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Wei Zhao[a]; Baoli Shi[a]
[a] Polymer Membrane Laboratory, College of Science, Northeast Forestry University, Harbin, China

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Removal of Volatile Organic Compounds from Water by Pervaporation Using Polyetherimide-Polyethersulfone Blend Hollow Fiber Membranes

Wei Zhao and Baoli Shi
Polymer Membrane Laboratory, College of Science,
Northeast Forestry University, Harbin, China

Abstract: Removal of volatile organic compounds (VOCs) such as 1,2-dichloroethane, trichloroethylene, chlorobenzene and toluene from water solutions through polyetherimide (PEI)-polyethersulfone (PES) blend hollow fiber membranes was investigated by pervaporation (PV) in this work. The separation performances of the membranes were researched by varying the spinning conditions (such as coagulation temperature and air gap distance) for the preparation of the hollow fibers and the operation conditions (such as velocity, concentration, and temperature of feed liquids). For the PEI-PES blend hollow fiber membrane prepared when the air gap was 7 cm and the temperature of coagulation bath was 45°C, it possessed high selectivity to the aqueous solutions containing 0.04 wt.% of VOCs at 20°C. The separation factors to 1,2-dichloroethane, trichloroethylene, chlorobenzene and toluene were 7069, 5759, 3952, and 3205, respectively. It was found that the pervaporation performance of the blend hollow fiber membrane was strongly related to the molecular size of the VOCs. The order of the selectivities was 1,2-dichloroethane > trichloroethylene > chlorobenzene > toluene.

Keywords: Hollow fiber membrane, pervaporation, polyetherimide, polyethersulfone, VOCs

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Address correspondence to Baoli Shi, College of Science, Northeast Forestry University, Harbin 150040, China. Tel.: +86-451-8219-2327. E-mail: shi_baoli@yahoo.com

INTRODUCTION

Volatile organic compounds (VOCs) such as 1,2-dichloroethane, trichloroethylene, chlorobenzene, and toluene are one of the main contaminants for our drinking water. These organic matters come from the wastewater discharged from some industries such as petroleum refineries, pharmaceutical, and chemical plants (1). These substances are dangerous to living creatures. At present, some techniques such as biological treatment, adsorption by active carbon, ozone processing, and air stripping in packed columns are used at industrial scale for the removal of VOCs (2). However, these methods are subjected to two limitations: expensive or inefficient. Consequently, a new technique with low-cost and high efficiency is needed to be developed.

Pervaporation (PV) is an effective membrane separation method to extract VOCs from dilute aqueous solutions at very low concentrations (0.01–0.05 wt.%) (3). Many kinds of polymeric membranes made from polyoctylmethylsiloxane (1), polydimethylsiloxane (4), polyphenylmethylsiloxane (5), and polyvinylidene fluoride (6) have been used for the removal of VOCs from water by PV process. Development of hollow fiber membrane for PV is attractive because hollow fiber membrane has many advantages than flat membrane, such as large surface area per volume ratio, self-supporting structure, and self-contained vacuum channel where feed can be supplied from the shell side while a vacuum can be applied on the lumen side (7). Consequently, hollow fiber membrane was widely used for the removal of contaminants from water (6,8).

Polyetherimide (PEI) is a kind of high performance resin. It is widely prepared to membranes for the separation of gas, vapor (9,10), and liquid mixtures (11,12). PEI is also proved as an attractive membrane material for PV (13). Polyethersulfone (PES) is an important polymer material. It is widely used as biomaterial (14,15) and pervaporation membrane material (16) because of its stability, excellent biocompatibility, and fiber spinning ability with appropriate morphology for hollow fiber. Blending PEI with PES to prepare hollow fiber membrane with high performance is a promising research to remove VOCs from water. To the best of our knowledge, using PEI-PES blend hollow fiber membrane to remove VOCs from water by PV process has not been reported until this work. In this study, PEI and PES blend hollow fiber membranes were prepared and used for the removal of VOCs (1,2-dichloroethane, trichloroethylene, toluene, and chlorobenzene) from water by PV technique. The effects of spinning condition for the preparation of hollow fibers and operating conditions on the PV performances were investigated in detail.

EXPERIMENTAL

Materials

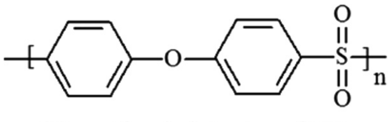
PES (Ultrason E 6020P) was purchased from BASF, Germany. PEI (ULTEM 1000) was purchased from GE, America. The chemical structures of PES and PEI are shown in Fig. 1. N-methyl-2-pyrrolidone (NMP), 1,2-dichloroethane, trichloroethylene, chlorobenzene, and toluene were purchased from Tianjin Kermel Chemical Reagents Development Center, China. Distilled water was used throughout this study.

