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Comparison of three membrane distillation configurations and seawater desalination by vacuum membrane distillation

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ABSTRACT

Three membrane distillation (MD) configurations, vacuum membrane distillation (VMD), sweeping gas membrane distillation (SGMD) and direct contact membrane distillation (DCMD), have been experimentally studied in a shell-and-tube capillary membrane module using sodium chloride aqueous solutions as feed. The flux, fresh water conductivity and desalination rate were compared. Preliminary experiments by VMD were carried out using seawater and sodium chloride aqueous solutions with the same salinity as seawater as feed. The influences of operating parameters: the flow rate, feed temperature, concentration, and permeate vacuum, have been investigated. The saline solution had higher flux than seawater since the membrane fouling. The membrane fouling was analyzed by SEM and the results indicate that embrane fouling is very serious in seawater desalination by VMD which resulting that the flux decreases obviously with operating time.

Keywords: Membrane distillation; Polyvinylidene fluoride (PVDF); Hydrophobic hollow fiber membrane; Vacuum membrane distillation (VMD); Sweeping gas membrane distillation (SGMD); Direct contact membrane distillation (DCMD)

1. Introduction

In light of the prevailing serious situation of shortage of fresh water resources, people increasingly seek seawater as fresh water source. At present the main implementation method of seawater desalination are multi-stage flash (MSF), multi-effect distillation (ME) and reverse osmosis (RO). However, still about 50 percent of the concentrated water is discharged. With the enhancement of people's awareness of environmental protection, the ecological environment pollution and hazard of the discharged concentrated water to the offshore and coastal zones are being paid more and more attention. Therefore, the concentrated drainage to seawater should be limited.

Membrane distillation (MD) is a novel process developed in recent years. It's being investigated worldwide as a low cost, energy saving alternative to conventional separation processes such as distillation and reverse osmosis (RO) [1,2]. The benefits of MD compared to other more popular separation processes mainly stem from the higher concentration feed or near to saturation at the feed side and the fresh water recovery may reach 80% for 3.5wt% salt water. So MD can be used as a new seawater desalination method or supplementary one for current technologies.

MD usually refers to a thermally driven transport of water vapor through a porous hydrophobic partition [1]. One side of the partition (the feed side) is always in contact with aqueous solution. The other side (the permeate side) may be brought into contact with four different phases: (1) with an aqueous solution, giving rise to the configuration called direct contact membrane distillation (DCMC), (2) with a sweeping gas. In this case the process is termed sweeping gas membrane distillation (SGMD), (3) with stagnant air gap plus a cold plate. This configuration is called air gap membrane distillation (AGMD) (4) with a vacuum volume. The process is called in this case

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vacuum membrane distillation (VMD) [3]. Much research had been carried out on the optimization of operation conditions as well as mass and heat transfer mechanism of the four MD methods [4–8]. Whereas, it's hard to choose the highest flux configuration for the reason that the membrane material and module configuration is different for different researchers. It is necessary to compare the flux of different configurations using the same membrane material and membrane module at different operating conditions to obtain the most efficient MD configuration.

In this paper contrast experiments were carried out on PVDF hollow fiber membrane to compare the efficiency of DCMD, SGMD and VMD using 3.5wt% salt solution as feed. The influence of feed concentration on fluxes was investigated. VMD presented the highest flux among the three MD configurations. Then the desalination experiment by VMD was carried out using seawater and sodium chloride aqueous solutions as feed. The influences operation parameters, feed temperature, feed velocity, concentration and downstream vacuum, on flux were tested and compared with salt solution as feed, which has the same salinity of 3.25wt% as raw seawater. After hardness being removed, Seawater (concentration factors 3) was concentrated again and the effect of concentration factors on flux was investigated. Finally the membrane fouling of seawater was investigated.

2. Experimental

A shell-and-tube capillary membrane module was used in this work to conduct the MD experiments. The polyvinylidene fluoride microporous hydrophobic capillaries were made by the Institute of Biological and Chemical Engineering of Tianjin Polytechnic University. The NaCl adopted is analytical pure made by chemical reagent 1st factory of Tianjin. The electronic balance was purchased from Tianma Instrument Plant, Tianjin, China. The DDS-11A conductivity meter was made by Leici Instrument Inc., Shanghai, China.

