FR(\%) = \left[\frac{(J_{wc} - J_{ww})}{(J_{wi} - J_{ww})} \right] \times 100 \quad (6)$$

2.4. Analytical methods

2.4.1. Water chemistry analyses

Feed water chemistry including pH, TDS, conductivity, turbidity, color, SS, DOC, and UV₂₅₄ are listed in Table 4. Water temperature, pH, and TDS were measured using a multi-meter. Turbidity was measured in NTU units via a turbidimeter and the measurements were carried out three times and an average value was used. The color was measured using a digital colority meter with a double-beam LED system. SS was calculated by weighing 1 L of the sample in GF/C. DOC was measured using total organic carbon analyzers and specific UV absorbance (SUVA) was calculated based on the DOC and UV₂₅₄ values.

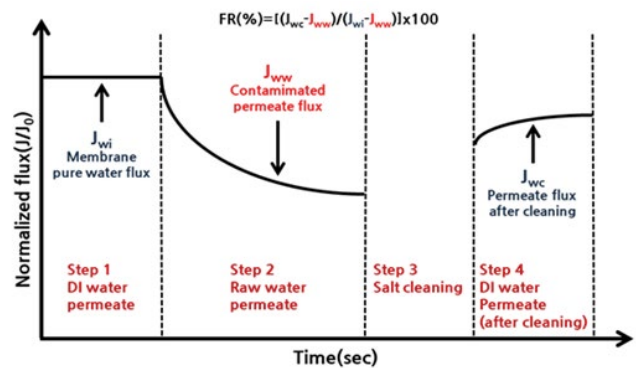


Fig. 4. Calculation of FR (%) from fouling and cleaning experiments.

2.4.2. FEEM and FTIR analyses

FTIR and FEEM analyses were performed to verify the salt cleaning efficiency (Table 5). There have been several studies using FTIR and FEEM to elucidate membrane fouling and cleaning mechanisms [22–26]. In this study, FTIR analysis was carried out with virgin, fouled, and cleaned membranes. By identifying the adsorption peaks obtained with each membrane, the degree of fouling as well as cleaning efficiency can be estimated qualitatively [22–24]. In the case of FEEM analysis, it was carried out with various samples including feed water and cleaning solution obtained during fouling and cleaning experiments. By comparing FEEM data from these samples, it can be determined how much EfOM foulants accumulated on the membrane surface have eluted from the membrane surface after salt cleaning. The specific location of FEEM peaks for representative EfOM foulants used in this study is shown in Fig. 5 [25,26].

3. Results and discussion

3.1. Salt cleaning of MF membrane fouled by single EfOM

For three EfOM foulants, including humic-, polysaccharide-, and protein-like substances, the fouling tendency and corresponding cleaning efficiency of each substance when each substance was present alone in the feed water have been evaluated. The concentration of each substance was adjusted to be 10 mg/L. Other feed water chemistry, as well as hydrodynamic operation conditions (i.e., initial flux and cross-flow velocity), was identical in all experiments. The results described below are shown in the order of humic-, polysaccharide-, and protein-like EfOM.

3.1.1. Humic-like EfOM

Humic acid (HA), a surrogate of humic-like EfOM, was used to evaluate salt cleaning efficiency. Flux decline curves

were obtained due to humic-like EfOM fouling in the absence and presence of Ca²⁺ (0.1 mM), and flux recovery curves were obtained after DI water and salt cleaning (0.3 M NaCl) as shown in Fig. 6. In all cases, flux decline due to humic-like EfOM fouling was severe (i.e., J/J_0 was less than 0.10). Flux recovery after salt cleaning was significant where J/J_0 after salt cleaning was up to 0.75. Membrane resistance (R_m), resistance after fouling (R_f), and resistance after cleaning (R_c) were listed in Table 6. Flux recovery (%) listed in Table 6 was calculated by Eq. (6) with corresponding flux data in Fig. 6. Flux recovery by salt cleaning was about 40% and 50% greater than DI water cleaning in the absence and presence of Ca²⁺, respectively. These results clearly show that salt cleaning is noticeably effective to recover the flux decline during fouling by

Table 3
Characteristics of real secondary wastewater effluent^a

Characteristic	Range	Average
Turbidity (NTU)	1.27–1.31	1.29
Color (PtCo)	40.5–41.1	40.8
COD (mg/L)	16.1–16.3	16.2
SS (mg/L)	5.13–5.23	5.18
T-N (mg/L)	7.8–7.9	7.9
T-P (mg/L)	0.5–0.7	0.6
DOC (mg/L)	10.5–11.1	10.8
UV ₂₅₄ (1/cm)	0.291–0.295	0.293
SUVA (L/mg m)	2.66–2.77	2.71
pH	7.93–7.97	7.95
TDS (mg/L)	380–396	388
Conductivity (μS/cm)	543–549	546
Ca ²⁺ (mg/L)	86.31–86.94	86.65

^aSample was collected from S-wastewater treatment plant located in Siheung city, South Korea.

