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Fouling-induced wetting of membranes in membrane distillation (MD) systems

Bomin Kim, Hyeongrak Cho, Jihyeok Choi, Jinsik Sohn, Sangho Lee*

School of Civil and Environmental Engineering, Kookmin University, Jeongneung-Dong, Seongbuk-Gu, Seoul, 136-702, Korea, Tel. +82-2-910-4529; Fax: +82-2-910-4939; email: sanghlee@kookmin.ac.kr (S. Lee), Tel. +82-2-910-5060; Fax: +82-2-910-8597; emails: bo6036@gmail.com (B. Kim), rhino@kookmin.ac.kr (H. Cho), cjh6563@gmail.com (J. Choi), jinsiksohn@kookmin.ac.kr (J. Sohn)

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ABSTRACT

One of the challenges of membrane distillation (MD) technology is the wetting of the membranes. However, relatively little information is available on membrane wetting induced by fouling in MD process. Accordingly, this study examines the MD membrane wetting caused by fouling under various conditions. Various feed solutions containing NaCl, $CaSO_4$, humic acid, alginate, and SDS were compared using polyvinylidene fluoride and polytetrafluoroethylene membranes in a series of MD experiments. Scanning electron microscope (SEM), liquid entry pressure and dynamic contact angle were used to interpret the results from the MD wetting experiments. Results showed that wetting was induced by severe fouling in the cases of 200,000 mg L^{-1} NaCl solution and 200,000 mg L^{-1} NaCl and 2,000 mg L^{-1} $CaSO_4$ solution. The organic matters (50 mg L^{-1} humic acid and 50 mg L^{-1} alginate) did not cause neither fouling nor wetting by themselves. On the other hand, the addition of 50 mg L^{-1} SDS accelerated wetting. Based on these experimental results, the wetting potentials for various combinations of foulants are presented.

Keywords: Membrane distillation (MD); Membrane wetting; Measurement; Prediction; Liquid entry pressure; Contact angle

1. Introduction

Membrane distillation (MD) is an emerging technology that can overcome the current limitations of reverse osmosis (RO) [1–4]. It is a thermally-driven separation process, in which only vapors transfer through a microporous hydrophobic membrane [3,5–7]. MD membranes are made of hydrophobic polymeric materials such as polyvinylidene fluoride (PVDF), polypropylene, and polytetrafluorethylene (PTFE) [4,8–12]. MD can treat high salinity feed solutions that RO cannot, including RO brine and wastewaters from shale gas industry [6,7,13,14]. MD can be easily combined with low grade energy sources, including solar thermal energy and waste heat from manufacturing or power plant [15–17].

However, as the feed solution is concentrated, the hydrophobicity of the MD membranes gradually decreases, leading to the penetration of feed water into the pores [18–21]. This phenomenon is called the wetting of membranes [22,23]. Membrane wetting is generally observed during the long-term operation of the MD process [24]. Factors affecting membrane wetting include transmembrane pressure, capillary condensation, scale deposition (inorganic fouling), organic fouling, surfactants, and membrane degradation [8,19,23,25]. The membrane wetting reduces the quality of product water and changes the flux through the membrane [21,26]. If no hydraulic pressure is applied, the flux is reduced due to membrane wetting. But the flux may increase if there is a net pressure difference between the feed and distillate side. Once the membrane wetting occurs, it is difficult to recover the membranes to their initial state [18,19]. This is why the membrane wetting is one of the most critical problems in MD [19,27].

Although many works have attempted to analyze the wetting phenomena in MD, there is still limited information available on its mechanism and prediction [23]. Moreover,

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* Corresponding author.

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there has been no systematic approach to elucidate how different foulants can lead to wetting in MD systems under various conditions [18,28,29]. The effect of interactions among different foulants on wetting has not been investigated yet. In this context, the objective of this study is to examine the MD membrane wetting induced by fouling under various conditions to broaden current understanding of mechanisms of wetting by different foulants. The results were analyzed in comparison with the parameters such as contact angle (CA) and liquid entry pressure (LEP) to provide insight into fundamental understanding of wetting phenomena in MD processes.

2. Materials and methods

2.1. MD membranes

Two hydrophobic microporous membranes were used in the experiments to compare wetting and fouling behaviors. The membrane used in the experiments were purchased from Merck Millipore Ltd of USA. One of them of was made of PVDF and the other one was made of PTFE. The characteristics of each membrane are shown in Table 1.

2.2. Feed solution

The model foulants used in this study were NaCl, $CaSO_4$, humic acid, and alginate. As an amphiphilic compound, sodium dodecyl sulfate (SDS) was used. The feed solutions were prepared by combining these foulants and SDS. The concentrations of the foulants were set to be high for accelerated fouling tests. The details on the experimental conditions are summarized in Table 2.

Table 1
Properties of PVDF and PTFE membranes

Product name	PVDF	PTFE
	GVHP (Millipore)	FGLP (Millipore)
Pore size (μm)	0.22	0.2
Thickness (μm)	125	150
Porosity (%)	75	85
Liquid entry pressure, LEP (bar)	1.91 ± 0.22	5.03 ± 0.14
Contact angle, CA (◦)	126.78 ± 1.0	140.3 ± 0.6

2.3. Direct contact membrane distillation wetting experiments

Each experiment was carried out to measure the propensity of wetting (or wetting potential) at a given condition. The experimental setup for direct contact MD (DCMD) is schematically illustrated in Fig. 1. The membrane cell was made of acrylic resin and its depth, width, and length were 2, 20, and 60 mm, respectively. The effective membrane area was 0.0012 m^2. The temperature and flow rates were maintained at 60°C and 0.7 L min^{-1} for the feed and 20°C and 0.4 L min^{-1} for the distillate. The volumes of feed solution and distillate were 1.0 and 1.5 L. The flow velocity of feed and permeate side through the membrane was 29.17 and 16.67 cm s^{-1}, respectively. The pressure differences between feed and permeate sides were negligible. The DCMD was operated with brine recycle and the feed solution was concentrated during the operation. The flux and distillate conductivity were continuously measured. In the beginning, the initial flux values for the PVDF and PTFE membranes were 12.0±0.5 and 26.0±1.0 kg m^{-2} h^{-1}, respectively. Thus, the flux results were expressed as the normalized flux, which is defined as the ratio of the flux at time t (J) to the initial flux (J_0).

The durations of experiments were different because wetting occurred at different times under different conditions. When wetting occurred near the beginning of the operation, it was impossible to carry out the experiment up to 30 h. Accordingly, the durations were adjusted depending on the progress of wetting and the minimum and maximum durations were set to 15 and 30 h, respectively.