The experimental setup shown in Fig. 1 is mainly composed by hot side circuit, cold side circuit and membrane module. All of the hot side circuits of three MD processes were combined by thermostatic water bath, magnetic pump, flow meter, pressure gauge and thermometer. The feed solution was circulated in the lumen side of the membrane module in all the experiments. However the cold side circuits of the MD processes are different.

The water flux was obtained by quantifying the collected distillate using an electronic balance in a given time. The salt rejection was obtained according to the concentration of the fresh water which was calculated from the conductivity measured by a conductivity meter.

3. Results and discussion

3.1. Performance comparison of three MD configurations

MD mechanism for pure water and salt solution has been intensively studied by many researchers. In this paper, we focused on the comparison of three configurations and application in seawater desalination.

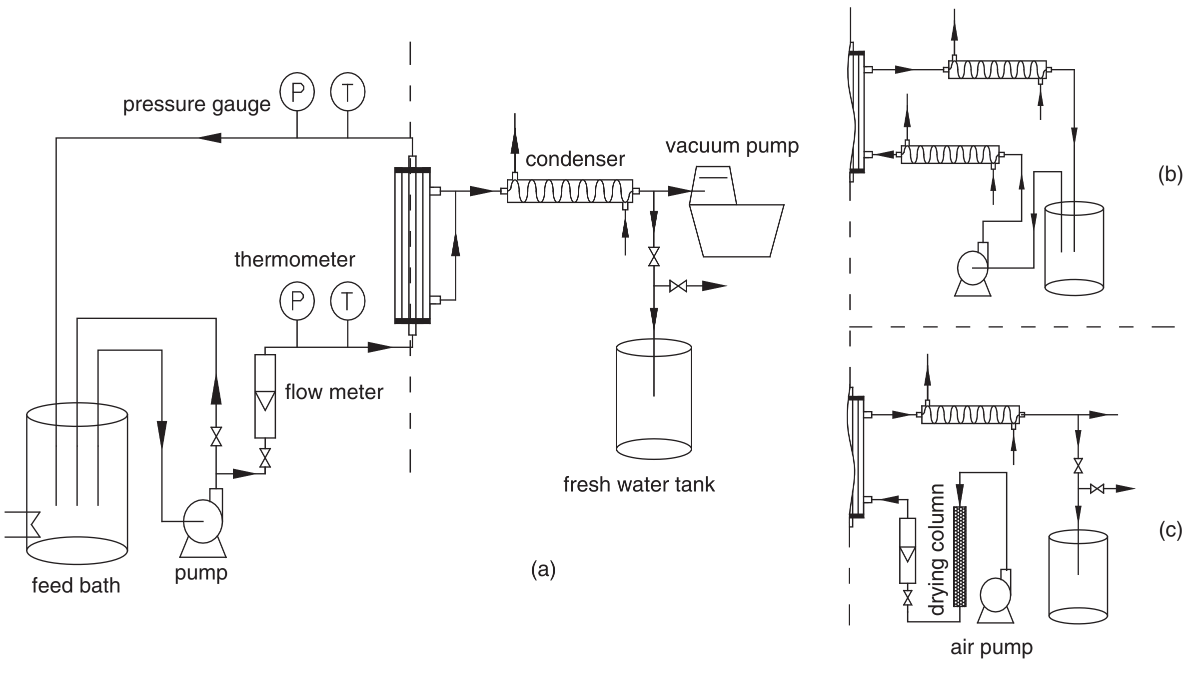

Fig. 1. Scheme of the MD experimental set-up.

Table 1
Parameters of membrane module in comparison of three MD configurations

Inner diameter	Thickness	Mean pore size	Porosity	Length	Area	Liquid entry pressure
1.0 mm	0.15 mm	0.16 μm	85%	23cm	0.03m^2	0.1 MPa

Firstly to compare the different MD configurations the effect of feed concentration on flux and salt rejection was investigated using NaCl solution at 70°C. The DCMD and SGMD were conducted at an inlet temperature of the fluid circulating in the shell side of the membrane module of about 20°C, while the VMD experiments were carried out at a vacuum pressure of 0.095 MPa. However, definitely all of the water vapor at every permeate side could be taken out of the membrane module and condensed. The principal characteristics of hollow fibers and membrane module are listed in Table 1.

