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Membrane distillation and novel integrated membrane process for reverse osmosis drained wastewater treatment

Wu Chunrui, Jia Yue, Chen Huayan, Wang Xuan, Lu Xiaolong*

Foster Base of State, Key Laboratory of Hollow Fiber Membrane Materials and Membrane Process, Institute of Biological and Chemical Engineering, Tianjin Polytechnic University, Tianjin 300160, People's Republic of China
Tel.: +86-22-2452 8750; Fax: +86-22-2452 8201; email: wuchunrui79@yahoo.com.cn, roseateyue@msn.com, chenhuayan@gmain.com, wangxuan0116@163.com, luxiaolong@263.net

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ABSTRACT

An integrated membrane process was constructed, which composed of immersing ultrafiltration(UF) cell as pretreatment step and vacuum membrane distillation (VMD) cell for both pure water reclamation from reverse osmosis (RO) drained wastewater and discharge reduction. The effect of feed temperature, velocity, and vacuum pressure at the pump side on the membrane performance in VMD process was studied. The performance of VMD process in the concentration of pretreated and untreated RO drained wastewater was compared. The surface morphology of the hydrophobic polyvinylidene fluoride hollow fiber membrane was observed by scanning electronic micrograph. Energy Dispersed Spectroscopy was also adopted to analyze the composition of the deposition on the membrane surface.

Using un-pretreated RO drained water as the feed, the initial flux of VMD was 22.6 kg/m^{2}h, and declined to 15.6 kg/m^{2}h as the concentration multiple reached four. The composition of contamination on membrane surface contains 32% calcium, 1.92% magnesium, and 1.41% sodium. Whereas the RO drained water was pretreated by hardness removal and UF, the VMD initial flux reached 25.6 kg/m^{2}h, and declined to 17.8 kg/m^{2}h as the concentration multiple got 10. The flux decreased to 11.8 kg/m^{2}h as the concentration multiple enhanced to 20. The contamination contains 26% sodium, 37% chlorine, and 2% calcium.

Keywords: Integrated membrane process; Vacuum membrane distillation; Reverse osmosis drained water; Hydrophobic membrane; Polyvinylidene fluoride hollow fiber membrane

1. Introduction

Reverse osmosis (RO) membrane technique had been used worldwide in the past several decades in sea/brackish water desalination and wastewater treatment processes, for the purpose of pure water production or water reclamation and reuse, as effective water treatment technique. But some problems also immersed concomitantly. The most important two problems may be relative low water production rate (about 50% in seawater desalination), and environmental pollution due to the drainage of concentrated water. It is needed to develop some effective methods or technique to overcome the problem [1].

Membrane distillation (MD) possesses obvious advantages comparing to RO technique, including higher rejection (theoretically 100%) for non-volatile components, higher water production rate and possibility for the treatment of solutions with high concentration, and so on [2–4]. MD process developed fast recently and

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*Corresponding author.

the research realm expanded from saline desalination to syrup concentration and wastewater treatment [5–8]. But the research on the treatment of RO concentrated and drained water was rare [9,10].

In this paper, an integrated membrane process was constructed, which composed of immersed ultrafiltration (UF) cell as pretreatment step and vacuum membrane distillation (VMD) cell for wastewater concentration and pure water production. The operation conditions of VMD process was optimized, the performance of VMD process in the concentration of pretreated and untreated RO drained wastewater was compared. The surface morphology of the hydrophobic polyvinylidene fluoride (PVDF) hollow fiber membrane was observed by scanning electronic micrograph (SEM). Energy Dispersed Spectroscopy (EDS) was also adopted to analyze the composition of the deposition on membrane surface.