Measurement of Contact Angle

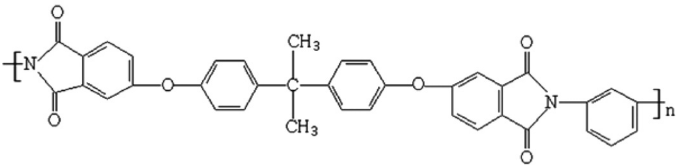
Contact angle (CA) technique was adopted to measure the hydrophobicity of PEI and PES flat sheet films on a contact angle meter (JC2000A, China) by means of sessile drop method at room temperature. The result was used to prove the feasibility of using PEI and PES to remove VOCs from water. For the CA measurement, distilled water was dropped onto 10 different sites on each film and an average value was obtained.

Preparation of Hollow Fiber Membranes

Dry/wet phase inversion method was used to make the blend hollow fiber membranes on a home- made spinning apparatus as shown in Fig. 2. PEI and PES materials were dried at 50°C for 48 h before use.



(1) Chemical structure of PES



(2) Chemical structure of PEI (ULTEM)

Figure 1. Chemical structures of PES and PEI.

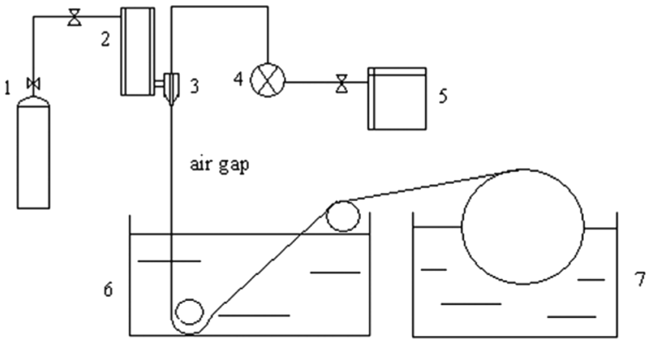


Figure 2. Schematic drawing of hollow fiber membrane spinning system: (1) nitrogen gas; (2) dope reservoir; (3) spinneret jet; (4) peristaltic pump; (5) water; (6) coagulation bath; (7) collection bath.

The composition of the spinning solutions was 16 wt.% PES/7 wt.% PEI/77 wt.% NMP. The spinning solutions were kept at 50°C for 12 h to degas. The procedure of spinning the hollow fibers was as follows: first, the spinning solution was loaded into a dope reservoir, then the solution was extruded from a spinneret by compressed nitrogen gas. At the same time, distilled water which was used as bore fluid was extruded from the center of the spinneret by a peristaltic pump. The air gap was 7 cm, 15 cm, 25 cm, and 35 cm. The nascent fibers entered freely into a coagulationv(water) bath without additional drawing. The temperature of the water bath was 15°C, 25°C, 35°C, and 45°C. At last, the fibers were collected in a collection bath. The hollow fibers were stored in distilled water for 48 h at ambient temperature, and then were dried in air.The temperature and humidity of the room were maintained at 20°C and 47%, respectively.

Membrane modules with an effective length of 34 cm were made by encasing eight hollow fibers in two glass tubes. The ends of the tubes and the fibers were sealed with epoxy resin. Each module was placed at ambient temperature for 48 h before measurements.

Characterization of Membrane Morphology

The structures of cross-section of the hollow fiber membranes fabricated at different conditions were characterized by a scanning electron microscope (FEI Quanta 200, USA). The dried hollow fibers were broken in liquid nitrogen and then sputtered with gold.

Pervaporation Experiment

The pervaporation apparatus for removing VOCs from water was described as Fig. 3. Mixtures of 1,2-dichloroethane, trichloroethylene, chlorobenzene and toluene with water were used as feed solutions, respectively. The total volume of the feed liquids was 6 L. The feed was extracted from the reservoir to the membrane module by a peristaltic pump. Sweeping method was used to collect the permeate. After being stabilized for an hour, the pervaporation experiment was started. The permeate was collected after being condensed in a cold trap by using liquid nitrogen. The samples were weighted by an electronic balance and the concentration was analyzed by a gas chromatography (GC-9A, Japan).