Fig. 2 compares the variation of flux with increasing feed concentration. The flux varies insensitively when the feed concentration was lower than 40 g · l^{-1} and sensitively higher than 80 g · l^{-1} for this experimental setting. The flux sequence for the three configurations is: VMD>DCMD>SGMD. According to the basic equation [9] to describe the water vapor transport in MD system relating between the flux (J) and the water vapor pressure difference across the membrane ($P_f - P_p$):

$$J = K_m \times (P_f - P_p) \tag{1}$$

where K_m is the membrane transport coefficient which is mainly related to the membrane permeability. P_f and P_p are the water vapor pressures at the feed side and the permeate side respectively. Since P_f is equal for the three MD configurations by Antonine equation, the difference of flux was caused only by P_p. For VMD, P_p was only 5 KPa according to the vacuum degree 0.095 MPa. For DCMD the temperature of de-ionized water used was 20°C. However the temperature at the membrane surface is higher than that of VMD for the higher thermal conductivity coefficient of liquid than gas. So P_p of DCMD is less than VMD. For SGMD sweeping air velocity and module length are two main limiting factors that influence the flux [10]. Both slow sweeping air and long membrane module result in long retention time of the water vapor which caused the increase of water vapor partial pressure at the permeate side. Additionally, more water vapor permeate the membrane would produce more water vapor at the permeate side [10] and induced higher steam partial pressure with the sweeping gas in the permeate side. So SGMD was limited by its flux for the reason that higher flux had higher steam partial pressure which limited the flux. Water vapor partial pressure at the permeate side for the VMD was the lowest one among these three configurations and the water vapor pressure difference of VMD reached the highest under the condition of equal mean flow rate, temperature and feed concentration.

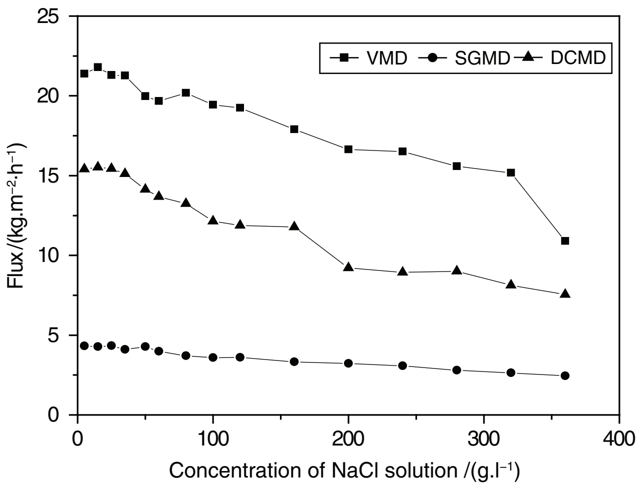

Fig. 2. Comparison of flux for three configurations at different feed concentration.
T_f = 70°C, v_f = 0.66 m · s^{-1}. VMD: P_p = –0.095 MPa; SGMD: v_p = 0.27 m · s^{-1}; DCMD: v_p = 0.02 m · s^{-1}.

From Fig. 2 it was observed that the VMD flux decreases sharply and the other two MD configurations decreases less evidently when the feed concentration is higher than 320 g · l^{-1}. The reason might be that higher flux of VMD induced more serious concentration polarization at the feed side than that of SGMD and DCMD. NaCl crystal might precipitate on the membrane surface for the serious temperature and concentration polarization and block the partial pores of the membrane, which decrease the VMD flux rapidly. The SEM pictures proved the existence of NaCl crystal as shown in Fig. 3.

The conductivity of fresh water in DCMD at the permeate side increased obviously when the feed concentration was higher than 150 g · l^{-1} as shown in Fig. 4. That might because that the NaCl crystal precipitated at the membrane surface of the feed and more microscale salt permeates through the membrane or the membrane wetting. For SGMD, even if the NaCl crystal precipitates at the outside of membrane surface the sweeping air still can not take it out of the membrane module and consequently the conductivity of fresh water was steady.