2.4. Determination of LEP

The LEP of the membranes were compared before and after the experiments. LEP is the pressure at which the liquid starts to penetrate the pores of the membrane, until the liquid passes through the membrane [4,19]. The LEP of membranes was measured as the hydraulic pressure was applied to the solution before the penetration of the solution through the

Table 2
Summary of experimental conditions

Component	Feed solution
Inorganic	NaCl (200,000 mg L^{-1})
	NaCl (200,000 mg L^{-1}) + SDS (50 mg L^{-1})
	$CaSO_4$ (2,000 mg L^{-1})
	$CaSO_4$ (2,000 mg L^{-1}) + SDS (50 mg L^{-1})
	NaCl (200,000 mg L^{-1}) + $CaSO_4$ (2,000 mg L^{-1})
	NaCl (200,000 mg L^{-1}) + $CaSO_4$ (2,000 mg L^{-1}) + SDS (50 mg L^{-1})
Organic	Humic acid (50 mg L^{-1}) + alginate (50 mg L^{-1})
	Humic acid (50 mg L^{-1}) + alginate (50 mg L^{-1}) + SDS (50 mg L^{-1})
Inorganic + Organic	NaCl + $CaSO_4$ (2,000 mg L^{-1}) + humic acid (50 mg L^{-1}) + alginate (50 mg L^{-1})
	NaCl + $CaSO_4$ (2,000 mg L^{-1}) + humic acid (50 mg L^{-1}) + alginate (50 mg L^{-1}) + SDS (50 mg L^{-1})

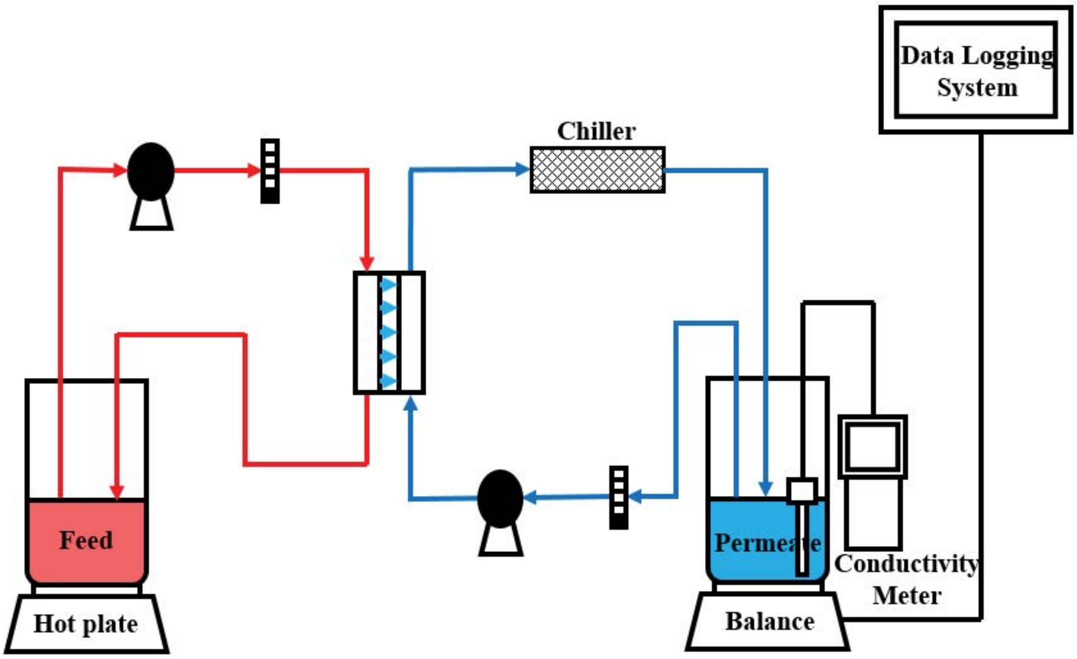


Fig. 1. Schematic diagram of laboratory scale DCMD system.

pores. The LEP values of the virgin membranes are shown in Table 1.

2.5. Determination of CA

The CA of the membranes was also compared before and after the experiments. In each case, CA was determined by measuring the angle between the membrane surface and the water drop on the membrane surface. As the wettability increases and the hydrophobicity of the membrane decreases, the CA decreases. CA was measured from six different places on each membrane and the average and standard deviations were presented. Table 1 shows the CA values of the PVDF and PTFE membranes.

2.6. Field emission scanning electron microscope

After the experiment, the surfaces of the membranes were observed using field emission scanning electron microscope (FE-SEM). A field emission electron microscope (JSM-7610F Prime) was used to identify morphology of scaling on membrane surface. In order to observe morphology of scaling, membranes were dried and coated by platinum. FE-SEM images confirmed the scale formation size and the pore clogging according to each experiments.

2.7. Pore size distribution

Capillary flow porometer (CFP-1500AEL) was used to measure pore size distributions of MD membranes before and after the experiments. First, the membrane samples were completely wetted using test solutions with constant surface tension. Then, the flow rates of air passing through the sample to the bottom were measured while the air pressure at the top of the sample varied. Based on these results, the pore size distributions were calculated.

3. Result and discussion

3.1. Wetting and fouling caused by inorganic and organic foulants

3.1.1. Inorganic foulants

Fig. 2 shows the changes in flux and conductivity for the PVDF and PTFE membranes during the MD experiments of feed solutions containing inorganic foulants such as NaCl and $CaSO_4$. The occurrence of wetting was detected by monitoring the permeate conductivity: If there is a significant increase in the permeate conductivity, it is likely that wetting occurs. As shown in Fig. 2a, which is the case that the feed solution containing NaCl of 200,000 mg L^{-1}, the conductivities increased at the operation time of 18 h for PVDF membrane and 8 h for PTFE membrane, indicating that wetting occurred in both membranes. Rapid declines of the flux were observed at 15 h for the PVDF membrane and 6 h for the PTFE membrane. Despite the difference of material and structure of PVDF and PTFE, the tendencies for fouling and scaling of the membrane surface were similar as shown in Fig. 3. Therefore, it can be concluded that the propensities of the fouling and wetting in these two membranes were similar except for the wetting time. The rate of flux decline was higher for the PTFE membrane than for the PVDF membrane because the initial flux for the PTFE membrane (~26 kg m^{-2} h^{-1}) was higher than that for the PVDF membrane (~12 kg m^{-2} h^{-1}).

As shown in Figs. 2a and c, the flux declined and conductivity increased when the solutions of NaCl 200,000 mg L^{-1} and NaCl 200,000 mg L^{-1} with $CaSO_4$ 2,000 mg L^{-1} were used as feeds. On the other hand, the flux declined but the conductivity did not increase for

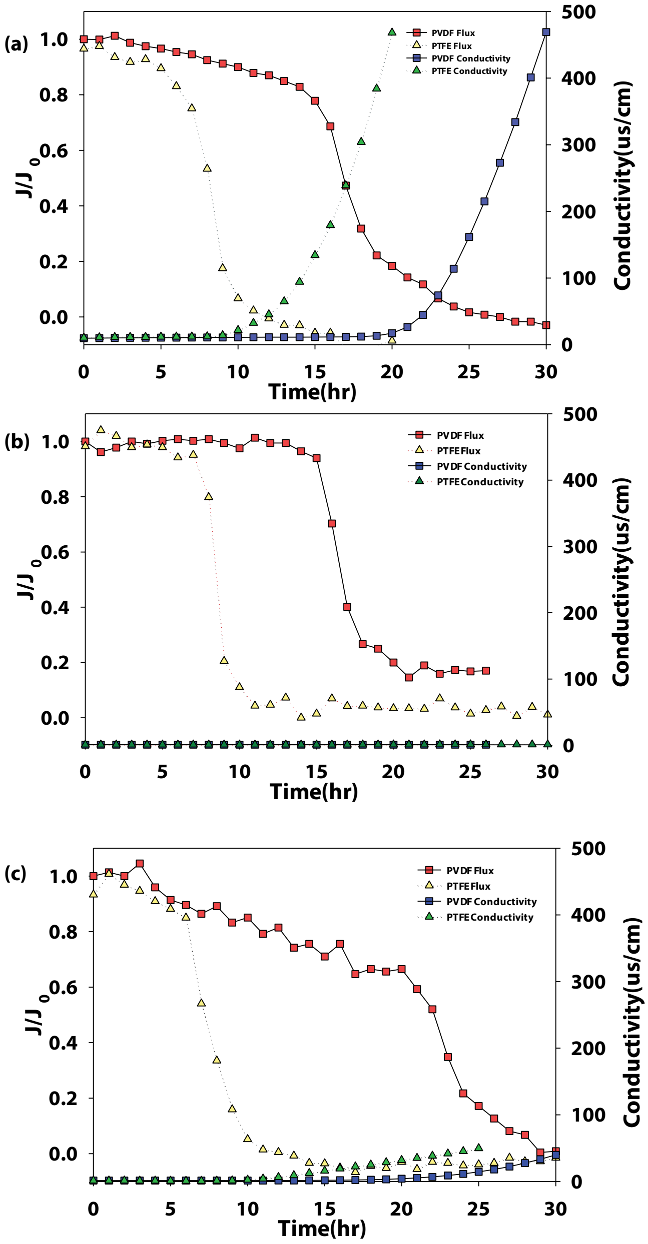


Fig. 2. Dependence of normalized flux and conductivity on time for PVDF and PTFE membranes using different feed solutions. (a) NaCl 200,000 mg L^{-1}, (b) $CaSO_4$ 2,000 mg L^{-1}, (c) NaCl 200,000 mg L^{-1} + $CaSO_4$ 2,000 mg L^{-1}.

