

Pervaporation Process with PDMS/PVDF Hollow Fiber Composite Membrane to Recycle Phenol from Coal Chemical Wastewater

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Abstract: To treat coal gasification wastewater containing phenol, polydimethylsiloxane (PDMS)/polyvinylidene fluoride (PVDF) hollow fiber composite membrane was made by dynamic negative pressure coating method, using PVDF hollow fiber membrane as base membrane, PDMS as modifying membrane material, to improve pervaporation performance of PDMS by the cross-linking modification. The influence of cross-linking agent, PDMS concentration, coating time on pervaporation performance of the composite membrane was investigated. Actual coal chemical wastewater with phenol concentration 1600-1800 mg/L, COD 13000-15000 mg/L was treated by the obtained PDMS/PVDF composite membrane, and at temperature 70°C, the flow rate of 10 L/h, pressure under membrane 3KPa, phenol flux 16.81 g/(m²·h), separation factor reaches 8.103.

Keywords: Hollow fiber composite membrane, dynamic negative pressure coating, cross-linking modification, pervaporation, coal chemical wastewater.

1. INTRODUCTION

Coal chemical industries result in a large amount of high concentration organic wastewater, mainly phenolic compounds, alkane, aromatic hydrocarbons, heterocyclic, ammonia nitrogen and cyanide, which are hard to be treated by traditional biological treatment. At the same time, phenolic is an important basic material in organic synthesis [1], so if large amount of phenolic substances be recovered or recycled, it would produce huge economic and environmental benefit.

Pervaporation is an industrial process with low energy consumption, being environmental friendly and promising, especially suitable for separating azeotrope, the isomers with same boiling point and thermosensitive substance [2]. In comparison with the plate-and-frame module, the hollow fiber membrane [3, 4] has the advantages of high-packing density, self-contained mechanical support, self-contained vacuum channel and economical superiority. The PDMS with side chain modification [5] has better pervaporation

performance and so PDMS/PVDF hollow fiber composite membrane was made by dynamic negative pressure coating method, and pervaporation performance of PDMS was improved by the cross-linking modification. The influence of cross-linking agent, PDMS concentration, coating time on the pervaporation performance of the composite membrane was investigated in this paper.

2. EXPERIMENTAL

2.1. Materials and Reagents

PVDF hollow fiber membrane module (pore size 0.16 μm, hollow fiber inner diameter 0.8mm, external diameter 1.16 mm, membrane area 553 cm², (Institute of Biological & Chemical Engineering, Tianjin Polytechnic University); polydimethylsiloxane (PDMS) with molecular weight 6000 (Heowns Biochem Technologies Co. Ltd.), tetraethoxysilane (Heowns Biochem Technologies Co. Ltd.), (3 - cyanide propyl) triethoxy silane (Heowns Biochem Technologies Co.Ltd.), dibutyltin dilaurate (Heowns Biochem Technologies Co. Ltd.), n-hexane, analytically pure (National Medicine Group Chemical Reagent Co. Ltd.) were used.

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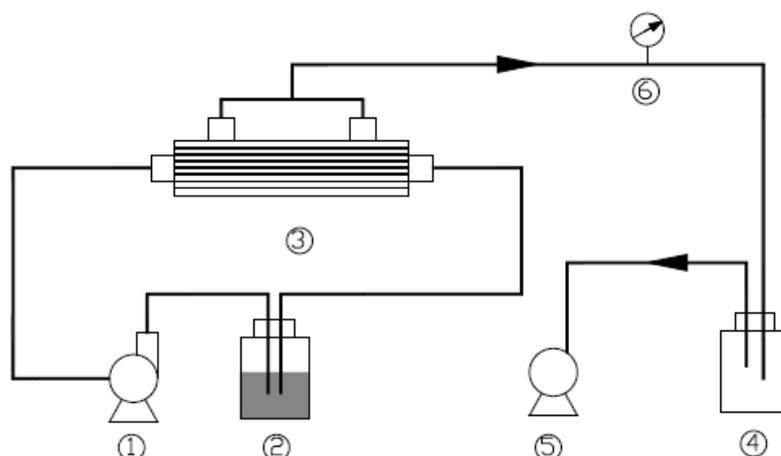


Figure 1: Coating process diagram. 1. Peristaltic pump; 2. Material liquid tank; 3. Hollow fiber membrane module; 4. Buffer bottle; 5. Vacuum pump; 6. Vacuum gauge.

2.2. Preparation of Composite Membrane

PDMS casting solution was prepared by dissolving PDMS, cross-linking agent and catalyst (dibutyltin dilaurate) with a certain mass ratio in n-hexane with continuous adding of n-hexane, stirring, centrifugating, and deaerating. PVDF membrane was activated by pumping the heated NaOH solution (65°C, concentration 2 mol/L) into hollow fiber membrane for 15min, then rinsing the membrane with deionized water till the effluent water pH being neutral. Composite membranes were prepared by a dynamic negative pressure coating method, as shown in Figure 1. Peristaltic pump was used to pump the PDMS casting solution into hollow fiber module, the flow direction of casting solution changed every 10min. Vacuum pump was used to produce certain negative pressure (0.06 MPa) in the hollow fiber membrane shell to form a composite layer after a certain time and cross-link last for 48 h in 30°C till the membrane being dry.

