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Two polymeric membranes, PTFE and PVDF, were employed in a direct contact membrane distillation system to investigate the effects of NaCl concentration, feed temperature, and flow rate on distillate flux and NaCl rejection. The distillate flux increases with increasing the feed flow rate or temperature, PTFE membrane has a higher distillate flux than that of PVDF, and PTFE membrane also has a larger solute rejection than that of PVDF membrane. The decrease of solute rejection by PVDF membrane is owing to the membrane pore wetting, especially at high feed temperature and flow rate. The membrane fouling tests under various feed compositions show that increasing NaCl concentration from 4.5 wt% to 10 wt% or the addition of $CaSO_4$ or BSA into NaCl solution does not cause severe fouling on the PTFE membrane. The distilled water flux recovery (FR) is about 0.96–0.97. The addition of $MgCl_2$ or $MgSO_4$ has a little significant fouling tendency, the distilled water FR is about 0.87–0.88.

Keywords direct contact membrane distillation; distillate flux; flux recovery; membrane fouling; PTFE; PVDF

INTRODUCTION

Membrane distillation (MD) is a thermally-driven separation process in which a hydrophobic microporous membrane separates a hot feed and a cold distillate. The hydrophobic nature of the membrane can prevent the wetting by the aqueous feed or distillate into the pores. The volatile components of the feed evaporate at the feed/membrane interface. These components subsequently diffuse through the air filling the membrane pores and condense at the other side of the membrane. When the condensation occurs at the membrane surface that a cold distillate stream is in direct contact with, the process is called the direct contact membrane distillation (DCMD). The driving force for water vapor transport is the vapor pressure difference which results from the temperature and composition of solutions at both the liquid-vapor interfaces.

The MD process is the combination of conventional distillation and membrane separations, and its main advantages are (1,2):

a. high purity in water product,
b. low operation pressure,
c. lower operating temperature than conventional distillation,
d. compactness in equipments,
e. heat integration ability with other heat source.

However, there are also some drawbacks that restrict the performance of the MD process, such as the transport resistances in the thermal and in the concentration boundary layers, exist in the fluids adjoining the membrane surface, and the problem of membrane fouling.

The transport resistances of the boundary layers can be reduced by increasing the disturbance near the membrane surface, such as inserting of channel spacers (3–5). And, the influences of temperature polarization and concentration polarization should be considered in modeling the performance of the MD process (6–8).

Because the membrane is in direct contact with the feed solution and the feed evaporates on the membrane surface, fouling is very likely to occur. The study about membrane fouling in DCMD showed that the accumulation rate of the membrane scale can be depressed by reducing the degree of polarization if NaCl solution was used as the feeding fluid; however, the depression effect was not obvious when real seawater was used as the feeding fluid (9). Other work indicated that when the NaCl concentration was higher than 25 wt%, the distillate flux decreased significantly, and the fouling rate was sensitive to the variances of the feed temperature and the flow rate (10). The treatment of wastewater by MD showed that the degree of membrane

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fouling increased with lowering feed temperature or increasing feed flow rate (11). In the case of concentrating the saline wastewater from animal intestines processing, the MD membrane was fouled not only by the NaCl, the presence of protein also caused membrane fouling (12). Membranes can be fouled by various constituents of the feed, such as polysaccharides, proteins, amino acid, humic substances, and multivalent ions in nanofiltration or ultrafiltration process (13,14).

The hydrophobic membranes, polyvinyldinefluoride (PVDF), and polytetrafluoroethylene (PTFE) are popularly used in the MD process for desalination application (15). However, the performance comparison between those membranes and the cause of membrane fouling due to various mono/multi-valent ions need to be studied further. In this work, the comparisons between the performances, the distillate flux, and the NaCl rejection, of those membranes in DCMD will be discussed. Experimental examinations will be conducted under various feed concentrations, flow rates, and temperatures. Then, the candidate membrane will be adopted for the membrane fouling tests. The constituents of the tested solutions include multivalent ions and protein.

MATERIALS AND METHODS

Experimental Setup and Membranes

The experimental setup for the DCMD operation in this work is shown in Fig. 1. The hot feed and cold distillate streams were circulated countercurrently through the MD module. The feed tank and the distillate tank were submerged in thermosets for setting the temperature difference between the feed side and the distillate side, and the temperatures were monitored using thermocouples. The increments of the distillate fluid were detected by electronic balance and the data were processed by personal computer.