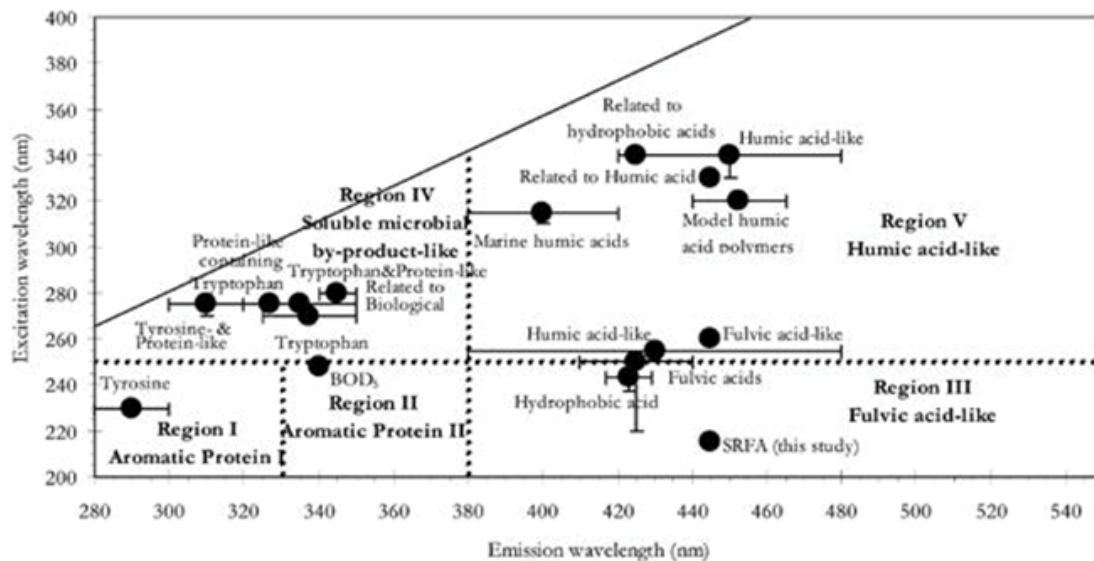


Fig. 5. Location of excitation–emission peaks (symbols) based on the literature reports and operationally defined excitation and emission wavelength boundaries (dashed lines) for five excitation–emission regions.

humic-like EfOM. Even more in the presence of Ca^{2+} , which assumed to accelerate organic fouling [2,3], salt cleaning was also effective. Briefly explained at this stage, the mechanism of salt cleaning is to destabilize the fouling layer due to osmotic destruction. The osmotic disruption proposed in this study is defined as disturbing the stable state of the boundary layer due to sudden osmotic pressure changes in the boundary layer. A more detailed description of the osmotic disruption will be made in the later part of this study with other experimental results.

3.1.2. Polysaccharide-like EfOM

Sodium alginate (SA), a surrogate of polysaccharide-like EfOM, was used to evaluate salt cleaning efficiency. Flux decline curves were obtained due to polysaccharide-like EfOM fouling in the absence (Fig. 7a) and presence of Ca^{2+} (0.1 mM; Fig 7b), and flux recovery curves were obtained after DI water and salt cleaning (0.3 M NaCl) as shown in Fig. 7. As shown in

Fig. 7a, in the absence of Ca^{2+} , flux was almost constant over the filtration period implying that polysaccharide-like EfOM in the absence of Ca^{2+} hardly fouled membrane. This result attributed to the fact that hydrophilic organic substance less fouled membrane than hydrophobic organic substances such as humic acids. Similar results have been reported previously [2,3]. Therefore, it was difficult to evaluate salt cleaning efficiency. Numerically by calculation, J/J_0 was almost 1.0 after salt cleaning. However, flux declined severely, in the presence of Ca^{2+} , as shown in Fig. 7b (i.e., J/J_0 was less than 0.07). The flux decline due to polysaccharide-like EfOM in the presence of Ca^{2+} was more significant compared with humic-like EfOM. This is due to the formation of a cross-linked gel-type fouling layer on the membrane surface [3,5,6].

Flux recovery after salt cleaning was significant where J/J_0 after salt cleaning was up to 0.85. Membrane resistance (R_m), resistance after fouling (R_f), and resistance after cleaning (R_c) were listed in Table 7. Flux recovery (%) listed in Table 7 was calculated by Eq. (6) with corresponding flux data in Fig. 7. Flux recovery by salt cleaning was much greater than DI water showing more than 75%. These results clearly show that salt cleaning is noticeably effective to recover the flux decline during fouling by polysaccharide-like EfOM even in the presence of Ca^{2+} . These results are quite consistent with previous research where the mechanisms of salt cleaning have been described as the combination of osmotic swelling

Table 4
Analytical methods

Categories	Detailed information
pH	HQ40d, HACH (Woodbridge, VA, USA)
Total dissolved solids (TDS)	HQ40d, HACH
Conductivity	HQ40d, HACH
Turbidity	2100AN, HACH
Color	DR6000, HACH
Suspended solid (SS)	WHATMAN GF/C, Electronic balance
Dissolved organic carbon (DOC)	TOC-LCPN, Shimadzu (Kyoto, Japan)
Ultraviolet absorbance at 254 nm (UV_{254})	DR6000, HACH

Table 5
Instruments used for FTIR and FEEM analyses

Instruments	Specification
FTIR	FTIR Spectrometer (Nicolet™ iS™ 50, Thermo Fisher Scientific (Waltham, MA USA))
FEEM	Spectro fluorophotometer (RF-6000, Shimadzu (Kyoto, Japan))

Table 6
Filtration resistances flux recovery corresponding to flux curves shown in Fig. 4

Resistance (m^{-1})	R_m	R_f	R_c	Flux recovery (%)
HA (DI cleaning)	1.74E+11	2.66E+12	1.35E+12	5
HA (Salt cleaning)	1.64E+11	2.46E+12	2.93E+11	48
HA + Ca^{2+} (DI cleaning)	1.7E+11	1.92E+12	6.5E+11	16
HA + Ca^{2+} (Salt cleaning)	1.62E+11	1.79E+12	2.16E+11	67