2.3. Pervaporation Performance Testing Process

The pervaporation performance of membrane was tested in pervaporation setup, shown in Figure 2, in which heated wastewater, from Qitaihe Baotailong Coal Chemical Co. Ltd, was pumped into the membrane reaction tank, the treated water recycled back into

waste water storage bottle. In membrane reaction tank, organic pollution in wastewater pervaporated into gas phase through membrane because of the negative pressure made by vacuum pump, then cooled and collected, the phenol concentration being determined by 4-Aminoantipyrine spectrophotometry. The characteristics of coal chemical wastewater were shown in Table 1. The wastewater mainly contain phenol, cresol, benzodiazepines, heterocyclic compounds and so on. 1L wastewater was used for test, and experimental operating conditions were as water temperature at 70°C, circulation flow rate fixed at 10L/h, pressure under membrane 3 KPa.

The pervaporation process evaluation index is the permeation flux and separation factor as formula (1-1) and (1-2):

$$J = \frac{W}{A \cdot \Delta t} \quad (1-1)$$

In which: J —permeation flux, g/(m²·h); W —permeation mass, g; A —membrane area, m²; Δt —operating time, h.

$$\alpha = \frac{Y_A / Y_B}{X_A / X_B} \quad (1-2)$$

Table 1: Characteristics of Coal Chemical Wastewater

Items	Value	Items	Value
COD	13000-15000 mg/L	SS	580-650 mg/L
pH	7.5-8.1	Color	Brown yellow
Phenol concentration	1600-1800 mg/L	Temperature	70-80 °C

In which: α —separation factor; Y_A —mass fraction of A in permeation(%); Y_R —mass fraction of B in permeation (%); X_A —mass fraction of A in feed (%); X_B —mass fraction of B in feed (%).

3. RESULTS AND DISCUSSION

3.1. Characterization of Coating Effect

The characterization of coating effect of membrane inner face was tested by contact angle test, scanning electron microscope (SEM), energy dispersive X-ray spectroscopy (EDS), as shown in Figure 3 for original PVDF membrane, activated PVDF membrane and composite membrane.

The contact angle between membrane and water was significant increased from original PVDF membrane (78.784°) to coated composite membrane (91.61°), so the coated hollow fiber membrane was more hydrophobic which means less water permeation and higher separation factor. Observation of SEM and EDS testing would illustrate that the original PVDF membrane had a large number of micropores on inner surface; the micropores became larger after activated, while the material composition was still polyvinylidene fluoride; which verified that polydimethylsiloxane was successfully coated on the activated membrane inner face, filling pores on the inner surface and formed the perfect dense endodermis. The SEM of original PVDF