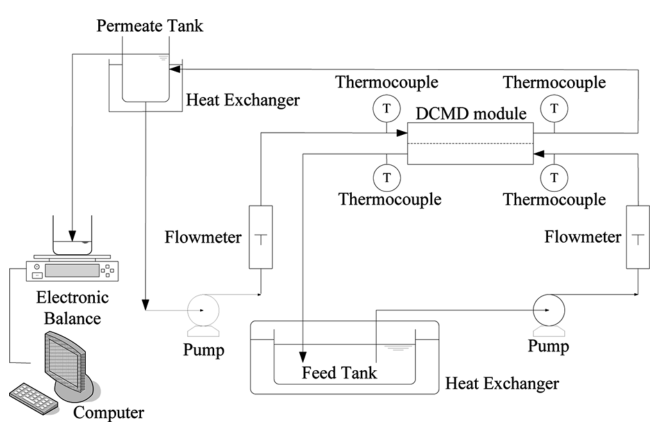

FIG. 1. Schematic diagram of DCMD experimental setup.

The detail of the DCMD module is illustrated as Fig. 2. The module consists of acrylic plates, rubber gaskets, spacer, and the membrane. The lower compartment is the hot feed channel and the upper one is for the cold distillate stream. The thickness of the gasket is 2 mm, and the effective length and width of the membrane are 20 and 10 cm, respectively. Two hydrophobic membranes, polyvinyldinefluoride (PVDF) and polytetrafluoroethylene (PTFE), were used in the experiments, and their characteristics are listed in Table 1.

Operating Conditions

In the experiments of permeate fluxes comparisons between PVDF and PTFE membrane, the feed temperatures were set from 313 to 323 K while the distillate side temperature was fixed at 293 K. The flow rate of feed varied from 0.6 to 0.9 l/min and the distillate side flow rate was 0.6 l/min. The feed solutions were 4.5 wt% and 10 wt% NaCl aqueous solutions. The permeate flux was measured until a steady flux was obtained for a specified operating condition.

In the experiments of the membrane fouling test, first, a fresh membrane was used to measure its initial permeate

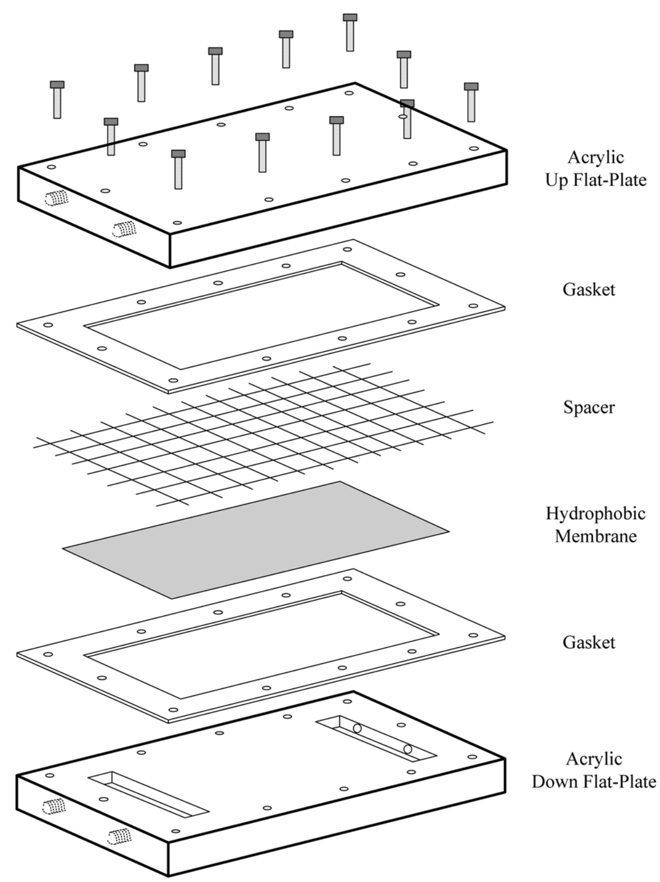

FIG. 2. The details of DCMD module.

TABLE 1
List of membrane characteristics

Material	Manufacturer	Type	Thickness (μm)	Pore size (μm)	Porosity (%)
PTFE	Toyo	Flat sheet	130	0.2	72
PVDF	GE osmonics	Flat sheet	175	0.3	–

flux with feed of distilled water at 323 K feed temperature and a 0.61/min flow rate. Then, the distilled water was replaced by a specified tested solution, and the permeate fluxes were measured at the same operating condition. After 24 hours operating, the final permeate flux through the fouled membrane was measured as the tested solution was replaced by the distilled water. The compositions of the tested solutions for the membrane fouling tests were summarized in Table 2.