the $CaSO_4$ 2,000 mg L^{-1} feed solution as shown in Fig. 2b. Accordingly, it was concluded that fouling and wetting occurred simultaneously with the feeds were the solutions of NaCl 200,000 mg L^{-1} and NaCl 200,000 mg L^{-1} with $CaSO_4$ 2,000 mg L^{-1}. On the other hand, only fouling occurred with the $CaSO_4$ 2,000 mg L^{-1} feed solution. As a matter of fact, fouling occurred prior to wetting. According to previous studies, the crystals of inorganic salts are formed not only on the membrane surface but also inside the pore walls. This leads to make the membranes more hydrophilic and the possibility of wetting increases.

Experiments were repeated using the feed solution containing $CaSO_4$ of 2,000 mg L^{-1} and results are shown in Fig. 2b. The flux decline was observed at the operation time of 16 h for the PVDF membrane and 5 h for the PTFE membrane. However, unlike the case with the NaCl feed solution, there was no increase in the feed conductivity during the operation time of 26 h for PVDF and 30 h for PTFE. This may be attributed to the different properties of inorganic crystals. If the crystallization occurs mainly on the surface of the membrane and the crystals cover the surface of membranes, pore wetting may not happen. As shown in Figs. 3a and b, the $CaSO_4$ crystals are larger than NaCl crystals and appear to exist only on the membrane surfaces.

Fig. 2c shows the case that the feed water containing NaCl of 200,000 mg L^{-1} and $CaSO_4$ of 2,000 mg L^{-1} was used for the MD experiment. Rapid drops in flux were found at 20 h for the PVDF membrane and 5 h for the PTFE membrane. The feed conductivity increased with time but it was not significantly high compared with the results in Fig. 2b. It is interesting to note that the mixtures of NaCl and $CaSO_4$ resulted in less severe wetting than NaCl. To interpret this, the following mechanism was proposed: As previously mentioned, the NaCl crystallization occurred not only on the membrane surface but also inside the pores but $CaSO_4$ crystallization occurred mainly on the membrane surface [30,31]. When both NaCl and $CaSO_4$ exist together, it appears that the NaCl crystal growth inside the pores may be interfered by the surface crystallization of $CaSO_4$. Since the surface of the membrane is blocked by the $CaSO_4$ scale formation, it causes fouling but retards the wetting.

This mechanism is supported by the SEM images. As expected, the size of the crystals in the presence of both NaCl and $CaSO_4$ (Fig. 3c) is larger than the NaCl crystals (Fig. 3a) but smaller than the $CaSO_4$ crystals (Fig. 3b). A larger amount of crystals were found in the case of the $CaSO_4$ solution (Fig. 3b) than the other feed solutions (Figs. 3a and c). This implies that $CaSO_4$ crystals were preferentially deposited on the membrane surface.

The SEM images for the cross-sections of the membranes are shown in Fig. 4. The crystals were observed inside the membranes when the NaCl solution and the NaCl/$CaSO_4$ solution were used as feeds (Figs. 4a and c). On the other hand, a thick layer of surface crystals was found in the case of the $CaSO_4$ solution (Fig. 4b). These results also support the proposed mechanism.

Fig. 5 shows the pore size distributions that were measured before and after MD experiments. In the case of PVDF membranes (Fig. 5a), the large pores were found at about 0.65–0.7 μm before the MD experiment. After the experiment, using the $CaSO_4$ solution, the size of large pores decreased to 0.58 μm. After the MD experiments using the NaCl solution and NaCl/$CaSO_4$ solution, the sizes were reduced to 0.46 and 0.48 μm. In the case of PTFE membranes (Fig. 5b), the pore sizes were slightly reduced when the NaCl solution and NaCl/$CaSO_4$ solution were used. But the difference was smaller in the PTFE membranes than in the PVDF membranes. This is probably because there were not many large pores in the PTFE membranes and their pore size distributions are more uniform than those of PVDF membranes.

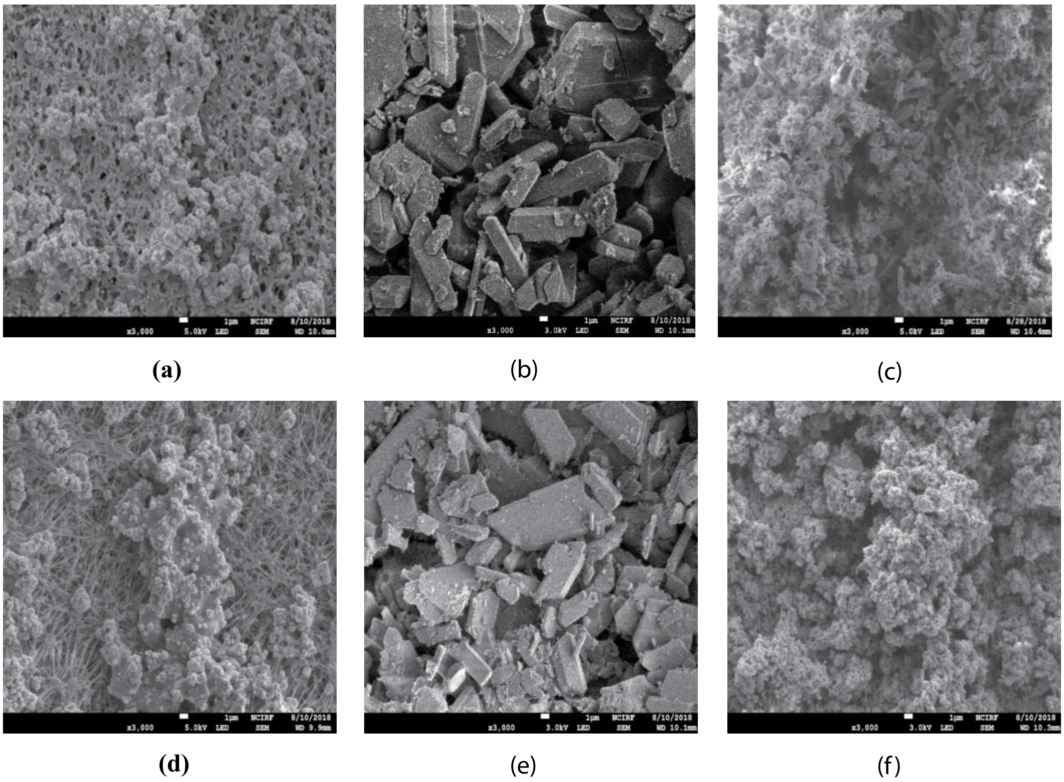


Fig. 3. SEM images of foulants on the membranes using different feed solutions. (a) PVDF membrane, NaCl 200,000 mg L^{-1}, (b) PVDF membrane, $CaSO_4$ 2,000 mg L^{-1}, (c) PVDF membrane, NaCl 200,000 mg L^{-1} + $CaSO_4$ 2,000 mg L^{-1}, (d) PTFE membrane, NaCl 200,000 mg L^{-1}, (e) PTFE membrane, $CaSO_4$ 2,000 mg L^{-1}, and (f) PTFE membrane, NaCl 200,000 mg L^{-1} + $CaSO_4$ 2,000 mg L^{-1}.