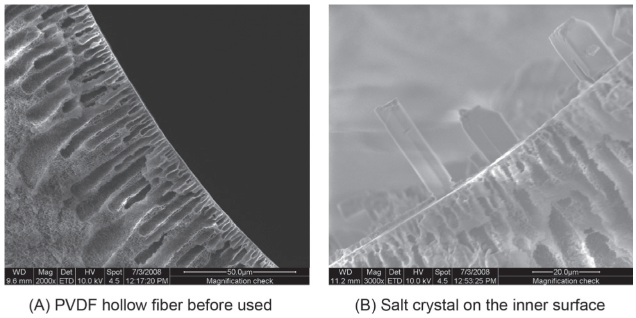

Fig. 3. Comparison of hollow fiber before and after being used.

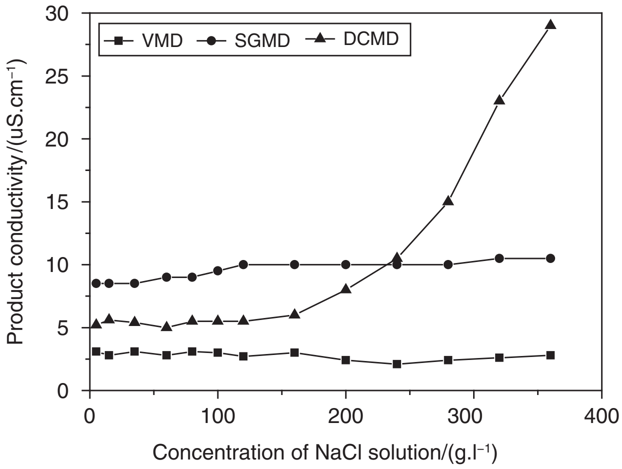

Fig. 4. Comparison of conductivity for three configurations at different feed concentration.
T_f = 70°C, v_f = 0.66 m · s^{-1}. VMD: P_p = −0.095 MPa; SGMD: v_p = 0.27 m · s^{-1}; DCMD: v_p = 0.02 m · s^{-1}.

3.2. *Effect of operating conditions on VMD flux with seawater as feed*

The MD configuration of maximal flux had been determined as VMD. The performance of VMD with seawater as feed was investigated as the function of

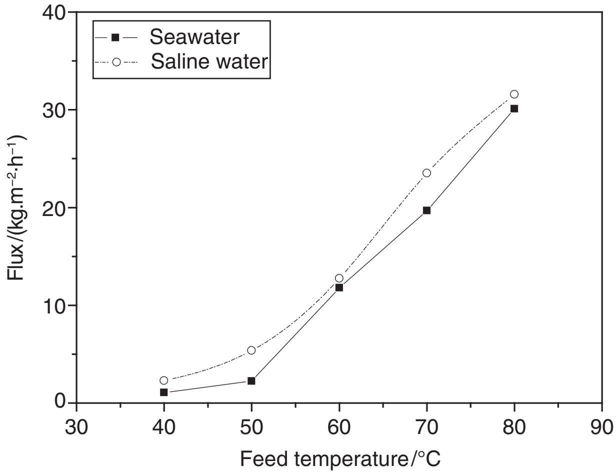

Fig. 5. Effect of feed temperature on flux. V_f = 0.51m.s^{-1}, Vacuum of pump: 0.095MPa.

feed temperature, feed velocity, downstream vacuum and feed concentration, meanwhile, compared with saline water. The saline water concentration is chosen at 3.5wt% to be the same as the seawater salinity. The seawater was retrieved from Bohai Sea and the main properties are listed in Table 2 and the PVDF hollow fiber parameters are listed in Table 3.