Analytical Methods

The concentration of NaCl in the distillate was measured by using the conductivity meter (DS-51, Horiba, Japan). The concentration of bovine serum albumin (BSA) in the solution was obtained by measuring the absorption of 280 mm wave length with UV/Vis spectrophotometer (UNICAM UV600, Thermo, USA). Then, the rejection of BSA by the membrane can be determined as $1–C_{b,p}/C_{b,f}$, where $C_{b,p}$ and $C_{b,f}$ were the concentrations of BSA in the distillate and feed, respectively.

The distillate rates of pure water, before and after each fouling test, through the membrane, were measured in order to determine and compare the extent of membrane fouling caused by various feed solutions. A flux recovery (FR) is defined as the ratio of the final distillate flux to the initial distillate flux. A smaller FR indicates a stronger fouling tendency by the tested solution.

TABLE 2
List of tested solutions and contact angles on fouled membrane

Test	Composition	Contact angle[b]
1	4.5 wt% NaCl	126.37°
2	10.0 wt% NaCl	128.42°
3	4.4 wt% NaCl, 0.1 wt% $CaSO_4$	127.20°
4	4.4 wt% NaCl, 0.1 wt% $MgCl_2$	126.96°
5	4.4 wt% NaCl, 0.1 wt% $MgSO_4$	127.47°
6	4.2 wt% NaCl, 0.1 wt% $CaSO_4$ 0.1 wt% $MgSO_4$, 0.1 wt% $MgCl_2$	128.47°
7	4.5 wt% NaCl, 0.05 wt% BSA[a]	123.80°

[a]BSA: bovine serum albumin.
[b]the measured contact angle of the fresh PTFE membrane: 130.25°.

In addition, the field-emission scanning electron microscopy (FESEM, LEO-1530, Schottky, Germany) was applied to observe the membrane morphologies before and after the fouling test, and the contact angle instrument (FTA-125, First Ten Angstrom, USA) was used to measure the contact angles of the membrane.

RESULTS AND DISCUSSION

Effect of Operating Parameters on Distillate Flux

Figure 3 showed the distillate fluxes of distilled water fed through the PTFE MD module under various flow rates and temperatures. A significant enhancement in the distillate flux was achieved by increasing the temperature difference between the feed side and the permeate side, while the flux was just slightly enhanced by increasing the flow rate. The increase in feed temperature increases the vapor pressure and results in a larger driving force for vapor to pass through the membrane pore. So, the flux increased significantly with the increase of feed temperature. The temperature polarization phenomenon was not changed apparently by increasing the flow rate because the flux increased slightly.

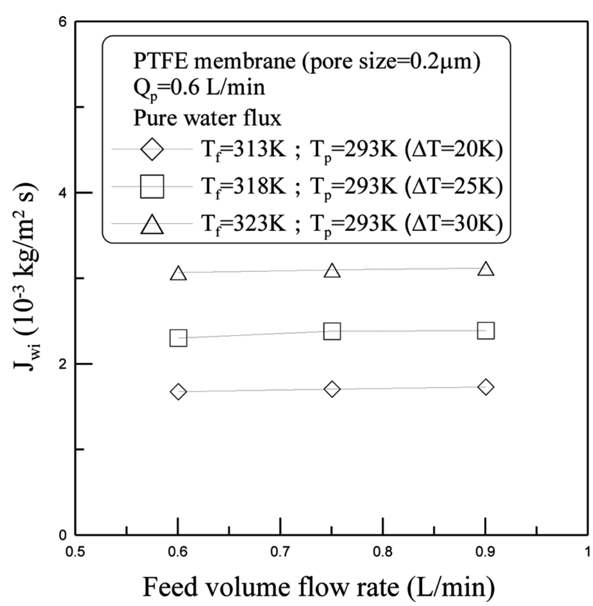

FIG. 3. Distillate fluxes through fresh PTFE membrane. Feed: distilled water.

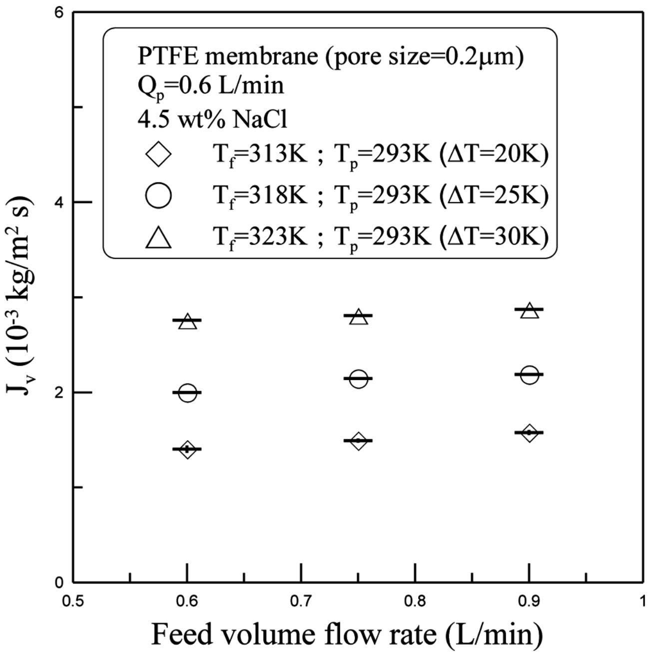

FIG. 4. Distillate fluxes through PTFE membrane. Feed: 4.5 wt% NaCl solution.