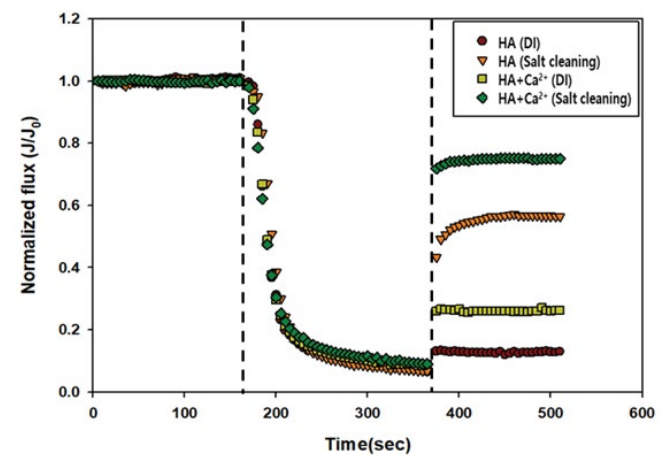


Fig. 6. Flux decline during fouling and recovery after cleaning for feed waters containing humic-like EfOM ('HA' and 'HA + Ca^{2+} ' for fouling in the absence and presence of Ca^{2+} , respectively; 'DI' and 'Salt cleaning' for cleaning with DI water and 0.3 M NaCl solution, respectively. This description applies similarly to later figures and tables).

and ion-exchange [19,20]. In the previous explanation, the concept of osmotic disruption was proposed, which is not exactly the same as osmotic swelling but can be considered as a similar concept. Following the loose of cross-linked gel-type fouling layer (i.e., usually formed with polysaccharide-like foulants in the presence of Ca^{2+}) due to osmotic disruption, the cross-transport between Ca^{2+} and Na^+ in the boundary of fouling layer, perhaps known as quantitative ion exchange [19,20], takes place since lots of Na^+ ions are convectively transported to the fouling layer diffusively, and consequently the diffusion of Ca^{2+} through the

boundary layer to bulk phase to meet an electro-neutrality. This description would be clearer in the results which will be shown in the later part of this study.

3.1.3. Protein-like EfOM

Bovine serum albumin (BSA), a surrogate of protein-like EfOM, was used to evaluate salt cleaning efficiency. Flux decline due to BSA fouling in the absence and presence of Ca^{2+} (0.1 mM) was presented in Figs. 8a and b, respectively, with the corresponding flux recovery after DI water and

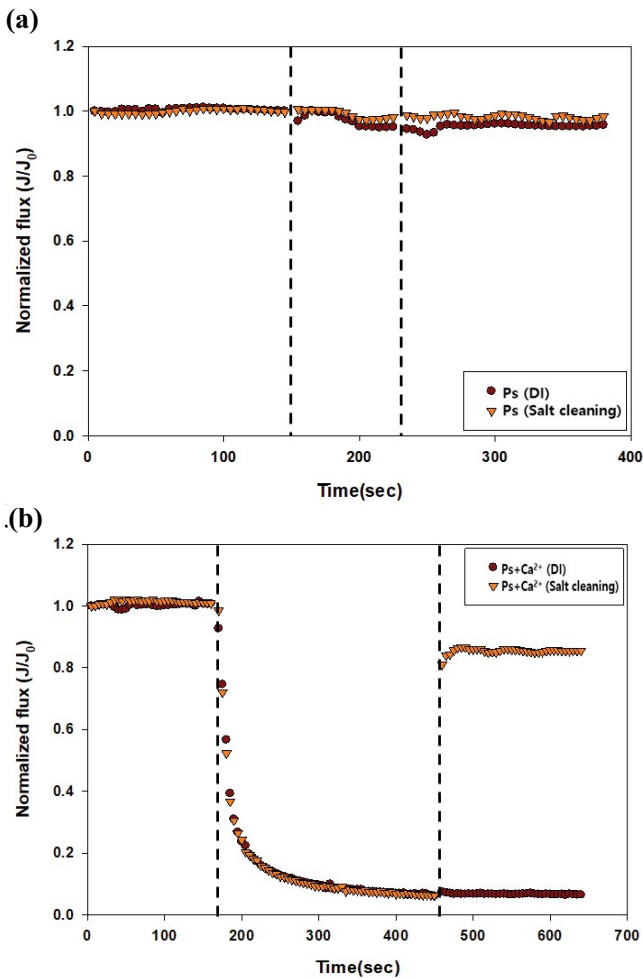


Fig. 7. Flux decline during fouling and recovery after cleaning for feed waters containing polysaccharide-like EfOM in the (a) absence and (b) presence of Ca^{2+} ('Ps' means polysaccharide).