Fig. 5 shows the influence of feed temperature on the mass flux, at the permeate side temperature 20°C, feed velocity 0.51 m.s^{-1} and the vacuum of pump 0.095 MPa. The fresh water conductivity was always kept less than 4 μS.cm^{-1}. The flux exhibits an exponential dependence on temperature as would be expected when considering the Antonine equation for vapor pressure of water [11]:

$$P_f = \exp\left(23.238 - \frac{3841}{T_f - 45}\right) \tag{2}$$

where P_f is the vapor pressure of water in Pa and T_f is the feed temperature in K. Feed concentration isn't included

Table 2
Raw seawater quality

pH	Conductivity (μS/cm)	Hardness (CaO, mg/l)	C_{Ca}^{2+} (mol/l)	C_{Mg}^{2+} (mol/l)	COD_{Mn} (mg/l)	SS (mg/l)	DS (g/l)	Density (°Be′)
8.21	35000	3557	12.55	1223	50.96	28	38.9	3.7

Table 3
Parameters of membrane module in seawater desalination by VMD

Inner diameter	Thickness	Mean pore size	Porosity	Module length	Area	Liquid entry pressure
0.8 mm	0.15 mm	0.16 μm	85%	10.2 cm	0.015 m^2	0.1 MPa

in this equation. With the feed temperature increasing from 40°C to 80°C, the flux of seawater as feed increases from 1.08 $kg.m^{-2}.h^{-1}$ to 30.1 $kg.m^{-2}.h^{-1}$. However the flux of saline water varies from 2.28 $kg.m^{-2}.h^{-1}$ to 31.56 $kg.m^{-2}.h^{-1}$ which is higher than that of seawater but has a consistent changing tendency. The reason that less flux of seawater than saline water may be attributed to the existence of much organic in seawater which probably blocked the membrane pores.

Fig. 6 shows the effect of feed velocity on flux at the feed and the permeate temperatures, 70°C and 20°C, respectively, and the downstream vacuum 0.095 MPa. The results indicate that the flow velocity has little effect on flux. However, the flow velocity has less effect on feed of seawater than on the saline water. For the membrane inner pore diameter is only 0.8 mm, Reynalds number, a measure of mixing intensity, estimated to be about 1000–2000 which means the feed flow in hollow fiber is in stagnation region during the velocity range of these experiments. So in these experiments feed velocity has little effect on flux. It can also be concluded that feed velocity shouldn't be the way to improve flux because of the great increase of energy consumption in speed increasing for hollow fiber membrane module. This conclusion can not be applied to flat sheet membranes.

The water vapor pressure difference across the membrane was mainly determined by the downstream pressure for VMD at constant feed temperature and the influence of downstream vacuum was indicated in Fig. 7. The pressure at the outlet of the membrane module shell side was employed to replace the downstream pressure for the difficulty in determining downstream vacuum. The vacuum was calculated according to the absolute pressure measured by a mercury manometer at the outlet of the membrane module shell side. Fig. 7 indicates that flux increases almost linearly with increasing downstream vacuum and the flux of saline water was still higher than that of seawater.

In the last set of traditional VMD experiments, the effect of feed concentration on flux was investigated. Concentration multiple is employed to replace seawater concentration for the hardness to determine seawater concentration. Fig. 8 shows that flux decreases obviously with feed concentration factors. According to the Antonine equation [12] considering the concentration:

$$P_f = \exp\left(23.238 - \frac{3841}{T_f - 45}\right)(1 - x_f)(1 - 0.5x_f - 10x_f^2) \quad (3)$$

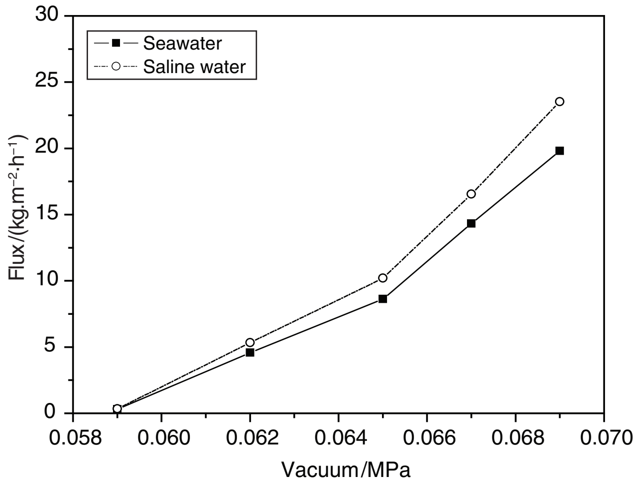

Fig. 7. Effect of vacuum on flux. T_f = 70°C, u_f = 0.51m.s^{-1}.