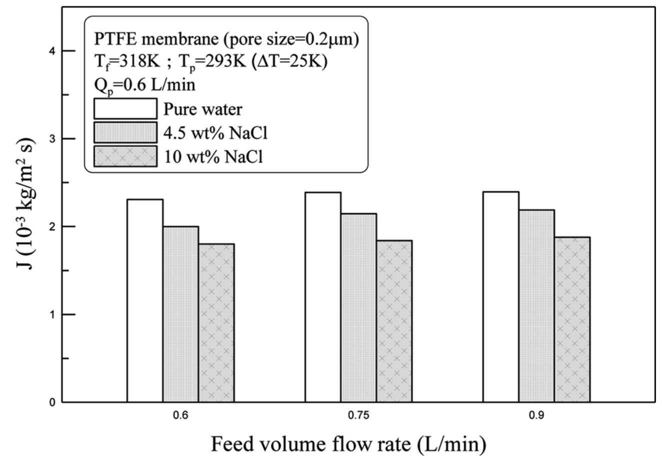

FIG. 6. Comparison of distillate fluxes under various feed concentrations.

The distillate fluxes of the feeds with 4.5 and 10 wt% NaCl concentrations were shown in Figs. 4 and 5, respectively. The increments in the distillate flux were also dominated by raising the feed temperature. And, both the temperature polarization and the concentration polarization were not disturbed significantly by the operated flow rates because the distillate flux varied slightly with the flow rate.

Figure 6 was the comparison of the distillate fluxes under various NaCl concentrations. It showed that the distillate flux decreased with the increase of feed concentration. For an aqueous solution, the activity coefficient of water or water vapour pressure decreases with the increase of solute concentration. Therefore, the flux decreased with increasing NaCl concentration due to the reduction in driving force for vapor to transport through the membrane pores.

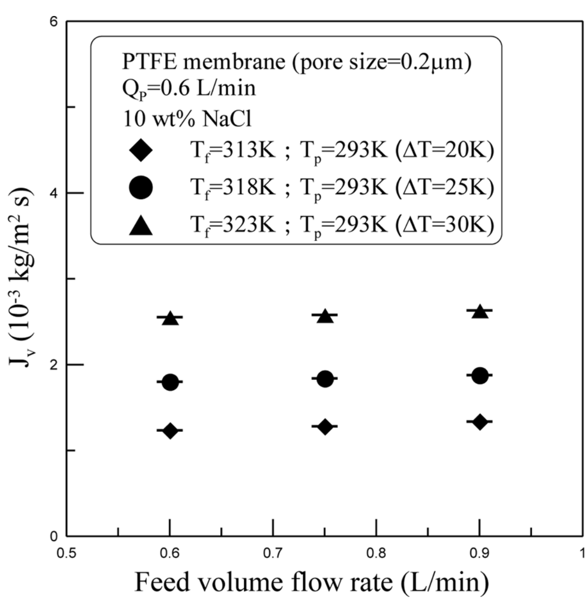

FIG. 5. Distillate fluxes through PTFE membrane. Feed: 10 wt% NaCl solution.

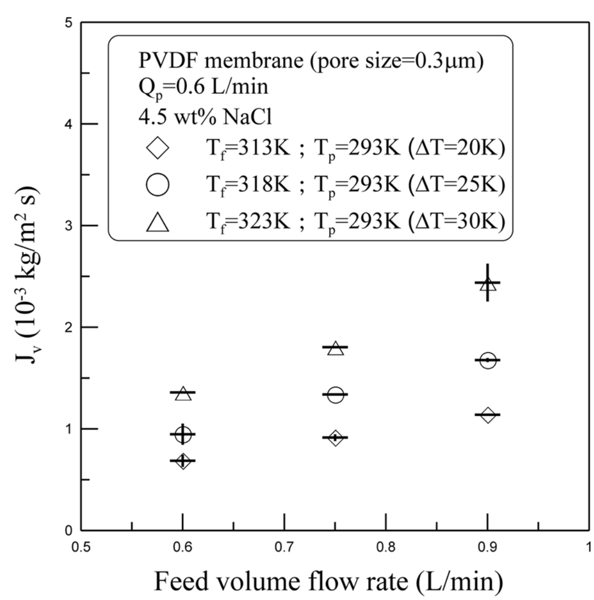

FIG. 7. Distillate fluxes through PVDF membrane. Feed: 4.5 wt% NaCl solution.