The pervaporation performance of different hollow fiber membranes prepared by varying the air gap (7 cm, 15 cm, 25 cm, and 35 cm) and the temperature of coagulation (15°C, 25°C, 35°C, and 45°C) was measured. The aqueous solutions of 1,2-dichloroethane, trichloroethylene, chlorobenzene, and toluene were choosen as the VOCs feeds. The concentrations of the feeds were 0.02 wt.%, 0.03 wt.%, 0.04 wt.%, and 0.05 wt.%, respectively. The velocities of the feeds in the membrane modules were 14 ml/min, 23.2 ml/min, 32.5 ml/min, and 40 ml/min. The temperatures of the feeds were 20°C, 30°C, 40°C, and 50°C. Permeation flux (J, $g/m^2 \cdot h$) was obtained as follows:

$$J = W/(t \times A)$$

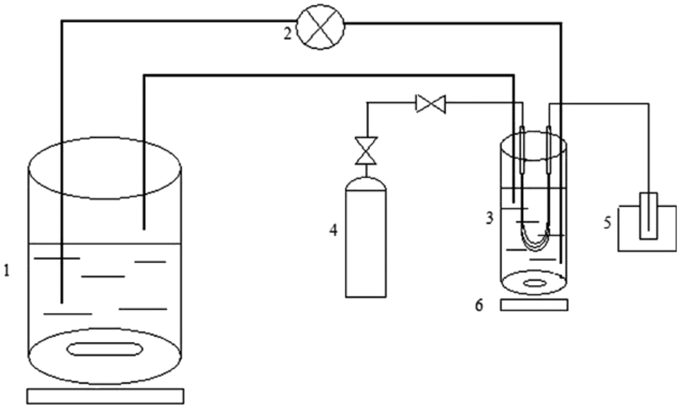


Figure 3. Schematic illustration of pervaporation apparatus: (1) feed reservoir; (2) peristaltic pump; (3) membrane module; (4) nitrogen gas; (5) cold trap; (6) magnetic stirrer.

Where W is the total mass of permeate, t is the permeation time, and A is the area (m^2) of membrane. Separation factor is calculated as follows:

$$\alpha_{VOC/H_2O} = (W_{VOC}/W_{H_2O})^P/(W_{VOC}/W_{H_2O})^F$$

Where $(W_{VOC}/W_{H2O})^P$ and $(W_{VOC}/W_{H2O})^F$ is the weight fraction of VOCs in permeate and feed solution, respectively.

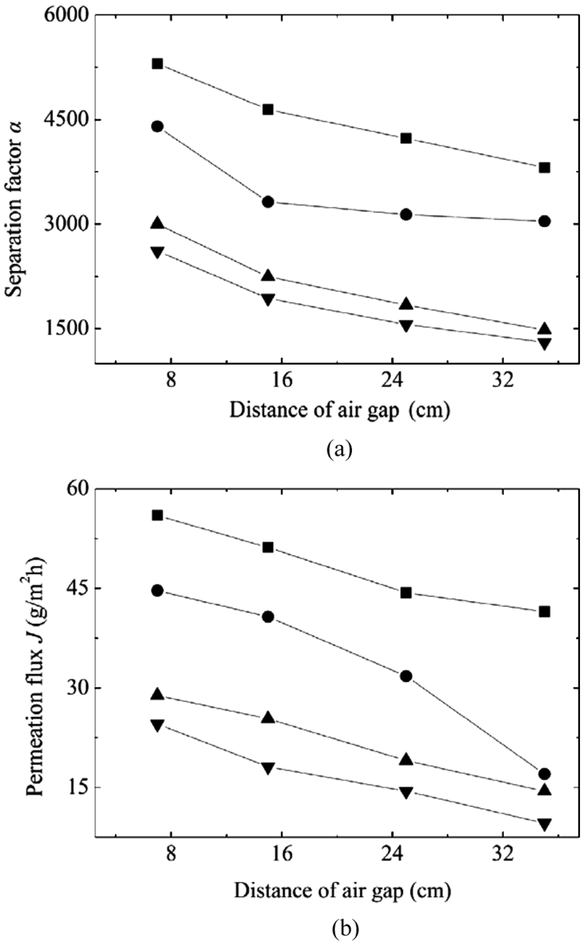
RESULTS AND DISCUSSION

Hydrophobicity of PEI and PES

The contact angles of water on the PEI and PES flat films were 109.5 and 102.5, respectively. It means that the two materials can not be wetted by water and possess hydrophobicity. In this experiment, the VOCs are hydrophobic molecules. Consequently, they have intensive interaction with PEI and PES, and the blend membranes prepared from PEI and PES will have good ability for the removal of VOCs from water.