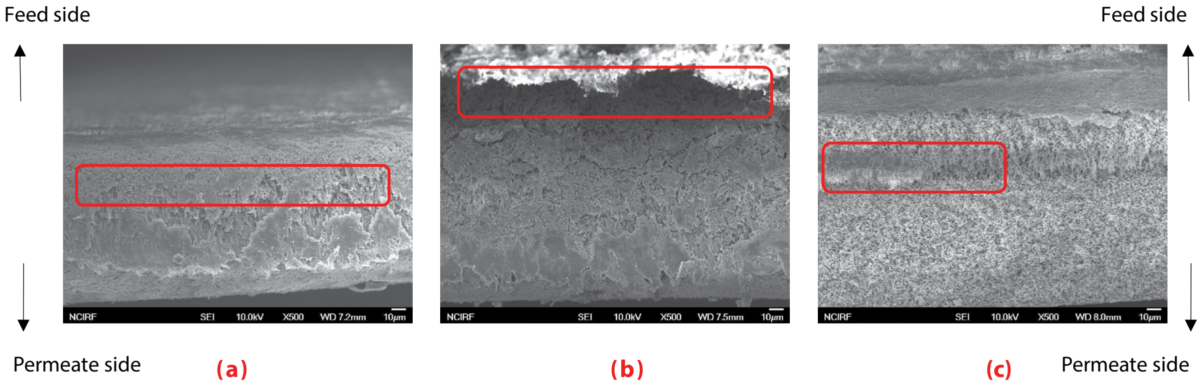


Fig. 4. Cross-sectional SEM images of foulants penetrating the membrane pores using inorganic feed solutions. Cross-sectional SEM images of PVDF membranes (a) NaCl 200,000 mg L^{-1}, (b) $CaSO_4$ 2,000 mg L^{-1}, and (c) NaCl 200,000 mg L^{-1} + $CaSO_4$ 2,000 mg L^{-1}. The red circles indicate crystal deposits.

3.1.2. Organic foulants

Fig. 6 shows the variations of flux and feed conductivity with time during the treatment of feed solution containing humic acid of 50 mg L^{-1} and alginate of 50 mg L^{-1}. Unlike the previous cases, neither fouling nor wetting was observed with the operation time, implying that the effect of the organic matters under those concentrations is negligible [32]. However, the SEM images in Fig. 7 show that the organic matters were deposited on the membrane surface. In other words, the deposition of the organic matters did not cause wetting as well as fouling. This is attributed to high permeability of such organic layers on the membrane surface, which do not affect the transport of water or vapor. Similar results were also reported in previous works [32–34].

3.1.3. Inorganic and organic foulants

The results of MD experiments using the feed solution containing NaCl, $CaSO_4$, humic acid, and alginate are illustrated in Fig. 8. The changes in flux and feed conductivity were similar to those in Fig. 2c. This finding can be

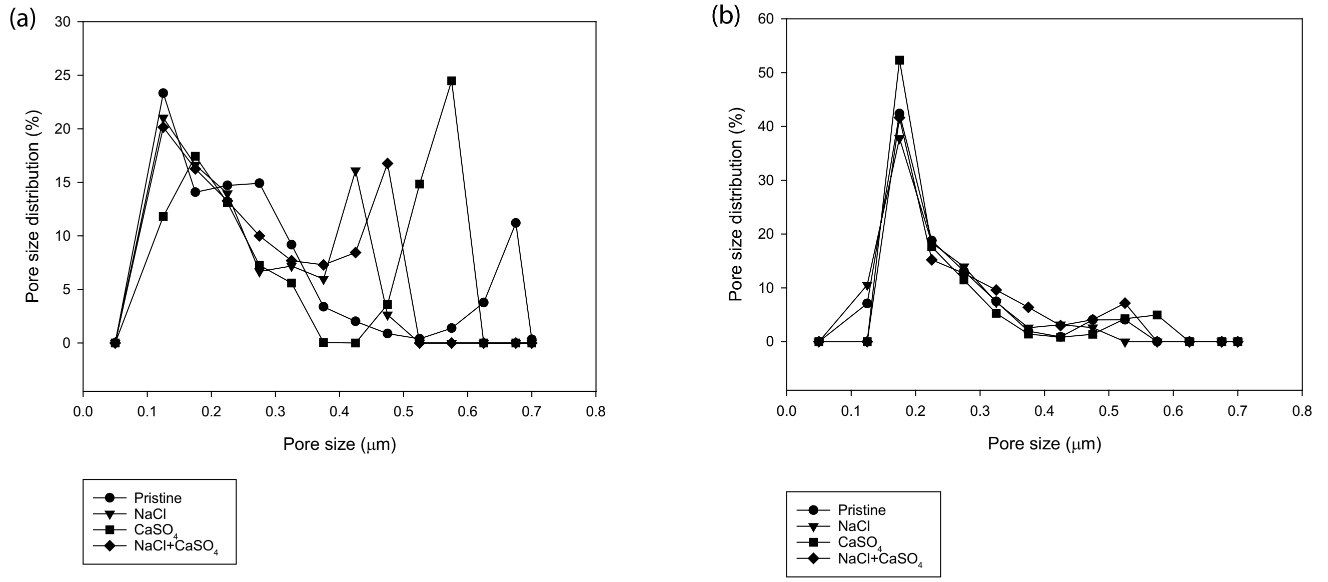


Fig. 5. Comparison of pore size distributions for MD membranes before and after the experiments. (a) PVDF membranes and (b) PTFE membranes.

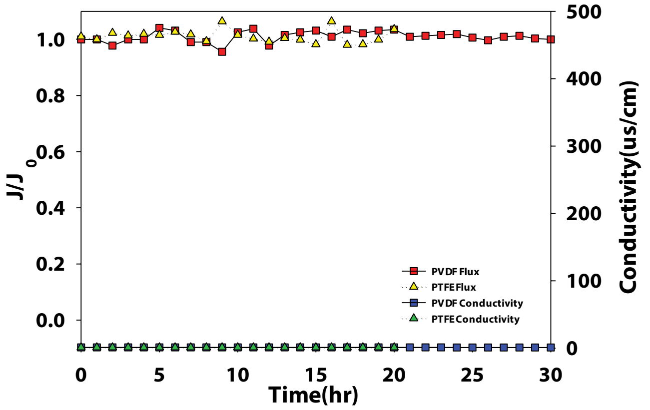


Fig. 6. Dependence of normalized flux and conductivity on time for PVDF and PTFE membranes using different feed solutions (HA 50 mg L^{-1} + AG 50 mg L^{-1}).

interpreted that the organic matters in the feed solution did not affect the wetting and fouling caused by the inorganic salts. As shown in Fig. 9, the organic matters appear to exist in the foulant layers on the membrane surface, leading to the slightly different morphologies. Nevertheless, it does not seem to be important enough in terms of wetting and fouling.