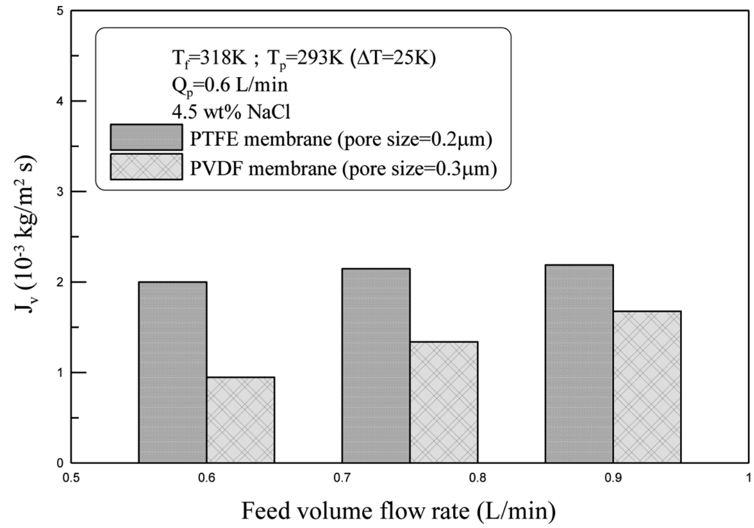

FIG. 8. Comparison of distillate fluxes between PTFE and PVDF membranes.

Comparison between PTFE and PVDF

Figure 7 was the experimental distillate fluxes through the PVDF MD module. The distillate fluxes increased with the increase in feed temperature or flow rate. However, as shown in Fig. 8, the distillate flux of PVDF membrane was low as compared to that of PTFE. On the other hand, the measured salt contents in distillates showed that the NaCl concentration in the distillate through PVDF membrane was obviously higher than through the PTFE membrane, especially at high flow rate and high temperature, as compared between Figs. 9 and 10. The high salt concentration of the distillate indicates that the membrane pores of PVDF could be wetted by the feed. In the case of wetting, the quality of the distillate would be unacceptable for desalination.

PTFE and PVDF are two common kinds of membrane materials applied in membrane distillation. The presented results show that the performance of the PTFE membrane is superior to the PVDF membrane.

Membrane Fouling

The PTFE membrane was used in the experiment of fouling test to investigate its durability in the operations contacting with various feed compounds. The measured

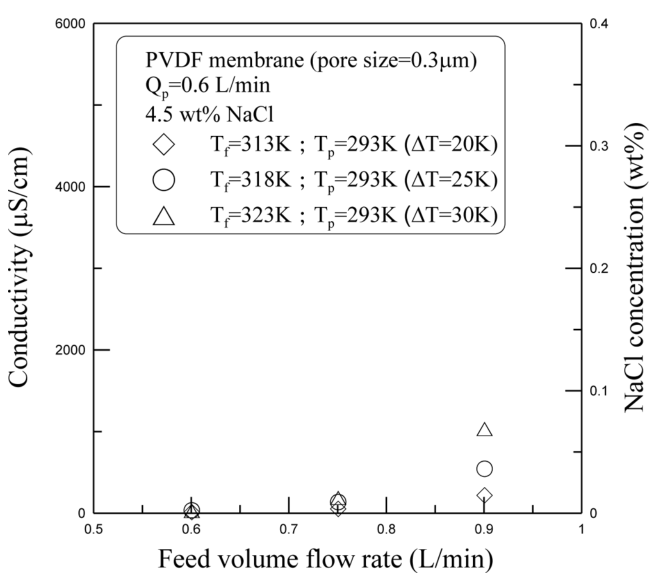

FIG. 9. Measured conductivities and NaCl concentrations in distillates. Membrane: PVDF, Feed: 4.5 wt% NaCl solution.