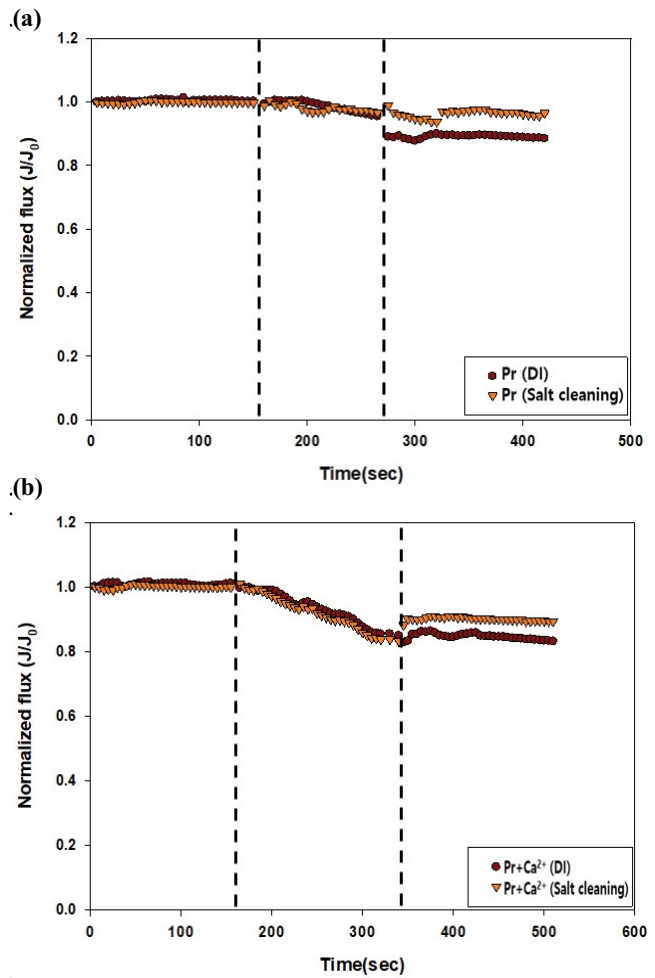


Fig. 8. Flux decline during fouling and recovery after cleaning for feed waters containing protein-like EfOM in the (a) absence and (b) presence of Ca^{2+} ('Pr' means protein).

Table 7
Filtration resistances flux recovery corresponding to flux curves shown in Fig. 5

Resistance (m^{-1})	R_m	R_f	R_c	Flux recovery (%)
Alginate (DI cleaning)	1.58E+11	1.66E+11	1.66E+11	2
Alginate (Salt cleaning)	1.58E+11	1.62E+11	1.6E+11	2
Alginate + Ca^{2+} (DI cleaning)	1.65E+11	2.71E+12	2.54E+12	1
Alginate + Ca^{2+} (Salt cleaning)	1.69E+11	2.68E+12	1.99E+11	79

salt cleaning (0.3 M NaCl). Flux decline in the presence of Ca^{2+} was slightly severer than that in the absence of Ca^{2+} . It seems that salt cleaning efficiency is not noticeable in all cases. This is due to the fact that much less flux decline occurred than the cases with humic-like EfOM (Fig. 6) and polysaccharide-like EfOM (Fig. 7b). However, in all cases, salt cleaning shows more flux recovery than DI water cleaning. Membrane resistance (R_m), resistance after fouling (R_f), and resistance after cleaning (R_c) were listed in Table 8. Flux recovery (%) listed in Table 8 was calculated by Eq. (6) with corresponding flux data in Fig. 8. It may be noted that the J/J_0 after DI water cleaning was lower than the J/J_0 at the final stage of fouling, and salt cleaning also shows negligible flux recovery even though the flux recovery after salt cleaning is visibly greater than DI water cleaning (Fig. 6a). This particular behavior is attributed to the characteristics of the protein. The osmotic shrinkage of protein molecules in certain conditions could lead to a denser fouling layer resulting in the increase of fouling layer resistance [27]. Therefore, caution may need to be taken into the case where the major EfOM of secondary wastewater is protein-like substances.

3.2. Salt cleaning of MF membrane fouled by mixed EfOM

In the previous discussion, it has been confirmed that salt cleaning was quite effective to clean the fouled membrane by the three representative EfOM foulants such as humic-like, polysaccharide-like, and protein-like substances. The efficiency of salt cleaning, however, was varied with the conditions applied such as types of EfOM and the presence of divalent cations. In this section, salt cleaning efficiency was evaluated using mixed EfOM. From the results in the previous section, it may be noted that the salt cleaning was quite promising especially for polysaccharide-like EfOM in the presence of Ca^{2+} . Therefore, the composition of mixed EfOM was varied by changing the portion of the polysaccharide content of the mixed EfOM. The total concentration of mixed EfOM was fixed to be 10 mg/L identical to the experiments shown in Section 3.1. The composition of mixed EfOM is listed in Table 2 in section 2 (i.e., HA: SA: BSA = 1:1:1, 1:1.5:1, 1:2:1, and 1:4:1). In all cases, feed water contains 0.1 mM Ca^{2+} and salt cleaning was performed with 0.3 M NaCl solution.

First, cleaning with DI water was carried out for the comparison with salt cleaning. The results are shown in Fig. 9. As shown in the figure, in all cases, quite severe flux decline was obtained and the extent of flux decline increased with increasing the sodium alginate (SA) content of the mixed EfOM (i.e., most severe flux decline for the mixing ratio of 1:4:1). It is clearly shown that, in all cases, DI water cleaning had little effect on flux recovery.