3.2. Effect of SDS on wetting and fouling by inorganic and/or organic foulants

3.2.1. Inorganic foulants with SDS

The addition of SDS on the feed solution affects the membrane properties. Table 3 shows the CAs and LEPs measured using the feed solution containing SDS of 50 mg L^{-1}. The CA reduced from 126.78° to 110.0° for the PVDF membrane and from 140.3° to 129° for the PTFE membrane. However, the changes in LEP were not significant. In the case of the PVDF membrane, the LEP was not changed by the addition of SDS (1.91 ± 0.22 bar → 1.92 ± 0.20 bar). In the case of the PTFE membrane, the LEP was slightly reduced from 5.03 ± 0.14 bar to 4.60 ± 0.31 bar. These results can be interpreted that the surface energy of the membranes was changed but the LEP was not significantly affected by the addition of SDS.

Fig. 10a depicts the flux and feed conductivity as a function of time in the presence of NaCl 200,000 mg L^{-1} and SDS 50 mg L^{-1}. Increases in the feed conductivity were found at 1 h for the PVDF membrane and 6 h for the PTFE membrane. Compared with Fig. 2a, which is the case of NaCl 200,000 mg L^{-1}, the wetting of membrane was accelerated by the addition of SDS. Moreover, more rapid flux declines were observed in the presence of SDS. Since SDS is a surfactant, it can reduce the hydrophobicity of the membranes, thereby resulting in rapid wetting of the membrane. It also causes the reduction in flux because the number of pores for vapor transport decreased with pore wetting.

The variations of flux and feed conductivity for the treatment of feed water containing $CaSO_4$ 2,000 mg L^{-1} and SDS 50 mg L^{-1} are presented as a function of time in Fig. 10b. The flux decline occurred at 1 h for the PVDF membrane and 8 h for the PTFE membrane, indicating that fouling was accelerated. Toward the end of the experiments, the feed conductivity slightly increases, indicating wetting. Considering the fact that there was no wetting by $CaSO_4$ scaling without SDS, the results can be interpreted that SDS induced wetting. It seems that the reduction in the hydrophobicity by SDS led to the penetration of feed water into some pores (partial wetting) [25].

Fig. 10c shows flux and feed conductivity in the cases that the feed contains NaCl 200,000 mg L^{-1}, $CaSO_4$ 2,000 mg L^{-1}, and SDS 50 mg L^{-1}. Again, wetting and fouling were accelerated by the addition of SDS. In the case of the PVDF membrane, the flux became zero within 2 h due to the

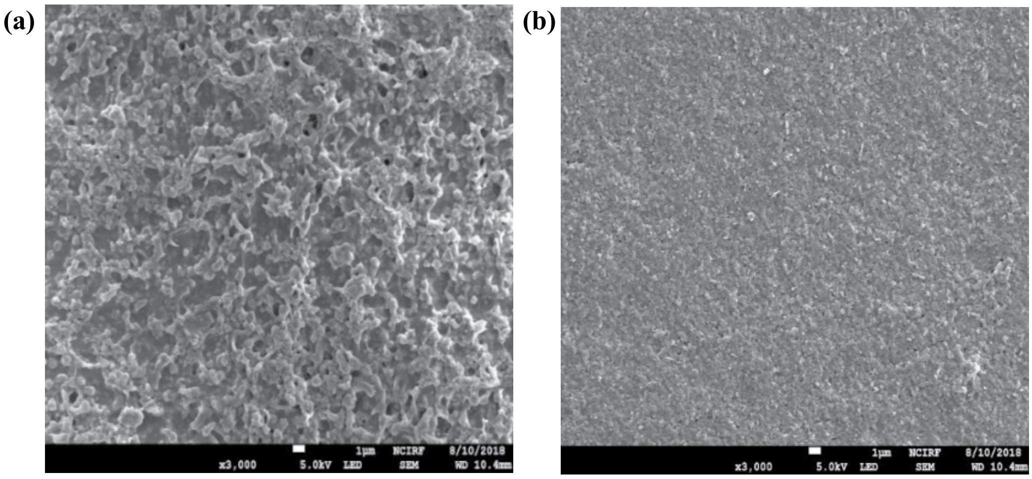


Fig. 7. SEM images of foulants on the membranes using different feed solutions. (a) PVDF membrane, HA 50 mg L^{-1} + AG 50 mg L^{-1}, (b) PTFE membrane, HA 50 mg L^{-1} + AG 50 mg L^{-1}.

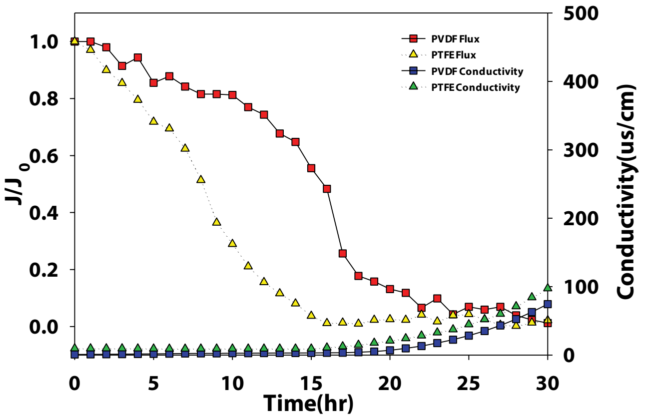


Fig. 8. Dependence of normalized flux and conductivity on time for PVDF and PTFE membranes using different feed solutions (NaCl 200,000 mg L^{-1} + $CaSO_4$ 2,000 mg L^{-1} + HA 50 mg L^{-1} + AG 50 mg L^{-1}).

severe fouling. In the case of PTFE membrane, the degrees of wetting became higher by SDS addition. If there is an enough pressure difference between the feed and permeate sides, pore wetting may result in flux increase. However, in this study, the feed and permeate pressures were almost same. Moreover, it seems that only a small portion of the pores were wetted (partial wetting). Accordingly, the flux did not increase with the occurrence of wetting.

The SEM images of the inorganic foulants on the membrane surfaces in the presence of SDS are compared in Fig. 11. Although the flux decline was more severe in the presence of SDS, the amounts of foulants seem to be smaller compared with the case without SDS (Fig. 3). This suggests that the flux decline could be caused by wetting as well as fouling. Since there is no transport of water vapor through the wetted pores, flux is reduced by wetting. In addition, water cannot be transported if there is no transmembrane pressure. Thus, it can be concluded that the existence of surfactants such as SDS results in not only wetting but also flux decline.

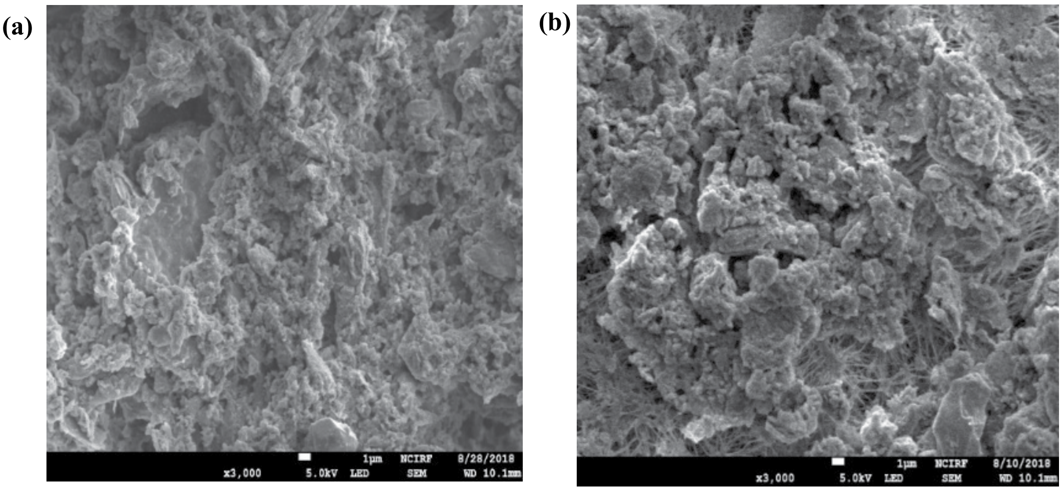
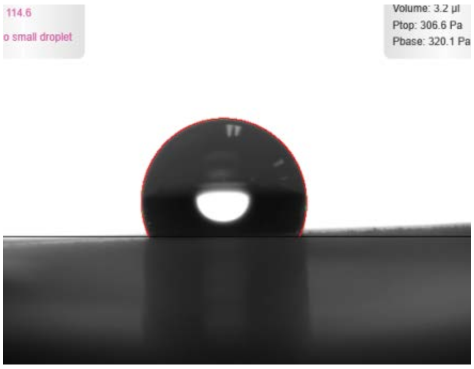
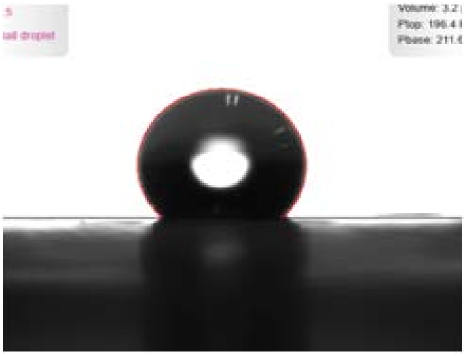