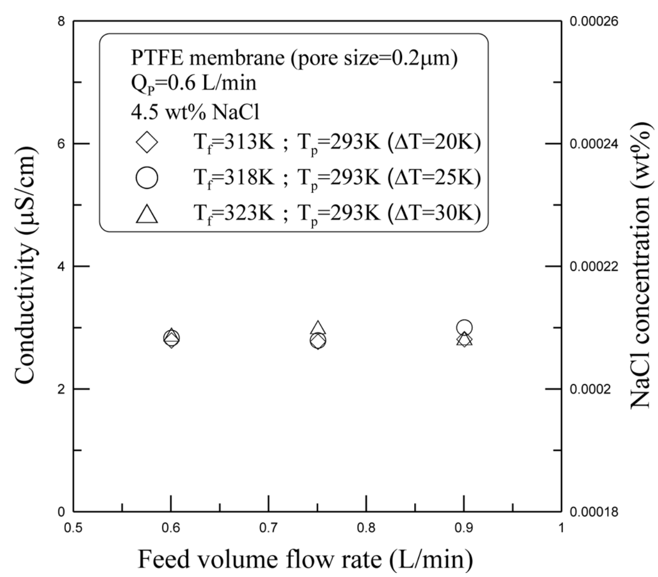

FIG. 10. Measured conductivities and NaCl concentrations in distillates. Membrane: PTFE, Feed: 4.5 wt% NaCl solution.

distillate fluxes of various tests are shown in Fig. 11. In each test, the final distillate flux was lower than the initial distillate flux. A different degree of fouling was formed on the PTFE membrane due to the variance in feed compositions. A comparison between Tests 1 and 2 showed that the increase of NaCl concentration from 4.5 to 10 wt% did not cause more severe fouling on the membrane. Their FRs were about 0.96–0.97. And, the addition of $CaSO_4$ or BSA into NaCl solution, Tests 3 or 7, also did not have a stronger fouling tendency. The measurement of BSA rejections showed that the BSA is almost totally rejected by the PTFE membrane.

It is noted that the addition of $MgCl_2$ or $MgSO_4$ caused a more significant fouling tendency on the PTFE membrane, as indicated by Tests 4, 5, and 6. The FR was about 0.87–0.88 for those cases.

Figure 12 was the SEM micrographs of the new membrane and the used membranes after the fouling test. The SEM images showed that some foulants were formed on the outer surface of the membrane, and in which most of the channels were not blocked by the foulants. Therefore, the fouled membrane still possessed a high FR.

The measured contact angles of water on the membranes were listed in Table 2. The contact angles of the used membranes were slightly lower than that of the new membrane. The foulants increased a little of the hydrophilicity on the PTFE membrane surface, especially the presence of BSA in the tested solution.