2. Experimental

The RO drained wastewater was obtained from the RO unit of the wastewater treatment system used in Yanshan Petrochemical Corporation. The composition of RO drained wastewater was shown in Table 1. PVDF hydrophobic hollow fiber membrane with a porosity of about 80%, pore size of 0.16 μm, inner diameter of 0.8 mm and membrane thickness of about 0.15 mm was prepared in our lab and used for VMD experiment. The hydrophobic hollow fiber membranes were fixed in a shell- and-tube membrane module, using a plastic cylinder with an inner diameter of 28 mm and length of 23 mm as the shell. The effective membrane area in each module is about 0.05 m^2.

The diagram of the integrated membrane process was shown in Fig. 1. The system composted a VMD cell and an UF filtration cell. The wastewater was pretreated by adding hardness and chemical oxygen demand (COD) removing reagent. The pretreated water was Pumped into the VMD cell and concentrated. The concentrated solution in VMD cell could be pumped back into UF filtration tank. Contaminants, such as Ca^{2+}, Mg^{2+}, and COD were removed by the addition of reagent. The filtered water obtained from the upper side of the UF module was pumped back into VMD bath. So higher water recovery rate was obtained and most water was reused.

3. Results and discussion

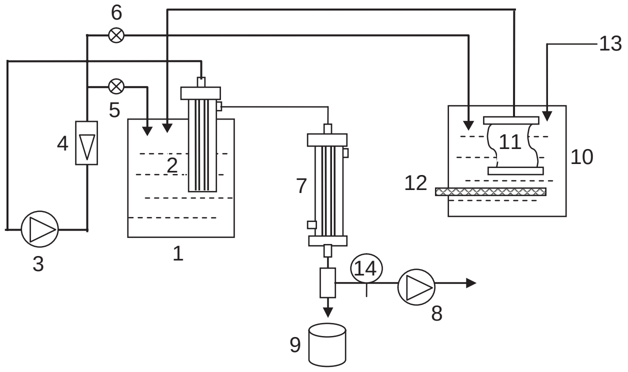
3.1. Effects of operation conditions on vacuum membrane distillation performance

Firstly, the effects of the operation conditions, such as the feed velocity, temperature and vacuum pressure at the vacuum pump side on the performance of VMD process were studied. The results were shown in Figs. 2–4.

The flux of VMD process only showed marginal increase as the feed velocity enhanced from 0.44 m/s to 1.33 m/s, as shown in Fig. 2. Fig. 3 shows that the flux increased linearly from 8.6 kg/m^2h to 22.6 kg/m^2h as the vacuum degree at the pump side increased from 0.07 MPa to 0.095 MPa, while the electronic conductivity of the product water was kept lower than 2 μS/cm. When tested at fixed conditions with certain membrane and module, the VMD coefficient was determined, and the flux of VMD process was just linearly relevant to the pressure difference, as expressed in Eq. (1) [11]:

$$N = B \cdot \Delta P_m = B(P_v(T_m) - P_{vacuum}) \tag{1}$$

Where N is the flux of VMD process, B is the MD coefficient, depending on membrane geometric characteristics



1. Feed water bath, 2. VMD module, 3. Pump, 4. Flow meter, 5 and 6. gauge, 7. Heat exchanger, 8. Vacuum pump, 9. Product tank, 10. Pretreatment tank, 11. Immersed UF module, 12. Bubble forming tube, 13. Reagent adding point, 14. Vacuum pressure gauge

Fig. 1. Experimental diagram of VMD integrated membrane process for RO drained wastewater treatment.

Table 1
The composition of the RO drained wastewater.

Conductivity (μS/cm)	Hardness($CaCO_3$) (mg/L)	CODcr (mg/L)	Na^+ (mg/L)	Ca^{2+} (mg/L)
5980	1621	118	858	407
Mg^{2+} (mg/L)	K^+ (mg/L)	Cl^- (mg/L)	NO_3^- (mg/L)	SO_4^{2-} (mg/L)
139	23	705	148	1498

and temperature, P_{vacuum} is the pressure in the vacuum side, and $P_v(T_m)$ is the vapor pressure in the membrane surface, at the membrane surface temperature, T_m.