Distance Effect of Air Gap on Pervaporation Performances

The distance effect of the air gap when preparing the PEI-PES blend hollow fiber membrane on the pervaporation performances is shown in Fig. 4. It shows that the permeation flux and the separation factor decrease with the increase of the distance of the air gap. Both the permeation and selectivity seem to deteriorate. The reason is that increasing the distance of the air gap will reduce the number of finger-like voids of the hollow fiber membranes and produce some defect structures on the surface of the hollow fibers at the same time. Chung et al. had found the same phenomenon when they researched polyimide and polyethersulfone hollow fiber membranes (17,18). When the nascent fibers passing through the air gap region, they will be stretched by gravity. This will induce the diameter of the fibers to shrink rapidly when the distance increases. According to the opinion of Chung et al., shrinking prevents the diffusion of coagulants, thus the macrovoids tend to disappear at a long distance the of air gap (18). In other words, the fibers prepared at short air gap have larger pore sizes than that at long air gap. A small cavity structure will enable VOCs to permeate difficultly (17,18). Figure 5 shows the SEM images of the cross section of the hollow fibers prepared at different distances of the air gap. The change in cross-section structures of these



(a)

(b)

Figure 4. Effect of distance of air gap on PV performances of hollow fiber membranes. Distance of air gap: 7 cm, 15 cm, 25 cm, and 35 cm. Temperature of coagulation: 45°C. Concentration of feed: 0.04 wt.% at 30°C. Velocity of feed: 32.5 ml/min. 1,2-dichloroethane (■); trichloroethylene (●); chlorobenzene (▲); toluene (▼).

membranes accords with the above opinion. Therefore, the flux decreased with the increase of the distance. In addition, although the membranes were inclined to form the structure with small cavities when the distance of the air gap increased, more defects may appear on the selective layer of the membranes because the drag action from gravity became stronger (17,18). Consequently, the selectivity factor decreased with the increase of air gap distance.

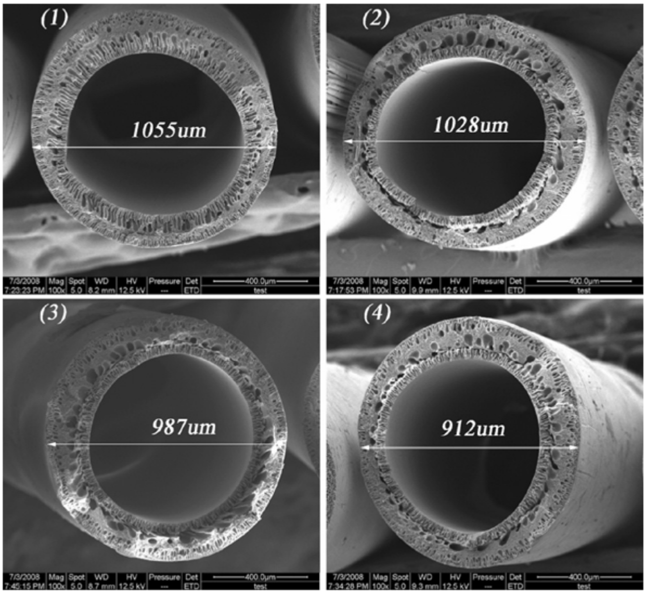


Figure 5. SEM images of cross section of hollow fiber prepared at the temperature of coagulation 45°C: (1>) air gap 7 cm; (2) air gap 15 cm; (3) air gap 25 cm; (4) air gap 35 cm.

Figure 4 shows that the order of selectivity and permeation flux is: 1,2-dichloroethane > trichloroethylene > chlorobenzene > toluene. The molar volume of 1,2-dichloroethane, trichloroethylene, chlorobenzene and toluene are 78.8 cm^3/mol, 90.2 cm^3/mol, 102.1 cm^3/mol, and 106.8 cm^3/mol, respectively. The order of pervaporation performance is reverse to that of the molecular size of the VOCs. The high selectivity to VOCs of the blend membrane attributes to PEI and PES are hydrophobic materials, and the four VOCs are hydrophobic molecules. As for the difference in the selectivity, it seems that their molecular sizes are the main factors. Small molecules permeate through the membranes easily than large molecules.

Effect of Coagulation Temperature on Pervaporation Performances

The effect of the temperature of coagulation on the flux and separation factor is shown in Fig. 6. It shows that with the increase of coagulation temperature, both the flux and the separation factor gradually increased. The structure morphology of the cross section of the hollow fibers prepared in coagulation at different temperatures is shown in Fig. 7. It clearly shows that when the temperature is high (e.g. 45°C), the membrane has a perfect finger-like and macrovoid structure. High temperature can decrease the viscosity of polymer spinning solution and enhance the exchange between the coagulation (water) and the solvent (NMP), tending to form macrovoids in the membrane.