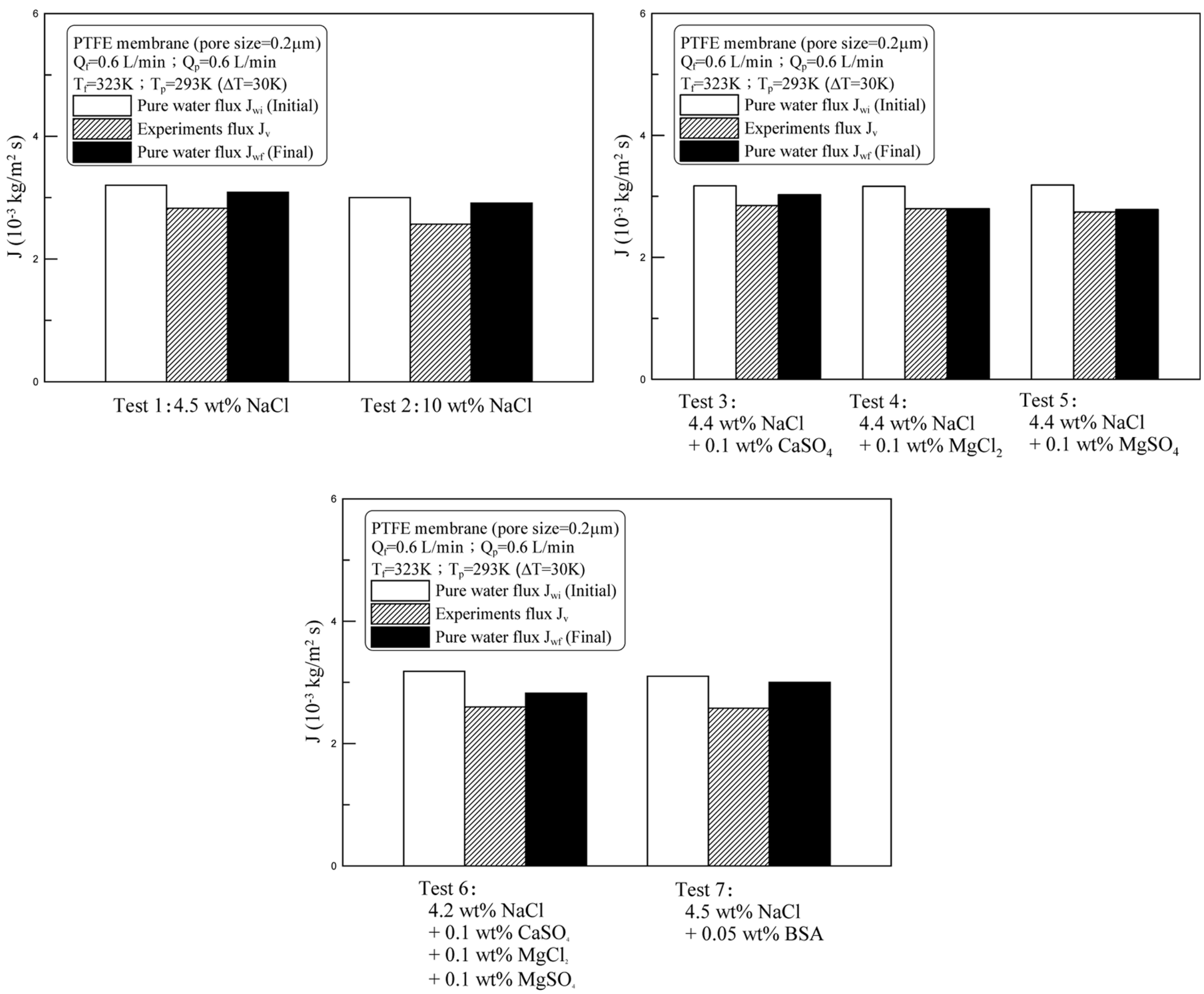

FIG. 11. Distillate fluxes under various membrane fouling tests.

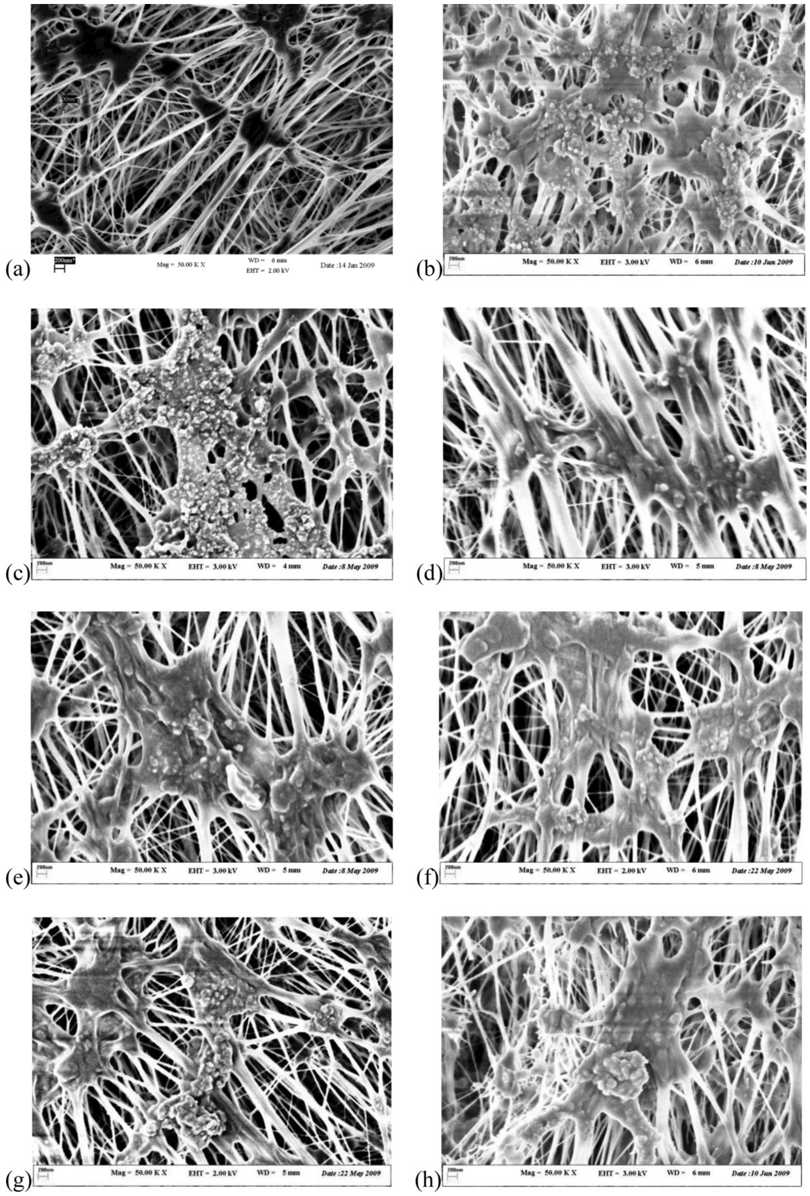

FIG. 12. SEM micrographs of fresh PTFE membrane and fouled membranes after testing. (a): fresh, (b): test 1, (c): test 2, (d): test 3, (e): test 4, (f): test 5, (g): test 6, and (h): test 7.