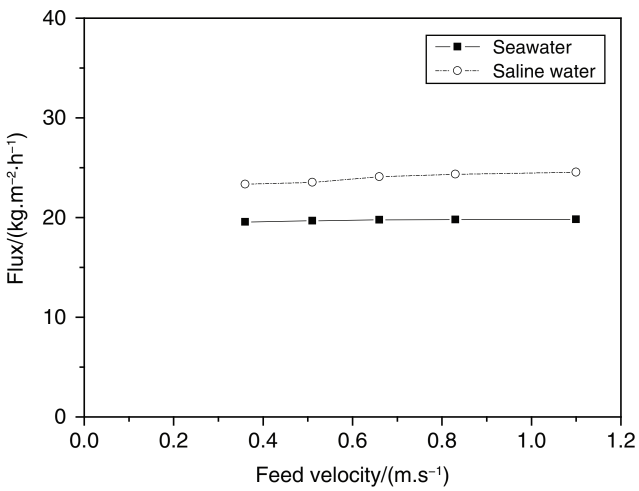

Fig. 6. Effect of feed velocity on flux. T_f = 70°C, Vacuum of pump: 0.095 MPa.

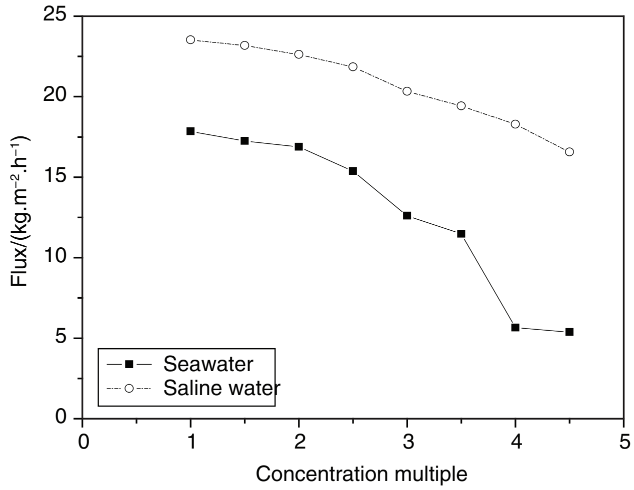

Fig. 8. Ef fect of concentration multiple on flux. T_f = 70°C, u_f = 0.51 m.s^{-1}, Vacuum of pump: 0.095 MPa.

where x_f is the molar fraction of feed solution, T_f is the feed temperature. However concentration multiple increases the feed concentration double which resulting in the water vapor partial pressure declines sharply and the flux decreases obviously.

All of the Figures of 5, 6, 7 and 8 show the result that the flux of saline water was higher than that of seawater. The less flux of seawater may be induced by the high organic contents and the suspended substance in it. The high content of organic suspension will block membrane pores with operating time and foul the membrane. The membrane fouling will be discussed in detail in latter part.

To test the quality of fresh water, conductivity vs. feed concentration multiple was shown in Fig. 9. The results indicate that the conductivity was a little high at the initial stage and then kept invariant but the maximal value was less than 5 μs.cm^{-1}. The changing conductivity was considered not caused by increasing concentration but by the volatile soluble matter contained in the hollow fiber which would be taken out by the water vapor. However the conductivity kept invariant at about 2 μs.cm^{-1}.

3.3. Secondary desalination after removal of organic and hardness

In VMD membrane fouling is unavoidable for high content of organic matter and hardness. Flux decreases obviously with time due to membrane fouling at given feed temperature, feed velocity, down stream vacuum and feed concentration.