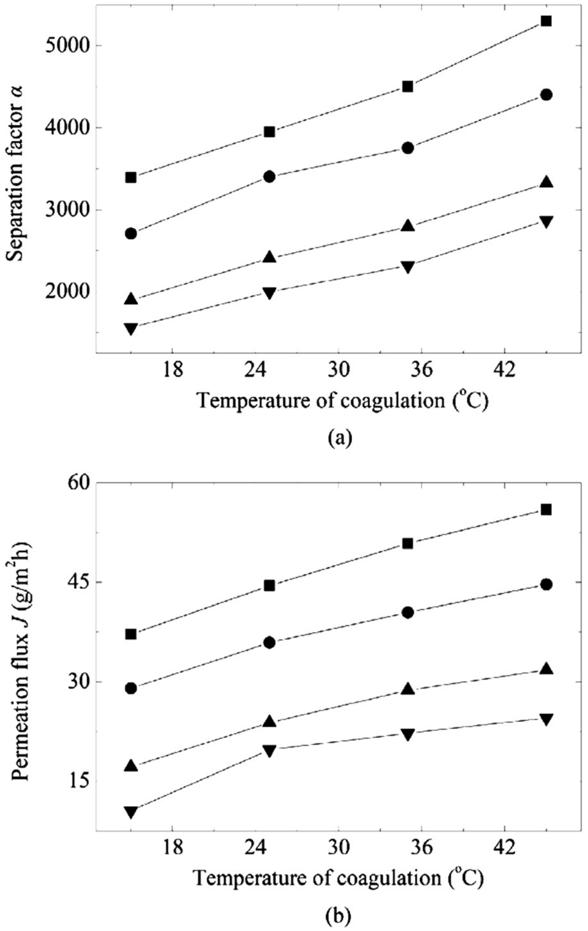


Figure 6. Effect of temperature of coagulation on PV performances of hollow fiber membranes. Temperature of coagulation: 15°C, 25°C, 35°C, and 45°C. Distance of air gap: 7 cm. Concentration of feed: 0.04 wt.% at 30°C. Velocity of feed: 32.5 ml/min. 1,2-dichloroethane (■); trichloroethylene (●); chlorobenzene (▲); toluene (▼).

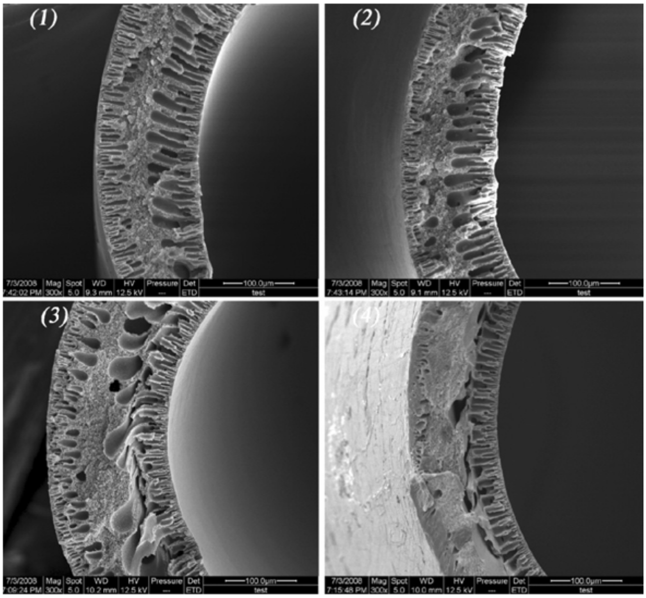


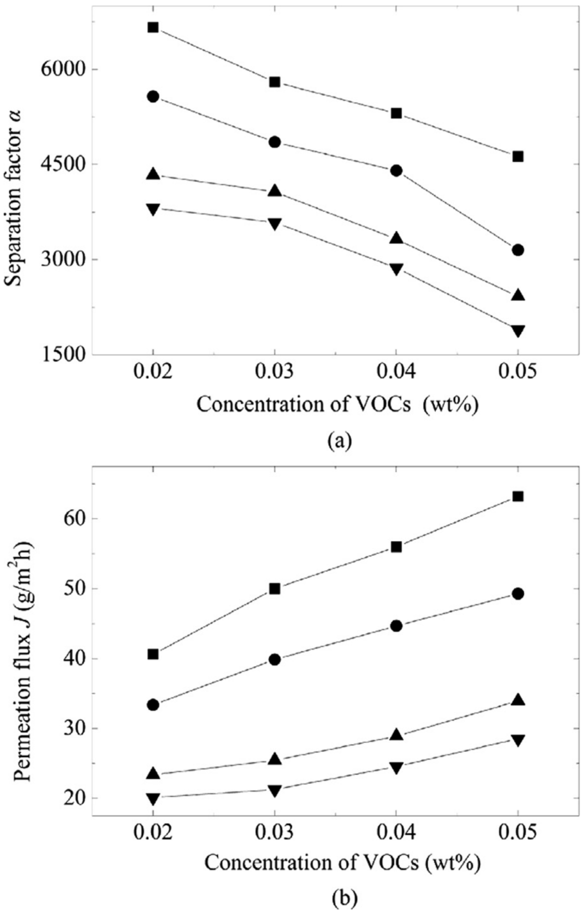
Figure 7. SEM images of hollow fibers prepared in water coagulation at various temperature: (1) 45°C; (2) 35°C; (3) 25°C; (4) 15°C. Air gap was 7 cm.