Next, salt cleaning was carried using mixed EfOM with different compositions of humic acid (HA), sodium alginate (SA), and BSA as shown in Fig. 10. There was no distinct relationship between SA content of the mixed EfOM and salt cleaning efficiency; however, flux recovery after salt cleaning was higher than 67% in all cases. When the SA content in the mixed EfOM increased from 30% to 60%, the flux recovery

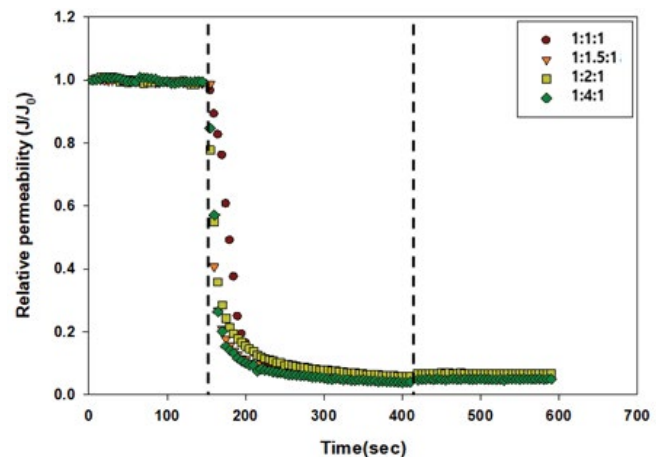


Fig. 9. Flux decline during fouling and recovery after DI water cleaning for feed waters containing mixed EfOM with different composition (e.g., 1:4:1 refers to the mixing ratio of HA:SA:BSA is 1:4:1).

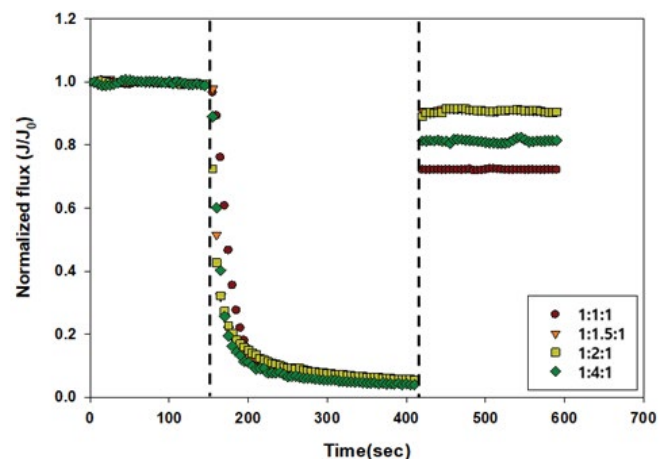


Fig. 10. Flux decline during fouling and recovery after salt cleaning for feed water containing mixed EfOM with different composition (e.g., 1:4:1 refers to the mixing ratio of HA:SA:BSA is 1:4:1).

Table 8
Filtration resistances flux recovery corresponding to flux curves shown in Fig. 6

Resistance (m^{-1})	R_m	R_f	R_c	Flux recovery (%)
BSA (DI cleaning)	1.59E+11	1.67E+11	1.8E+11	–
BSA (Salt cleaning)	1.58E+11	1.63E+11	1.64E+11	1
BSA + Ca^{2+} (DI cleaning)	1.68E+11	1.86E+11	2.03E+11	–
BSA + Ca^{2+} (Salt cleaning)	1.66E+11	1.86E+11	1.86E+11	5

was increased, but when the SA content was increased to 80%, the flux recovery was decreased but still higher than that of 30%. This observation may be related to the threshold concentration. Regardless of this threshold phenomenon, it is sure that salt cleaning could be a promising tool to clean the EfOM-fouled membrane as, in most cases, polysaccharide-like EfOM has been known to be the major EfOM [7,8,10]. As discussed previously, the reason why salt cleaning has an excellent effect on cleaning fouled membrane by polysaccharide-EfOM could be attributed to the combined mechanisms of osmotic disruption (i.e., known as osmotic swelling in the previous studies [19,20]) and cross-transport of Na⁺ and Ca²⁺ (i.e., known as quantitative ion exchange in the previous studies [19,20]) through the boundary of the fouling layer. These salt cleaning mechanisms allow the loose of the cross-linked gel-type fouling layer and make it easy to be detached from the membrane surface and, thus, the removal from the membrane surface by crossflow shear effect.

3.3. Evaluation of salt cleaning applicability using real secondary wastewater

To evaluate the applicability of salt cleaning to practical process, a real secondary wastewater effluent collected from the ‘S’ wastewater treatment plant at Siheung city (Gyeonggi-do, South Korea) was tested. The characteristics of the secondary wastewater effluent were listed in Table 3. All the experimental conditions were the same as those applied to the previous fouling and cleaning experiments using the representatives of EfOM substances. First, the influence of salt concentration of cleaning solution on salt cleaning efficiency was investigated. Then, periodic salt cleaning similar to the practical cleaning method was carried out to see if it could prevent the continuous flux decline during MF of the secondary wastewater effluent.

3.3.1. Influence of salt concentration

The salt concentration of salt cleaning solutions was varied to be 0.3, 0.6, and 0.9 M NaCl. As shown in Fig. 11

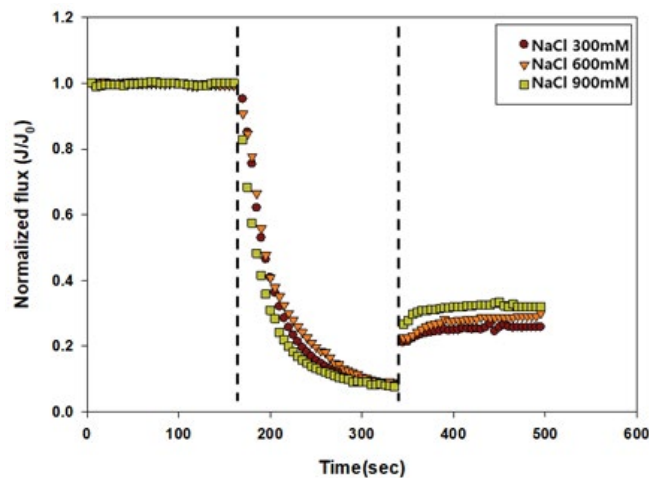


Fig. 11. Membrane permeability for real plant raw water experiment with various concentration of salt solution cleaning.