Fig. 9. SEM images of foulants on the membranes using different feed solutions. (a) PVDF membrane, NaCl 200,000 mg L^{-1} + $CaSO_4$ 2,000mg L^{-1} + HA 50 mg L^{-1} + AG 50 mg L^{-1}, (b) PTFE membrane, NaCl 200,000 mg L^{-1} + $CaSO_4$ 2,000 mg L^{-1} + HA 50 mg L^{-1} + AG 50 mg L^{-1}.

Table 3
CA and LEP values using only SDS 50 mg L^{-1}

	PVDF	PTFE
Contact Angle, CA (◦)		
	110 ± 5	129 ± 7
Liquid entry pressure, LEP (bar)	1.92 ± 0.20	4.60 ± 0.31

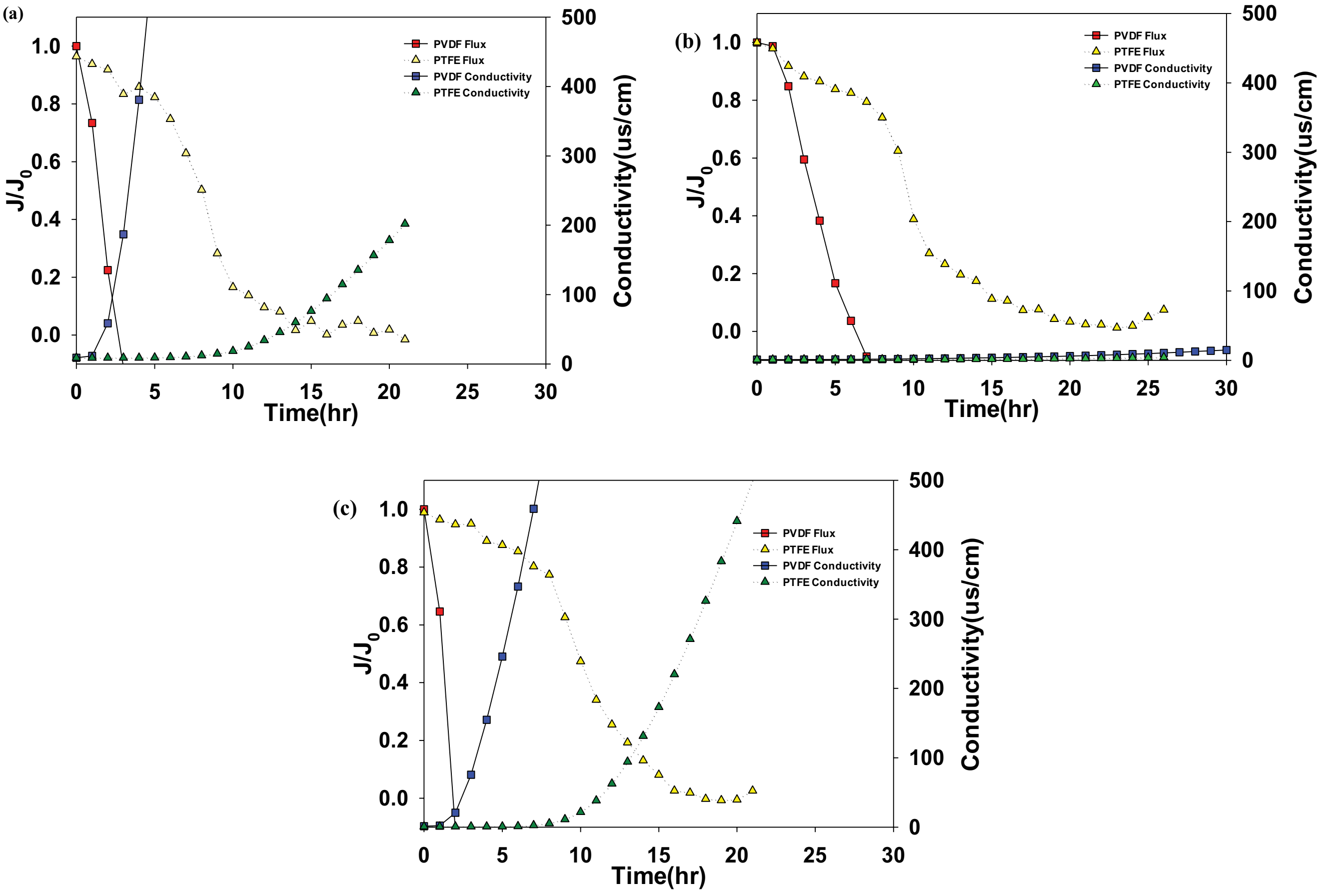


Fig. 10. Dependence of normalized flux and conductivity on time for PVDF and PTFE membranes using different feed solutions. (a) NaCl 200,000 mg L^{-1} + SDS 50 mg L^{-1}, (b) $CaSO_4$ 2,000 mg L^{-1} + SDS 50 mg L^{-1}, (c) NaCl 200,000 mg L^{-1} + $CaSO_4$ 2,000 mg L^{-1} + SDS 50 mg L^{-1}.

3.2.2. Organic foulants with SDS

Unlike the cases of inorganic foulants with SDS, no wetting was observed by SDS in the case of organic foulants in the feed water, as illustrated in Fig. 12. Although SDS reduces the hydrophobicity of the membranes, it does not seem to be enough to cause wetting in the presence of the organic matters. The SEM images shown in Fig. 13 are similar to