Effect of Feed Concentration on Pervaporation Performances

The effect of VOCs concentration in the feeds on the pervaporation performances of the blend hollow fiber membranes is shown in Fig. 8. It shows that the separation factor decreases but the flux increases with the increase of the VOCs concentration in the feeds. Generally, hydrophobic polymers can be easily swollen by organic hydrophobic solvents. When more VOCs molecules permeate in the PEI-PES blend membrane, the flexibility of the polymer chains will increase, which make the VOCs molecules to transport through the membrane more easily.

Effect of Temperature of Feed on Pervaporation Performances

The effect of the temperature of the feeds on the pervaporation performance of the blend hollow fiber membranes is shown in Fig. 9. It shows that the permeation flux increases but the separation factor decreases when the temperature of the feeds increases. The phenomenon is due to the fact that the movement of the polymer chains increases with the increase of temperature. Consequently, for the VOCs molecules permeating through the membrane, the resistance decreases with the



(a)

(b)

Figure 8. Effect of concentration of VOCs in feed on PV performances. Concentration of VOCs in feed: 0.02 wt.%, 0.03 wt.%, 0.04 wt.% and 0.05 wt.%. Temperature of feed: 30°C. Velocity of feed: 32.5 ml/min. Distance of air gap: 7 cm. Temperature of coagulation: 45°C. 1,2-dichloroethane (■); trichloroethylene (•); chlorobenzene (▲); toluene (▼).

increase of temperature. The same effect will exist in water molecules. Therefore, the flux increases but the separation factor decreases.

Effect of Velocity of Feed on Pervaporation Performances

The effect of the velocity of the feeds on the pervaporation performance of the membranes is shown in Fig. 10. It shows that with the increase of

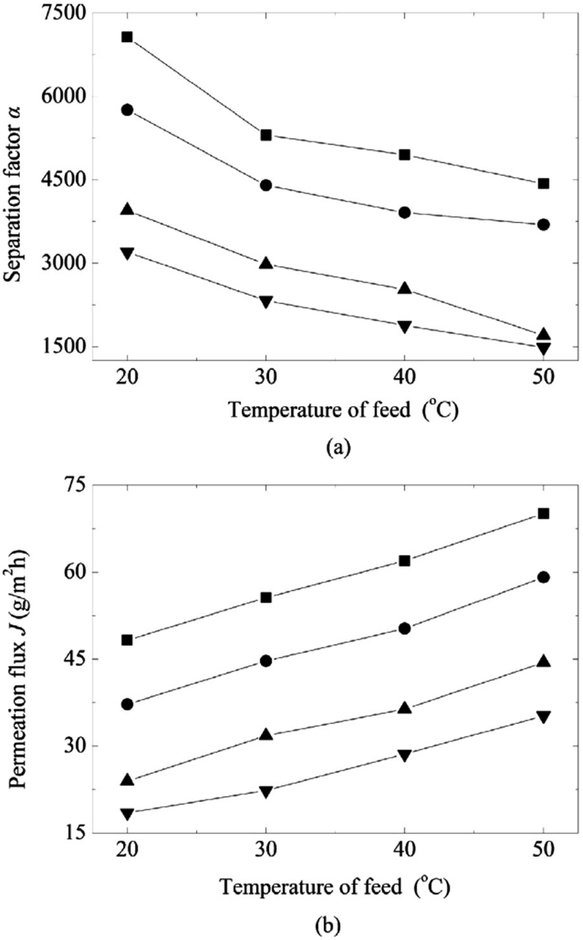


Figure 9. Effect of temperature of feed on PV performance. Temperature of feed: 20°C, 30°C, 40°C and 50°C. Concentration of feed: 0.04 wt.%. Velocity of feed: 32.5 ml/min. Distance of air gap: 7 cm. Temperature of coagulation: 45°C. 1,2-dichloroethane (■); trichloroethylene (●); chlorobenzene (▲); toluene (▼).

the velocity of the feeds, both the separation factor and the permeation flux increase. For most of the membrane separation processes, the phenomenon of concentration polarization widely exists, which makes the separation ability of the membranes to become poor. Increasing the velocity of feed is an effective method to weaken the influence from the concentration polarization, especially when the diffusivity of solute in solution is low (19). In this experiment, the phenomenon of concentration polarization should exist.