The linear decrease of the vacuum pressure resulted in a linear increase of the pressure difference on the two sides of the membrane, and thus resulted in the linear enhancement of flux.

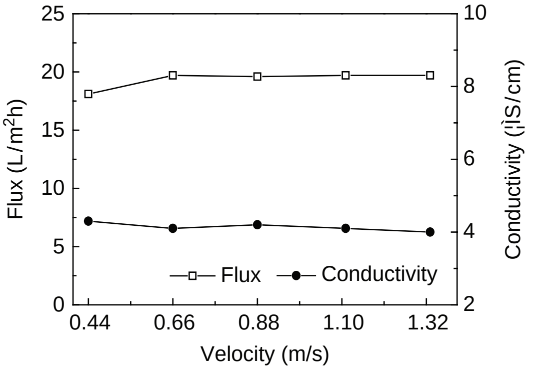


Fig. 2. Effect of feed velocity on VMD performance, tested at 70° with a pressure of −0.09 MPa.

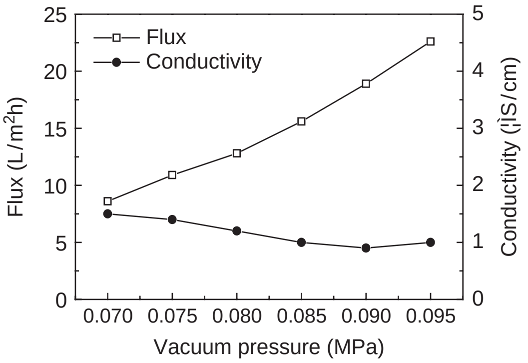


Fig. 3. Effect of vacuum pressure on VMD performance, tested at 70° with a feed velocity of 0.66 m/s.

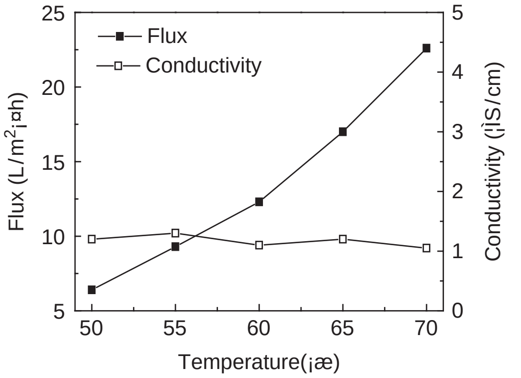


Fig. 4. Effect of feed temperature on VMD performance, tested with a pressure of −0.095 MPa, and feed velocity of 0.66 m/s.

Figure 4 shows that the conductivity of the product water was kept lower than 2 μS/cm when the feed temperature increased from 50° to 70°. While the flux was increased from 6.4 kg/m^{2}h to 22.6 kg/m^{2}h.

In VMD, most of the selectivity or separation is attributed to vapor–liquid equilibrium at the liquid–vapor interface. The water vapor pressure at the liquid–vapor interface (in Pa) is related with the temperature (in K) at the interface, according to Antoine's equation, which is represented in Eq. (2):

$$P_v(T) = \exp\left(23.1964 - \frac{3816.44}{T_m - 46.13}\right) \tag{2}$$

What's more, the Knudsen mechanism is dominant in the transmembrane mass transfer according to Dusty Gas Model, and the following explicit expression for MD coefficient, B, is achieved in Eq. (3) [12]:

$$B = 1.064 \cdot \frac{r\varepsilon}{dt} \cdot \left(\frac{M}{RT_m}\right)^{1/2} \tag{3}$$

Where, r is the radius of the pores, e is the porosity, d is the thickness, and t is the pore tortuosity of the membrane. M is the molecular mass of water, R is the gas constant, and T_m is the temperature at the membrane surface, or the water–vapor interface.