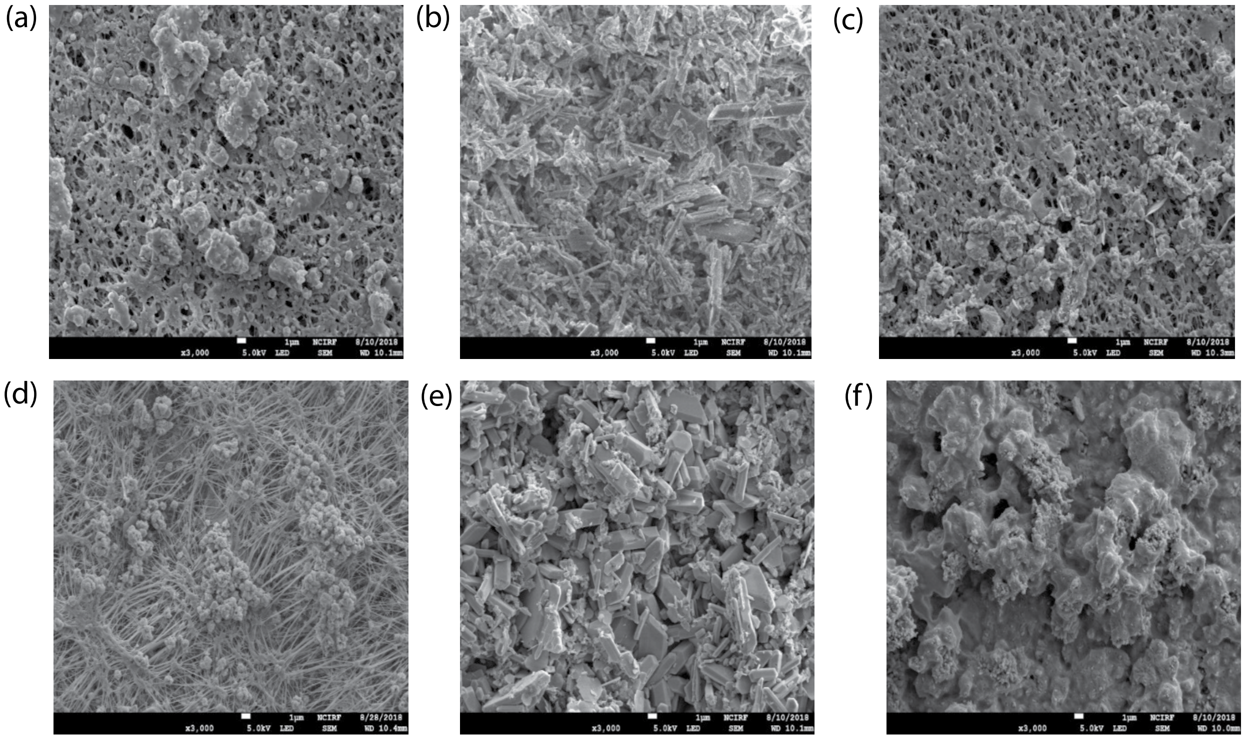


Fig. 11. SEM images of foulants on the membranes using different feed solutions. (a) PVDF membrane, NaCl 200,000 mg L^{-1} + SDS 50 mg L^{-1}, (b) PVDF membrane, $CaSO_4$ 2,000 mg L^{-1} + SDS 50 mg L^{-1}, (c) PVDF membrane, NaCl 200,000 mg L^{-1} + $CaSO_4$ 2,000 mg L^{-1} + SDS 50 mg L^{-1}, (d) PTFE membrane, NaCl 200,000 mg L^{-1} + SDS 50 mg L^{-1}, (e) PTFE membrane, $CaSO_4$ 2,000 mg L^{-1} + SDS 50 mg L^{-1}, (f) PTFE membrane, NaCl 200,000 mg L^{-1} + $CaSO_4$ 2,000 mg L^{-1} + SDS 50 mg L^{-1}.

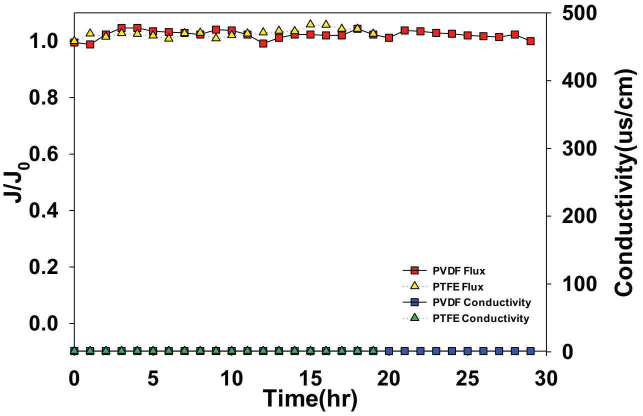


Fig. 12. Dependence of normalized flux and conductivity on time for PVDF and PTFE membranes using different feed solutions (HA 50 mg L^{-1} + AG 50 mg L^{-1} + SDS 50 mg L^{-1}).

those without SDS. This finding can be interpreted that the addition of 50 mg L^{-1} SDS was not enough to induce wetting and fouling by organic matters such as humic acid and alginate.

3.2.3. Inorganic and organic foulants with SDS

Fig. 14 shows the flux and feed water conductivity as a function of time for the feed water containing NaCl of 200,000 mg L^{-1}, $CaSO_4$ of 2,000 mg L^{-1}, humic acid of 50 mg L^{-1}, alginate of 50 mg L^{-1}, and SDS of 50 mg L^{-1}. As expected, SDS increases the rate of wetting and flux decline. In both membranes, the flux rapidly decreased from the beginning. The feed conductivity increased faster in the PVDF membrane than in the PTFE membrane, suggesting that the progress of wetting was faster in the PVDF membrane. This is attributed to the combined effect of inorganic foulants, organic matters, and SDS. Although the PTFE membrane is more hydrophobic, the adsorption of organic matters and SDS reduces its hydrophobicity. However, high hydrophobicity of PTFE membrane is somewhat resistant to the SDS of 50 mg L^{-1}. The SEM images are presented in Fig. 15, indicating that the morphologies of the foulants on the surfaces for the two membranes were different. Although the membranes were not fully covered by the foulants, the flux was low in both cases. This can be interpreted that the flux decline resulted from not only fouling but also wetting.

3.3. Changes in contact angle and liquid entry pressure by wetting

After each MD experiment, the membrane was taken from the module and its CA and LEP were measured. If these properties are changed, it is likely that the wetting property of the membrane is also changed. The results are summarized in Table 4. As expected, the CA and LEP were substantially reduced in the cases that the wetting phenomena were observed. On the other hand, the CA and LEP were not greatly changed for the feed solutions that did not result in wetting.

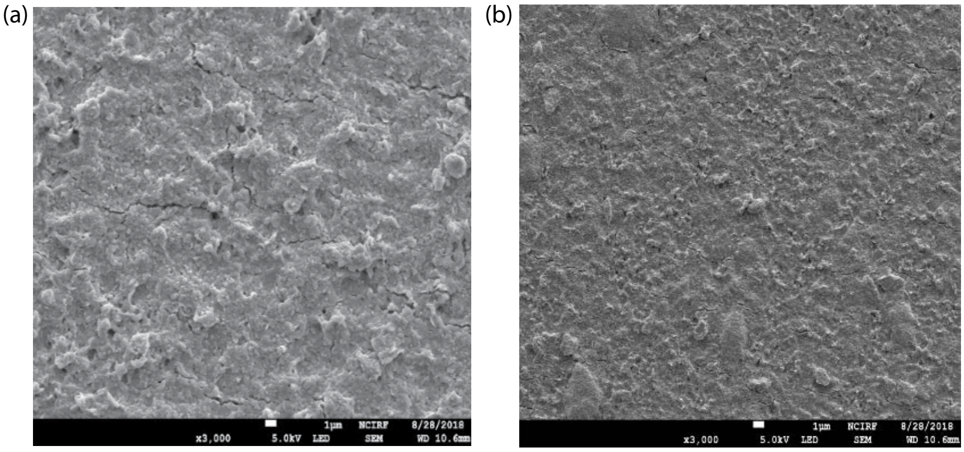


Fig. 13. SEM images of foulants on the membranes using different feed solutions. (a) PVDF membrane, HA 50 mg L^{-1} + AG 50 mg L^{-1} + SDS 50 mg L^{-1}, (b) PTFE membrane, HA 50 mg L^{-1} + AG 50 mg L^{-1} + SDS 50 mg L^{-1}.