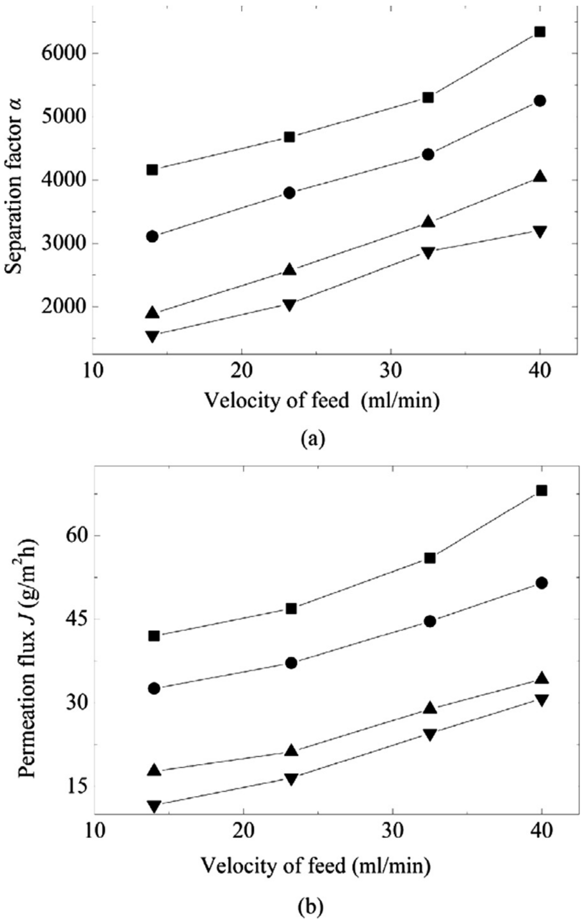


Figure 10. Effect of velocity of feed on PV performance. Velocity of feed: 14 ml/min, 23.2 ml/min, 32.5 ml/min and 40 ml/min. Concentration of feed: 0.04 wt.% at 30°C. Distance of air gap: 7 cm. Temperature of coagulation: 45°C. 1,2-dichloroethane (■); trichloroethylene (●); chlorobenzene (▲); toluene (▼).

Comparison of Selectivity to VOCs between PV and Simple Evaporation Process

The content of VOC in the head space of aqueous solution can be calculated as follows:

$$y_B = P_B/P$$

Table 1. Comparison of selectivity to VOCs between PV and simple evaporation process at 20°C

VOC aqueous solution (0.04 wt.%)	VOC molar fraction y_B ($\times 10^{-4}$) in vapor for evaporation	VOC molar fraction in permeate for PV
1,2-dichloroethane	2.74	0.354
Trichloroethylene	1.92	0.249
Chlorobenzene	0.51	0.204
Toluene	0.98	0.201

$$P_B = P_B^* \times \gamma_B \times x_B$$

Where y_B is the molar fraction of VOC in the head space of vapor, P_B is the vapor pressure of the VOC, P is the total pressure, P_B^* is the saturated vapor pressure of the VOC, γ_B is the activity coefficient and x_B is the molar fraction of the VOC in the aqueous solution. Due to the feed liquids in this experiment are very dilute solutions, γ_B can be taken as 1.

Table 1 lists the comparison of the selectivity to VOCs between PV and simple evaporation process. y_B was calculated to the aqueous solutions containing 0.04 wt.% of VOCs at 20°C. The PV results were taken from a blend membrane prepared when the air gap was 7 cm and the temperature of coagulation bath was 45°C. The data show that the concentrations of VOCs in PV permeation are thousand times over the concentration of the corresponding VOCs in the vapor of a simple evaporation process. Therefore, using the PV technique to remove VOCs from water is preponderant.

CONCLUSION

The pervaporation performances of the PEI-PES blend hollow fiber membranes were affected by both the spinning conditions and the separation conditions. The blend membranes showed high VOC/water selectivity and permeation flux to the VOCs aqueous solutions. The order of the selectivity was 1,2-dichloroethane > trichloroethylene > chlorobenzene > toluene. When the distance of the air gap, the temperature of the coagulation for preparing the blend membrane and the velocity of the feed were 7 cm, 45°C and 32.5 ml/min, respectively, to the aqueous solutions containing 0.04 wt.% VOCs at 20°C, the separation factors of the prepared membrane to 1,2-dichloroethane, trichloroethylene, chlorobenzene and toluene were 7069, 5759, 3952, and 3205, respectively. Consequently, the PEI-PES blend material is valuable for further research of separating VOCs from water by the pervaporation technique.