According to the flux recovery tests and membrane surface morphology measurements, the PTFE membrane has a good durability in contact with various feed compounds. However, a longer test cycle is necessary in the further study.

CONCLUSION

In this study, PTFE and PVDF membranes were employed in a direct contact membrane distillation system to investigate the effects of NaCl concentration, feed temperature, and flow rate on distillate flux and NaCl rejection. The membrane fouling tests for PTFE were also conducted under various NaCl concentrations and feed compositions. The fouled membranes were detected by the FESEM images and contact angle measurements.

Generally, the distillate flux increases with the increase of the feed flow rate or feed temperature. The applied PTFE membrane has a higher distillate flux than that of PVDFs, and the solute rejection by the PTFE membrane is also larger than that of the PVDF membrane, especially under the condition of the high feed flow rate and temperature. The transmission of the solute through the PVDF membrane is due to the membrane pore wetting at high feed flow rate and temperature.

Increasing NaCl concentration from 4.5 to 10 wt% does not cause more severe fouling on the membrane. The distilled water flux recovery is about 0.96–0.97. The addition of $CaSO_4$ or BSA into NaCl solution does not cause further fouling. However, the addition of $MgCl_2$ or $MgSO_4$ has a more significant fouling tendency on the PTFE membrane, and the distilled water FR is reduced to about 0.87–0.88. Though some foulants are formed and there is little change of hydrophobicity on the membrane surface, the PTFE membrane has a good durability in the direct contact membrane distillation under various feed compositions.

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REFERENCES

1. Smolders, K.; Franken, A.C.M. (1989) Terminology of membrane distillation. *Desalination*, 72: 249.
2. Lawson, K.W.; Lloyd, D.R. (1997) Review. Membrane distillation. *J. Membr. Sci.*, 124: 1.
3. Martinez, L.; Vazquez-Gonzalez, M.I.; Florido-Diaz, F.J. (1998) Study of membrane distillation using channel spacers. *J. Membr. Sci.*, 144: 45.
4. Martínez, L.; Rodríguez-Maroto, J.M. (2006) Characterization of membrane distillation modules and analysis of mass flux enhancement by channel spacers. *J. Membr. Sci.*, 274: 123.
5. Martínez, L.; Rodríguez-Maroto, J.M. (2006) Effects of membrane and module design on flux in direct contact membrane distillation. *Desalination*, 205: 97.
6. Schofield, R.W.; Fane, A.G.; Fell, C.J.D. (1987) Heat and mass transfer in membrane distillation. *J. Membr. Sci.*, 33: 299.
7. Schofield, R.W.; Fane, A.G.; Fell, C.J.D.; Macoun, R. (1990) Factors affecting flux in membrane distillation. *Desalination*, 77: 279.
8. Tomaszewska, M.; Gryta, M.; Morawski, A.W. (1994) A study of separation by the direct-contact membrane distillation process. *Sep. Technol.*, 4: 244.
9. Hsu, S.T.; Cheng, K.T.; Chiou, J.S. (2002) Seawater desalination by direct membrane distillation. *Desalination*, 143: 279.
10. Yun, Y.; Ma, R.; Zhang, W.; Fane, A.G.; Li, J. (2006) Direct contact membrane distillation mechanism for high concentration NaCl solutions. *Desalination*, 188: 251.
11. Gryta, M. (2008) Fouling in direct contact membrane distillation process. *J. Membr. Sci.*, 325: 383.
12. Gryta, M.; Grzechulska, J.; Morawski, A.W. (2003) Membrane distillation of NaCl solution containing natural organic matter. *J. Membr. Sci.*, 223: 11.
13. Cho, J.; Amy, G.; Pellegrino, J.; Yoon, Y. (1998) Characterization of clean and natural organic matter (NOM) fouled NF and UF membranes, and foulants characterization. *Desalination*, 118: 101.
14. Schäfer, A.I.; Fane, A.G.; Waite, T.D. (1998) Nanofiltration of natural organic matter: Removal, fouling and the influence of multivalent ions. *Desalination*, 118: 109.
15. Martínez, L.; Rodríguez-Maroto, J.M. (2008) Membrane thickness reduction effects on direct contact membrane distillation performance. *J. Membr. Sci.*, 312: 143.