and listed in Table 9, the efficiency of salt cleaning in terms of flux recovery increased from 18% to 25% with increasing salt concentration from 0.3 to 0.9 M. In the previous results shown in Figs. 6 and 7, flux recovery after salt cleaning was more than 40%. The reasons for less flux recovery for the real secondary wastewater effluent than for the feed water made using the representatives of EfOM substances could be followed. First, as shown in Table 3, the real secondary wastewater effluent contains lots of other materials than EfOM, which results in the forming of a much complex fouling layer. Next, the SUVA value is about 2.7, which implies that humic-like substances are more abundant than polysaccharide-like substances. This condition may not be favorable for salt cleaning as shown in Fig. 10. Finally, calcium concentration of the secondary wastewater is about 0.7 mM. This is seven times higher than the calcium concentration of the feed water containing representatives of EfOM substance. As discussed previously, calcium ions play an important role in the cross-linked gel-type fouling layer in combination with organic matter. Therefore, there might be lots of thick and dense fouling layer after salt cleaning. However, for the purpose of maintenance cleaning, 10%–20% flux recovery could be enough if this value can be obtained periodically.

3.3.2. Application of periodic salt cleaning

Based on the above experimental results, it is confirmed that salt cleaning to some extent is effective to clean the fouled membrane by the real secondary wastewater effluent.

Table 9 Membrane resistivity and flux recovery for real plant raw water experiment with various concentration of salt solution cleaning

Resistance (m ⁻¹)	R _m	R _f	R _c	Fluxrecovery (%)
0.3 M NaCl	1.65E+11	1.92E+12	6.38E+11	18
0.6 M NaCl	1.72E+11	2.27E+12	6.74E+11	21
0.9 M NaCl	1.58E+11	1.6E+12	5.23E+11	25

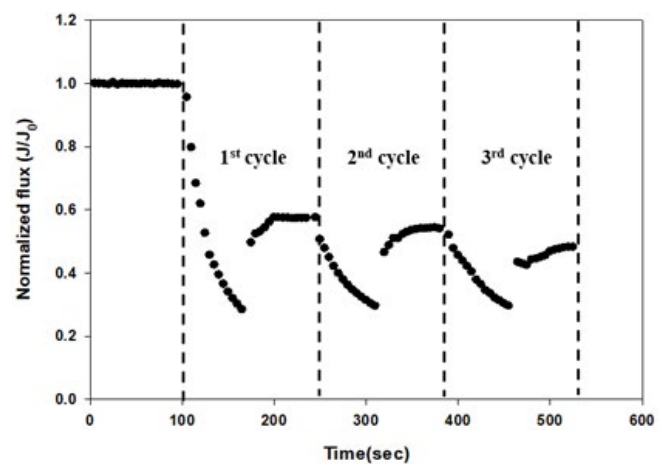


Fig. 12. Membrane permeability for real plant raw water with continuous experiment.

Table 10
Membrane resistivity and flux recovery for real plant raw water with continuous experiment

Resistance (m^{-1})	R_m	R_f	R_c	Flux recovery (%)
1st cycle	3.75E+11	1.31E+12	6.52E+11	30
2nd cycle	6.52E+11	1.27E+12	6.92E+11	25
3rd cycle	6.92E+11	1.26E+12	7.75E+11	19

Therefore, in this section, the periodic salt cleaning was applied to see if the continuous flux decline could be prevented. The results are shown in Fig. 12 and Table 10. In the first cycle, J/J_0 of the fouled membrane was measured to be 0.284 and recovered to 0.574 after salt cleaning. In the second cycle, J/J_0 of the fouled membrane was measured to be 0.296 and recovered to 0.540 after salt cleaning. In the final cycle, J/J_0 of the fouled membrane was measured to be 0.296 and recovered to 0.482 after salt cleaning. In terms of flux recovery, as listed in Table 9, the flux recovery reduced from 30% for the first cycle to 19% to the final cycle. However, the flux recovery of 19% for the final cycle is still enough to maintain an acceptable permeation allowing more filtration without CIP. These results clearly showed that the continuous flux decline

could be prevented in an acceptable manner by applying the periodic salt cleaning implying that salt cleaning could be a proper maintenance cleaning method.