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REFERENCES

1. Konieczny, K.; Bodzek, M.; Panek, D. (2008) Removal of volatile compounds from the wastewaters by use of pervaporation. *Desalination*, *223* (1–3): 344.
2. Ghoreyshi, A.A.; Jahanshahi, M.; Peyvandi, K. (2008) Modeling of volatile organic compounds removal from water by pervaporation process. *Desalination*, *222* (1–3): 410.
3. Panek, D.; Konieczny, K. (2007) Preparation and applying the membranes with carbon black to pervaporation of toluene from the diluted aqueous solutions. *Sep. Purif. Technol.*, *57* (3): 507.
4. Li, L.; Xiao, Z.Y.; Zhang, Z.B.; Tan, S.J. (2004) Pervaporation of acetic acid/water mixtures through carbon molecular sieve-filled PDMS membranes. *Chem. Eng. J.*, *97* (1): 83.
5. Luo, Y.; Tan, S.J.; Wang, H.; Wu, F.W.; Liu, X.M.; Li, L.; Zhang, Z.B. (2008) PPMS composite membranes for the concentration of organics from aqueous solutions by pervaporation. *Chem. Eng. J.*, *137* (3): 496.
6. Jian, K.; Pintauro, P.N. (1997) Asymmetric PVDF hollow-fiber membranes for organic/water pervaporation separations. *J. Membr. Sci.*, *135* (1): 41.
7. Teoh, M.M.; Chung, T.S.; Wang, K.Y.; Guiver, M.D. (2008) Exploring Torlon/P84 co-polyamide-imide blended hollow fibers and their chemical cross-linking modifications for pervaporation dehydration of isopropanol. *Sep. Purifi. Technol.*, *61* (3): 404.
8. Mishima, S.; Nakagawa, T. (2003) Characterization of Graft Polymerization of Fluoroalkyl Methacrylate onto PDMS Hollow-Fiber Membranes and Their Permselectivity for Volatile Organic Compounds. *J. Appl. Polym. Sci.*, *88* (6): 1573.
9. Kneifel, K.; Peinemann, K.V. (1992) Preparation of hollow fiber membranes from polyetherimide for gas separation. *J. Membr. Sci.*, *65* (3): 295.
10. Wang, D.; Li, K.; Teo, W.K. (1998) Preparation and characterization of polyetherimide asymmetric hollow fiber membranes for gas separation. *J. Membr. Sci.*, *138* (2): 193.
11. Huang, R.Y.M.; Feng, X.S. (1992) Pervaporation of water ethanol mixtures by an aromatic polyetherimide membrane. *Sep. Sci. Technol.*, *27* (12): 1583.

12. Huang, R.Y.M.; Feng, X.S. (1993) Dehydration of isopropanol by pervaporation using aromatic polyetherimide membranes. *Sep. Sci. Technol.*, *28* (11–12): 2035.
13. Wang, Y.; Jiang, L.Y.; Matsuura, T.; Chung, T.S.; Goh, S.H. (2008) Investigation of the fundamental differences between polyamide-imide (PAI) and polyetherimide (PEI) membranes for isopropanol dehydration via pervaporation. *J. Membr. Sci.*, *318* (1–2): 217.
14. Barzin, J.; Feng, C.; Khulbe, K.C.; Matsuura, T.; Madaeni, S.S.; Mirzadeh, H. (2004) Characterization of polyethersulfone hemodialysis membrane by ultrafiltration and atomic force microscopy. *J. Membr. Sci.*, *237* (1–2): 77.
15. Sun, S.D.; Yue, Y.L.; Huang, X.H.; Meng, D.Y. (2003) Protein adsorption on blood-contact membranes. *J. Membr. Sci.*, *222* (1–2): 3.
16. Liu, R.X.; Qiao, X.Y.; Chung, T.S. (2007) Dual-layer P84/polyethersulfone hollow fibers for pervaporation dehydration of isopropanol. *J. Membr. Sci.*, *294* (1–2): 103.
17. Liu, R.X.; Qiao, X.Y.; Chung, T.S. (2005) The development of high performance P84 co-polyimide hollow fibers for pervaporation dehydration of isopropanol. *Chem. Eng. Sci.*, *60* (23): 6674.
18. Chung, T.S.; Hu, X.D. (1997) Effect of air-gap distance on the morphology and thermal properties of polyethersulfone hollow fibers. *J. Appl. Polym. Sci.*, *66* (6): 1067.
19. Peng, M.; Vane, L.M.; Liu, S.X. (2003) Recent advances in VOCs removal from water by pervaporation. *J. Hazard. Mater.*, *98* (1–3): 69.