So, the VMD flux, N, could be rewritten as Eq. (4):

$$N = 1.064 \cdot \frac{r\varepsilon}{dt} \cdot \left(\frac{M}{RT_m}\right)^{1/2} \cdot \left[\exp\left(23.1964 - \frac{3816.44}{T_m - 46.13}\right) - P_{vacuum}\right] \tag{4}$$

The increase of feed temperature throw light on VMD flux from the two aspects, and the increase of flux with the feed temperature was the combination of the two aspects.

3.2. Reverse osmosis wastewater concentration by the integrated process

The RO drained wastewater was then concentrated by the integrated VMD process. The VMD experiment was carried out without any pretreatment to the wastewater, with feed temperature of 70°, velocity of 0.66 m/s, and vacuum pressure of 0.095 MPa. The VMD performance during the concentration process was studied. The variation of flux and product conductivity was illustrated in Fig. 5.

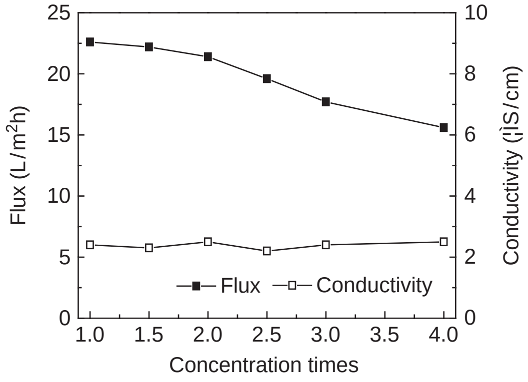


Fig. 5. VMD performance in RO drained water treatment, tested at 70° with a pressure of –0.095 MPa, and feed velocity of 0.66 m/s.

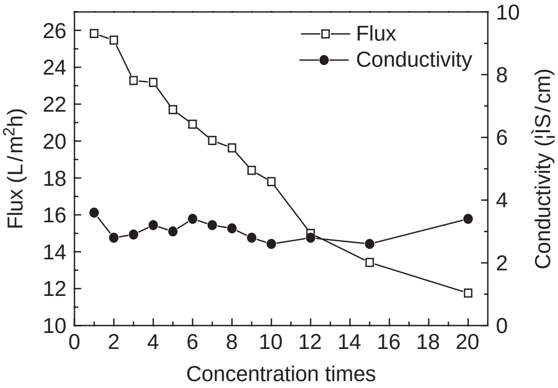


Fig. 7. VMD performance in RO drained wastewater concentration, tested at 70°, –0.095 MPa, 0.66 m/s.

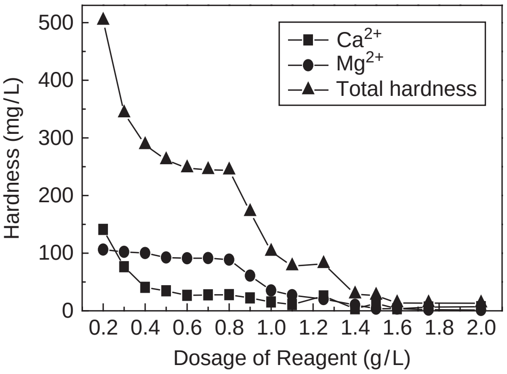


Fig. 6. Effect of the reagent dosage on the hardness of the RO drained wastewater.

From Fig. 5, one can see that the product conductivity was kept at about 2.4 μS/cm. The initial flux was about 22.6 kg/m²h, and declined gradually to about 15.6 kg/m²h, as the concentration multiple increased upto four.

To improve the VMD performance, increase total water reclamation and fulfill discharge reduction, the RO drained wastewater was pretreated in the UF filtration cell. The hardness composition, Ca^{2+} and Mg^{2+} was removed from the solution by adding hardness removing reagent. The variation of the solution hardness with the dosage of the reagent was shown in Fig. 6. The total hardness of the wastewater decreased to about 25 mg/L as the dosage of reagent reached 1.5 g/L. The solution was then sent into the VMD cell through the immersed UF membrane by a pump.