3.4. FEEM and FTIR analyses for evaluating salt cleaning effectiveness

3.4.1. Fluorescence excitation–emission matrix

FEEM analyses were carried out with samples from the real secondary wastewater effluent, DI water cleaning solution, and salt cleaning solution. The specific wavelength range of organic substances is as follows: excitation/emission (Ex/Em) wavelength of 220–270 nm/280–330 nm (Region I)

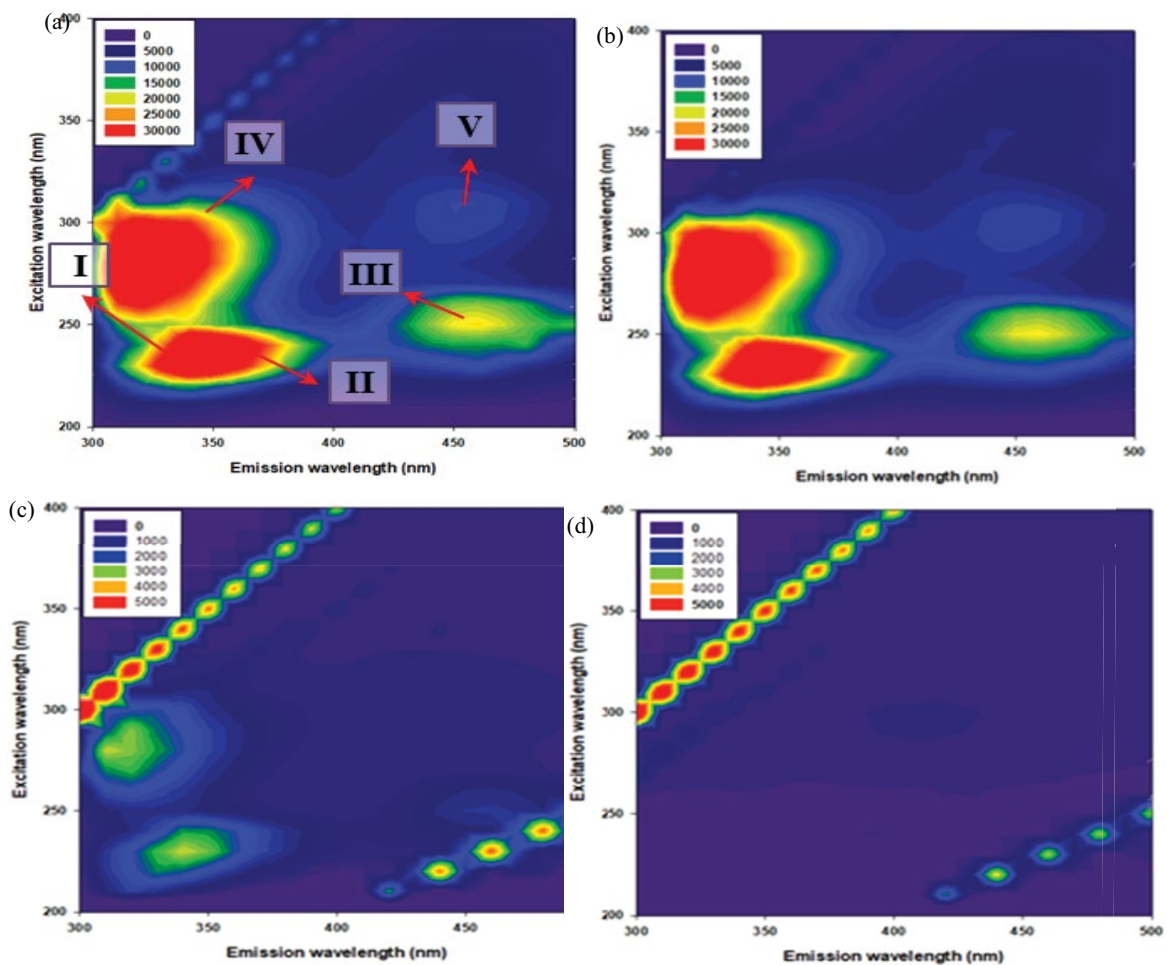


Fig. 13. FEEM measurements for (a) the secondary wastewater effluent, (b) MF permeate, (c) salt cleaning solution, and (d) DI water cleaning solution.

as well as 220–270 nm/330–380 nm (Region II) is the range of aromatic proteins, 270–340 nm/380–540 nm (Region V) nm is the range of humic acid, 270–440 nm/280–380 nm (Region IV) is the range of SMPs, and 230–280 nm/380–540 nm (Region III) is the range of fulvic acid.

As shown in Fig. 13, aromatic protein, fulvic acid, humic acid, and SMPs were present in the secondary wastewater effluent in the scale range from 0 to 30,000. Among them, SMPs and aromatic proteins seemed to be the abundant organic substances (Fig. 13a). In the case of the DI cleaning solution (Fig. 13d), there is almost no elution of organic substances from the membrane surface. However, there is a noticeable elution of organic substances (i.e., SMPs and aromatic protein) from the membrane surface for salt cleaning solution (Fig. 13c). In this study, even though the results from FEEM analyses did not give precise information on how much EfOM on the membrane surface detached from the membrane surface by salt cleaning, the tendency of foulant detachment from the membrane surface was identified.

3.4.2. Fourier transform infrared spectroscopy

FTIR measurements were performed on the virgin membrane first for comparison. Membranes fouled by the secondary wastewater effluent were cleaned by DI water and salt solution. FTIR measurements were also performed with these membranes. By comparing the FTIR peaks of the cleaned membrane to those of virgin membranes, the efficiency of the corresponding cleanings could be estimated. The results from FTIR analyses are shown in Fig. 14.

As shown in the figure, the functional groups for the cleaned membrane by DI water were 3,300 cm^{-1} indicating the O–H stretch of the polysaccharides and 2,900 cm^{-1} indicating the humic substances of the aliphatic C–H stretch, 1,650 cm^{-1} as C=O bonds representing the primary amide

of protein, 1,420 cm^{-1} as symmetric carboxylate stretch and 1,100 cm^{-1} as asymmetric CO–O–C stretch. Some of these groups did not show in FTIR spectra for the virgin membrane. This implies that most organic foulants remained after DI water cleaning. However, FTIR peaks corresponding to these functional groups for the cleaned membrane by salt solution significantly reduced in both peak number and peak size. This implies that salt cleaning was effective to detach the organic foulants (i.e., SMPs, protein, polysaccharide) from the membrane surface having many similar FTIR spectra to that for the virgin membrane. Similar to FEEM results, FTIR results also showed that salt cleaning actually detached some EfOM substances accumulated on the membrane surface.