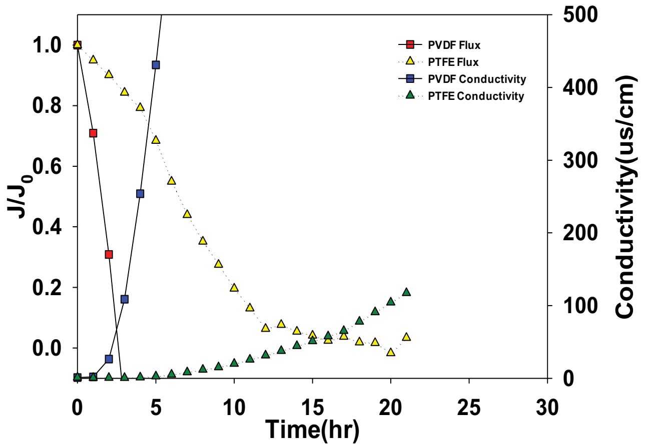


Fig. 14. Dependence of normalized flux and conductivity on time for PVDF and PTFE membranes using different feed solutions (NaCl 200,000 mg L^{-1} + $CaSO_4$ 2,000 mg L^{-1} + HA 50 mg L^{-1} + AG 50 mg L^{-1} + SDS 50 mg L^{-1}).

3.4. Correlation of fouling and wetting with feed water compositions

Table 5 summarizes a qualitative correlation between feed composition and wetting caused by fouling. The high TDS solution including NaCl of 200,000 mg L^{-1} resulted in both fouling and wetting but the $CaSO_4$ solution only caused fouling. If NaCl and $CaSO_4$ were mixed, the wetting propensity was reduced due to the interference of $CaSO_4$ scales with wetting by NaCl crystals. With the addition of SDS, the $CaSO_4$ solution results in a moderate wetting because the hydrophobicity of the membrane was reduced. The feed solution containing HA and AG did not cause wetting and fouling without and with SDS, indicating that their wetting potential was low. When all the foulants and SDS were included in the feed solution, wetting was observed as well as flux decline. Due to the higher initial flux, the PTFE membrane showed higher wetting tendency than the PVDF membrane although the initial hydrophobicity of the PTFE membrane is higher. In summary, the wetting potential for foulants in feed waters is systematically presented in Table 5, which helps to qualitatively predict the occurrence of wetting.

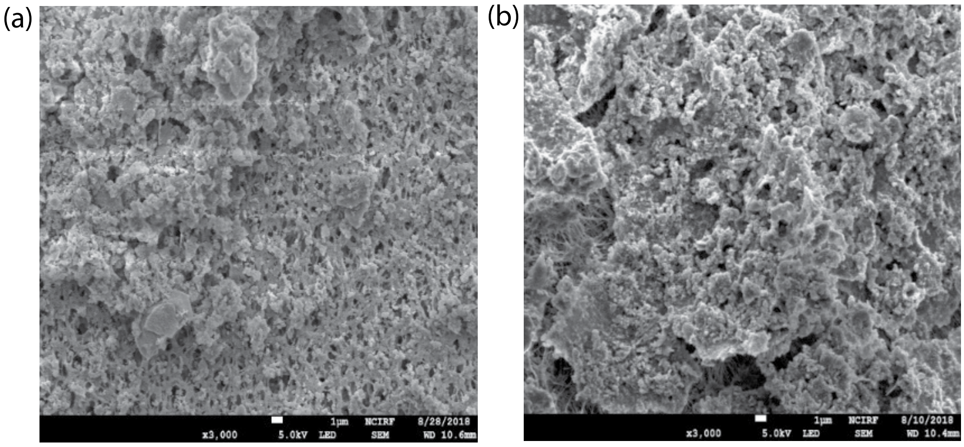


Fig. 15. SEM images of foulants on the membranes using different feed solutions. (a) PVDF membrane, NaCl 200,000 mg L^{-1} + $CaSO_4$ 2,000 mg L^{-1} + HA 50 mg L^{-1} + AG 50 mg L^{-1} + SDS 50 mg L^{-1}, (b) PTFE membrane, NaCl 200,000 mg L^{-1} + $CaSO_4$ 2,000 mg L^{-1} + HA 50 mg L^{-1} + AG 50 mg L^{-1} + SDS 50 mg L^{-1}.

Table 4
Summary of contact angle and liquid entry pressure before and after MD experiments

Feed types	PVDF membrane		PTFE membrane	
	Contact angle (°)	Liquid entry pressure (bar)	Contact angle (°)	Liquid entry pressure (bar)
Control (before the experiments)	126.8	1.91	140.3	5.03
SDS	110.5	1.92	129.7	4.6
NaCl	81	1.49	123	2.7
NaCl + SDS	69	0.1	90	0.6
$CaSO_4$	0	2.08	0	4.5
$CaSO_4$ + SDS	0	1.24	0	1.6
NaCl + $CaSO_4$	69	1.33	77	2.68
NaCl + $CaSO_4$ + SDS	46	0.2	51	1
Humic acid + alginate	88	2.01	103	4.7
Humic acid + alginate + SDS	98	1.88	76	4.1
NaCl + $CaSO_4$ + humic acid + alginate	5	0.61	12.5	2.37
NaCl + $CaSO_4$ + humic acid + alginate + SDS	59	0.93	49	0.1

Table 5
Summary of MD experimental results for wetting potential analysis

Membrane	High TDS	Scale forming ions	Organics	SDS	Wetting	Fouling
PVDF	✓	–	–	–	○	○
	–	✓	–	–	×	○
	–	–	✓	–	×	×
	✓	✓	–	–	△	○
	✓	✓	✓	–	△	○
	–	–	–	✓	×	×
	✓	–	–	✓	○	○
	–	✓	–	✓	△	○
	–	–	✓	✓	×	×
	✓	✓	–	✓	○	○
	✓	✓	✓	✓	○	○
PTFE	✓	–	–	–	○	○
	–	✓	–	–	×	○
	–	–	✓	–	×	×
	✓	✓	–	–	△	○
	✓	✓	✓	–	△	○
	–	–	–	✓	×	×
	✓	–	–	✓	○	○
	–	✓	–	✓	△	○
	–	–	✓	✓	×	×
	✓	✓	–	✓	○	○
	✓	✓	✓	✓	○	○

✓: Included; –: not included; ○: significant; △: moderate; ×: negligible.

4. Conclusions

In this study, the wetting behaviors of MD membranes caused by fouling were analyzed through a series of laboratory scale MD experiments. The following conclusions were obtained:

- High TDS feed solution showed a high potential for wetting as well as fouling. However, scale-forming ions such as $CaSO_4$ did not result in wetting within the conditions considered in this study. This is attributed to different properties between NaCl crystals and $CaSO_4$ scales, which can be confirmed by SEM analysis.

- The organic matters such as humic acid and alginate resulted in negligible fouling and wetting. Although foulant layers were formed, they cause neither fouling nor wetting due to their porous properties.
- The addition of 50 mg L^{-1} SDS to the feed solutions containing inorganic ions accelerated the wetting of membranes. However, SDS did not induce the wetting by the organic matters.
- When the feed solution contained all the inorganic/organic foulants as well as SDS, a serious wetting was observed, leading to flux decline not only by fouling but also by pore wetting.
- Under the same operating conditions, the PTFE membranes showed a higher initial flux than the PVDF membrane. Accordingly, the extent of wetting was greater for the PTFE membrane.
- After the experiments, the CA and LEP were changed, which are related to wetting. The wetting caused by foulants in feed waters was systematically analyzed to provide a table that helps to qualitatively forecast wetting under a given feed composition.

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