Flocculant was applied to reduce the organic content and the lime milk was employed to remove the hardness in the concentration of seawater to 3 times. The main properties of brine after the organic matter and hardness being removed are listed in Table 4. The flux of the two types of feeds, raw seawater and the concentration seawater to 3 times after being removed organic matter and hardness, was compared and the results are shown in Fig. 10. The flux was improved greatly after removing the organic matter and hardness compared with the raw seawater at the given feed temperature,

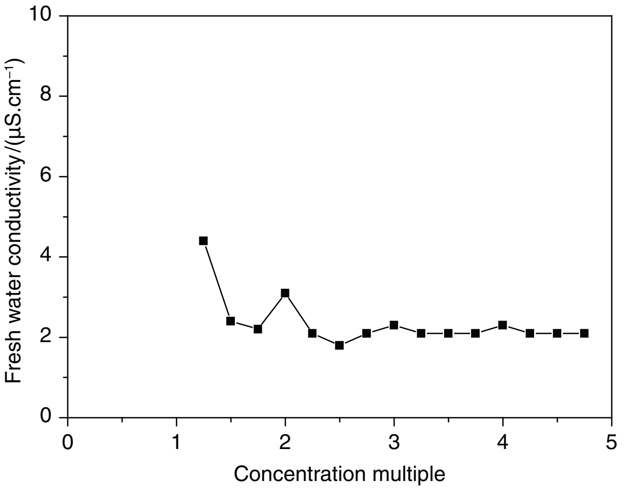

Fig. 9. Fresh water conductivity under different concentration multiple.

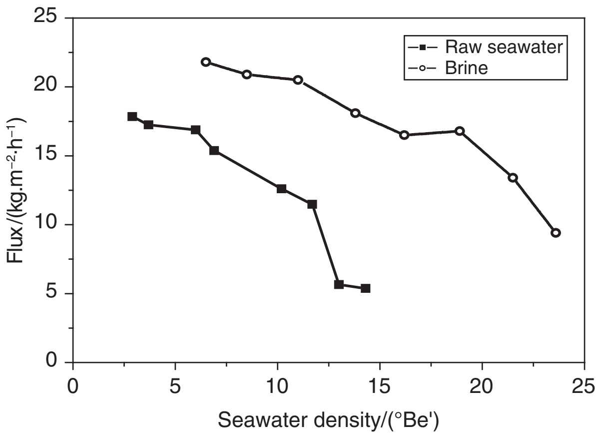

Fig. 10. Flux comparison of the first and second concentration. T_f = 70°C, u_f = 0.51m.s^{-1}, Vacuum of pump: 0.095 MPa.

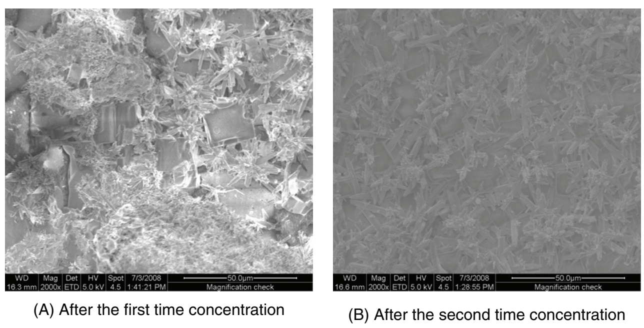

Fig. 11. Membrane fouling of VMD.

Table 4
Brine quality after being removed the organic and hardness

pH	Conductivity (μS/cm)	Hardness (CaO, mg/l)	C_{Ca}^{2+} (mol/l)	C_{Mg}^{2+} (mol/l)	COD_{Mn} (mg/l)	SS (mg/l)	DS (g/l)	Density (°Be′)
10	18000	0	0	0	18.8	4.5	114	6.5

feed velocity and permeate vacuum and same density. Here feed concentration is represented by density in °Be′ since seawater density increases linearly with the concentration. Fig. 11(A) and (B) indicates that the inner surface of membrane mainly fouled by organic and inorganic crystals for the first and the second concentration, respectively.

4. Conclusions

VMD is the most efficient configuration among the three MD configurations, VMD, SGMD and DCMD by presenting the highest flux and desalination rate, and the lowest fresh water conductivity

According to the results concluded from the MD configurations comparison, VMD is chosen to be applied in seawater desalination. The influence of feed temperature, velocity concentration and permeate vacuum on flux and conductivity is investigated. The results show that flux increases obviously with increasing feed temperature and permeate vacuum, keeps invariant with increasing feed velocity, and decreases sharply with the increasing feed concentration multiple. The saline water with same salinity as seawater has a higher flux due to less membrane fouling.

Membrane fouling is very serious in seawater desalination by VMD which resulting that the flux decreases obviously with operating time.

Acknowledgements

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