The pretreated RO drained wastewater was concentrated by VMD process. The experiment was carried out with feed temperature of 70°, velocity of 0.66 m/s, and vacuum pressure of 0.095 MPa. The VMD performance during the concentration process was studied. The variation of flux and product conductivity was illustrated in Fig. 7.

Fig. 7 shows that the conductivity of the product water was kept below 3.5 μS/cm even the concentration multiple reached 20. The initial flux of the process was 25.6 kg/m²h, and got to 11.8 kg/m²h when the concentration multiple reached 20. The flux was 17.8 kg/m²h when the concentration multiple was 10, which is higher than the 15.6 kg/m²h, obtained in the concentration of the untreated wastewater as the concentration multiple was four.

SEM was used to observe the inner surface morphology of the membranes used in the wastewater concentration process. Fig. 8(a) is the surface of the initial membrane, Fig. 8(b) is the membrane fulfilled the four times concentration of the un-pretreated wastewater, Fig. 8(c) is the membrane used for the 20 times concentration of the pretreated wastewater, and Fig. 8(d) is the membrane being washed by dilute hydrochloric acid after the 20 times concentration of pretreated wastewater.

Comparison between Fig. 8(a) and (b) illustrates the contamination of the membrane surface. The EDS analysis of the contamination showed it contains 32% calcium, 1.92% magnesium, and 1.41% sodium. The deposition of calcium and magnesium on the membrane surface is the main reason for membrane fouling in the four times concentration process of the un-pretreated wastewater. From Fig. 8(c), we can see quite different morphology of the deposition on membrane surface. The EDS analysis of the membrane surface showed the composition of the contamination contains 26% sodium, 37% chlorine, and 2% calcium.

The contaminated membrane could be easily cleaned by dilute hydrochloric acid solution. Fig. 8(d) shows that the surface morphology of the washed membrane is