4. Conclusions

In this study, the effects of salt cleaning on EfOM fouling of MF membranes in the wastewater reclamation process were investigated. By executing continuous fouling and cleaning experiments with a novel home-made membrane cell, the extent of flux decline during fouling and flux recovery after cleaning was measured. Humic acid (HA), sodium alginate (SA), and BSA were used as the surrogates of humic-like, polysaccharide-like, and protein-like EfOM substances, respectively.

First, when EfOM substances were used alone, salt cleaning was effective to recover the flux declined during fouling by all substances such as HA, SA, and BSA. Especially, salt cleaning was quite effective to weaken the structural integrity of the cross-linked gel-type fouling layer formed by polysaccharide-like substances in the presence of Ca^{2+} . This fouling layer has been known to be hardly detached from the membrane surface and, thus, the problematic during MF pretreatment in wastewater reclamation. The mechanisms of salt cleaning have been described as the combination of

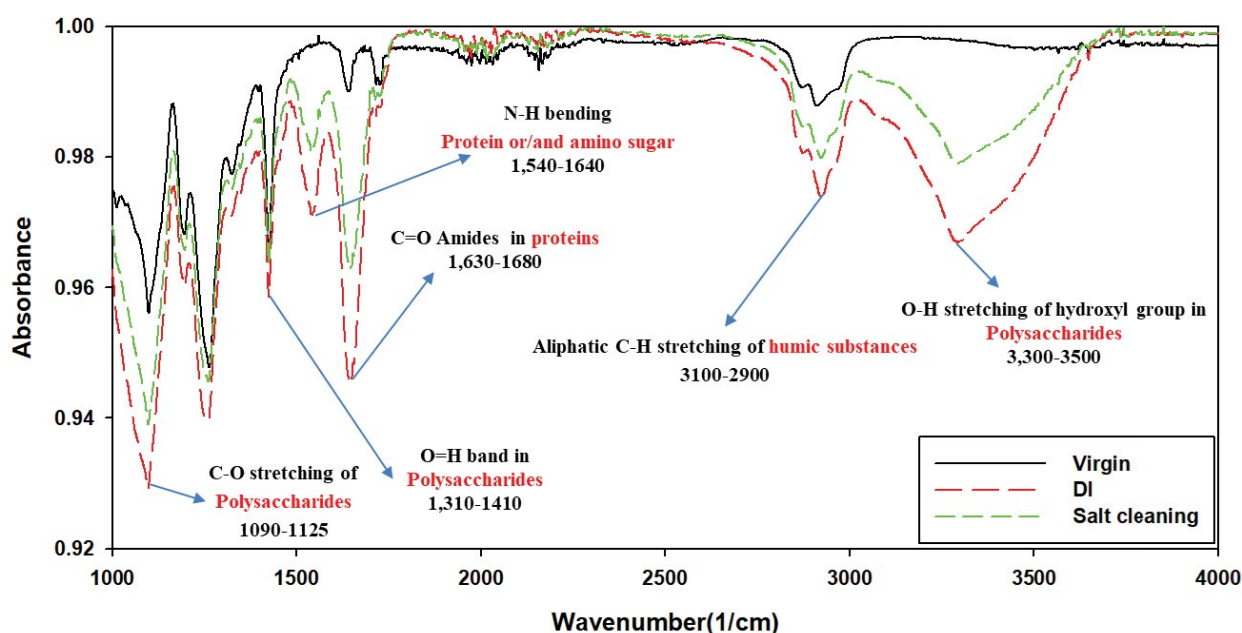


Fig. 14. FTIR measurements with virgin membrane, membrane after DI water cleaning, and membrane after salt cleaning.

(i) osmotic disruption resulting in the loose of fouling layer and (ii) cross-transport of Ca^{2+} and Na^+ in the boundary of the fouling layer. Later, this description was proved to be quite reasonable based on other experimental results including FEEM and FTIR results. These salt cleaning mechanisms were confirmed through FEEM and FTIR analyses showing that EfOM foulants accumulated on the membrane surface eluted significantly after salt cleaning. Next, when EfOM substances used in combination, salt cleaning was also effective to recover the flux declined during fouling by mixed EfOM containing HA, SA, and BSA. In general, salt cleaning efficiency increased with increasing the SA content of the mixed EfOM. This implies that salt cleaning can be a promising tool to effectively clean the fouled membrane during wastewater reclamation as the polysaccharide-like substances have been considered to be one of the most important EfOM substances.

The applicability of salt cleaning has been investigated using real secondary wastewater effluent. The results showed that salt cleaning could recover to some extent the flux declined after the filtration of the secondary wastewater effluent. In addition, the continuous flux decline during MF of the secondary wastewater effluent was efficiently prevented by the periodic application of salt cleaning. Therefore, proper salt cleaning for the purpose of maintenance could lead to preventing the frequent application of CIP which may cause problems such as membrane damage and cleaning waste disposal. Based on the result shown in this study, it can be suggested that salt cleaning could be an economical and green sustainable solution to solve EfOM fouling during wastewater reclamation.

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