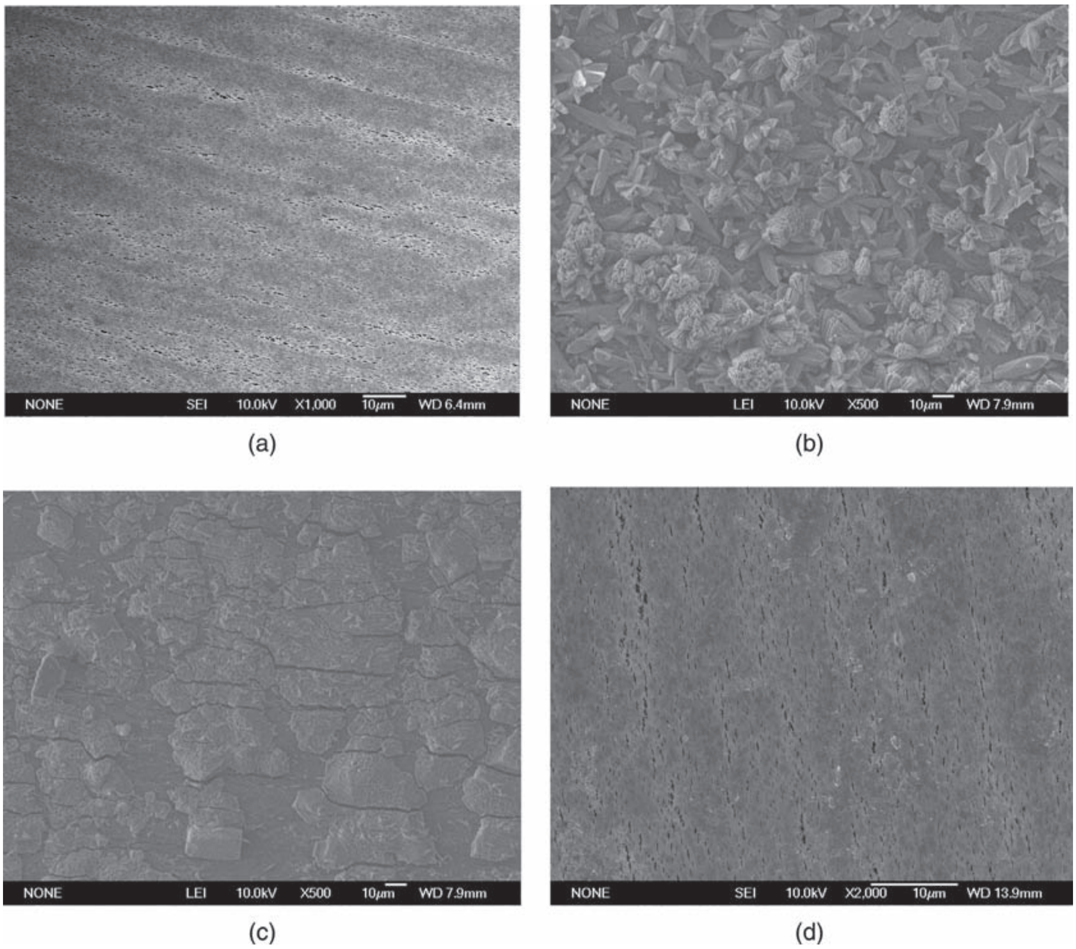


Fig. 8. SEM photograph of the inner surface of the hollow fiber membranes. (a) initial membrane, (b) and (c) are membranes contaminated in VMD process, (d) membrane washed by hydrochloric acid

same as the initial membrane, only a little contaminant left on the surface. The VMD flux of the washed membrane was about 24.7 kg/m^{2}h. The recovery rate of the membrane flux was about 97%.

4. Conclusion

An integrated membrane process was constructed, which composted of immersing UF cell as pretreatment step and VMD cell for wastewater concentration and pure water production. The effect of feed temperature, velocity, and vacuum pressure at the pump side on the membrane performance in VMD process was studied. The performance of VMD process in the concentration of pretreated and untreated RO drained wastewater was compared. The hardness removal pretreatment improved the VMD performance during the concentration of RO drained wastewater greatly. When untreated RO drained water was used as the feed, the VMD initial flux was 22.6 kg/m^{2}h, and declined to 15.6 kg/m^{2}h as the concentration multiple reached four. Whereas, if the RO drained water was pretreated by hardness removal, the VMD initial flux reached 25.6 kg/m^{2}h, and declined to 17.8 kg/m^{2}h as the concentration multiple increased to 10. The flux decreased to 11.8 kg/m^{2}h as the concentration multiple was enhanced to 20.

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References

[1] E. Drioli, F. Lagana, A. Criscuoli and G. Barbieri, Desalination 122 (1999) 141–145.

[2] M.S. El-Bourawi, Z. Ding, R. Ma and M. Khayet, J. Membr. Sci., 285 (2006) 4–29.

[3] K.W. Lawson and D.R. Lloyd, J. Membr. Sci., 124 (1997) 1–25.

[4] A.M. Alklaibi and N. Lior, Desalination, 171 (2004) 111–131.

[5] S. Al Obaidan, E. Curcio, G. Di Profio and E. Drioli, Desalination Water Treat., 10 (2009) 210–219.

[6] M. Gryta, M. Tomaszewska and K. Karakulski, Desalination, 198 (2006) 67–73.

[7] M. Qtaishat, T. Matsuura, M. Khayet and K.C. Khulbe, Desalination Water Treat., 5 (2009) 91–98.

[8] A.M. Alklaibi, Desalination, 223 (2008) 375–385.

[9] F. Macedonio, E. Curcio and E. Drioli, Desalination, 203 (2007) 260–276.

[10] D. Qu, J. Wang, L. Wang, D. Hou, Z. Luan and B. Wang, Sep. Purif. Technol., 67 (2009) 21–25.

[11] R.W. Schofield, A.G. Fane and C.J.D. Fell, J. Membr. Sci., 33 (1987) 299–313.

[12] S. Bandini, A. Saavedra and G.C. Sarti, AIChE J., 43 (2) (1997) 398–408.