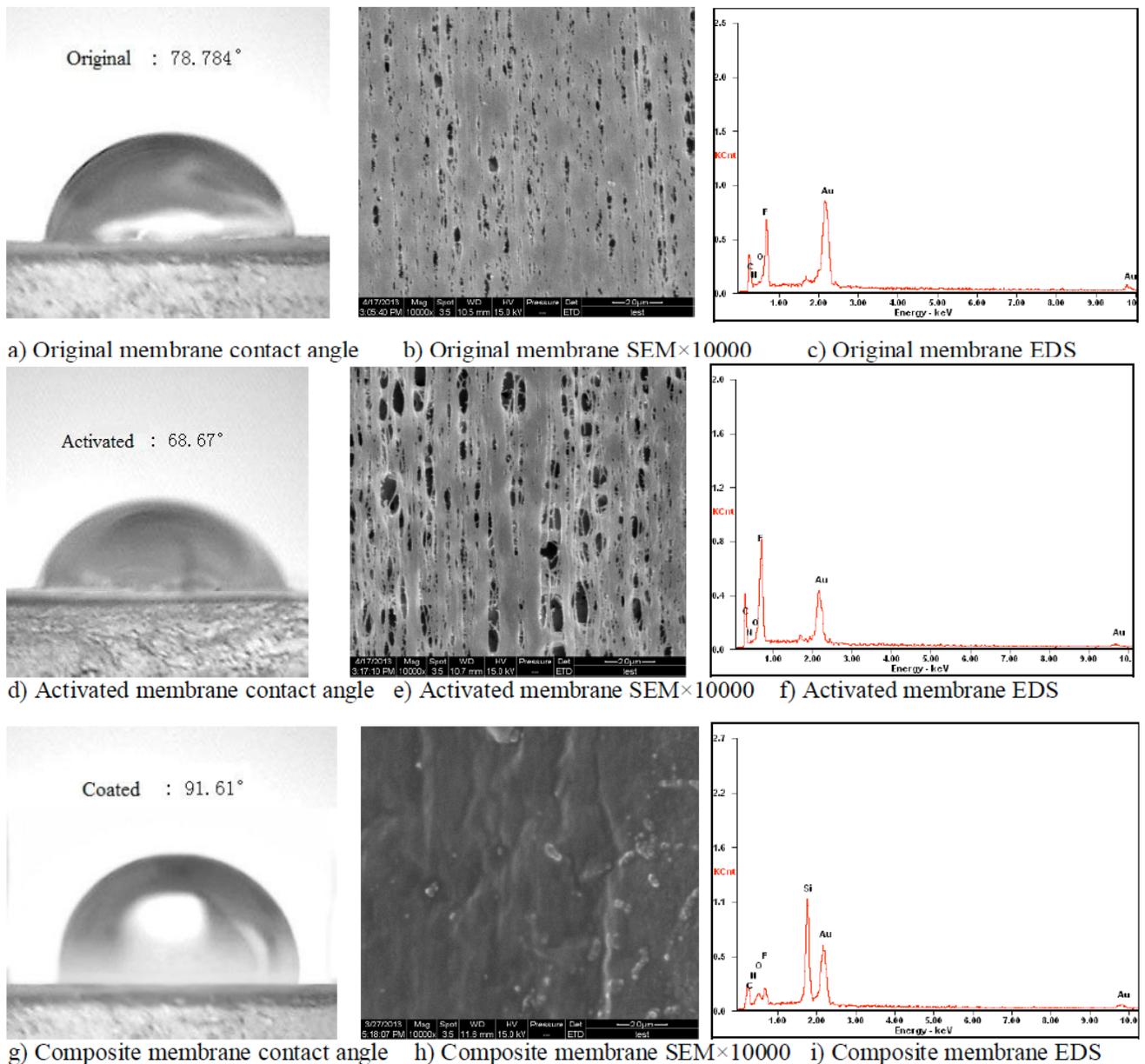


Figure 3: Membrane inner surface characterization.

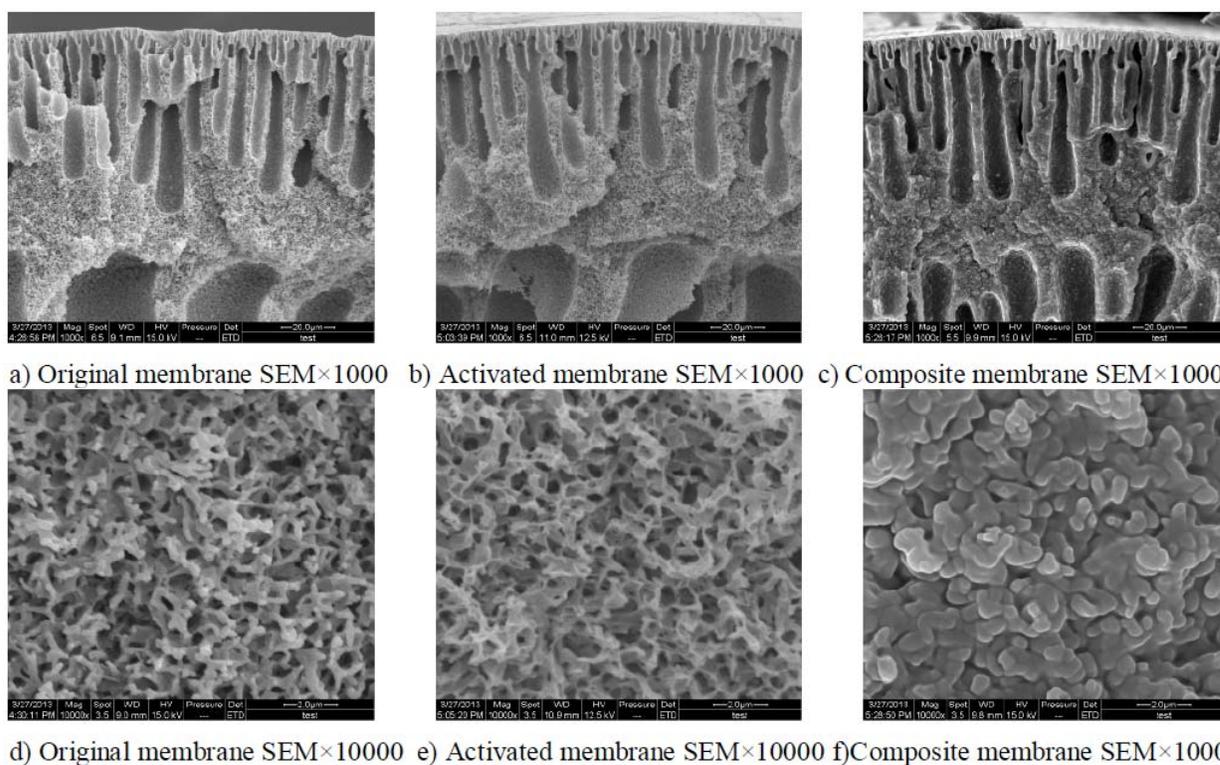


Figure 4: SEM pictures of hollow fiber membrane cross section.

membrane, activated PVDF membrane and composite membrane were shown in Figure 4.

The morphology change of original PVDF membrane, activated PVDF membrane, coated composite membrane could be easily observed by the cross section SEM pattern. The original PVDF membrane has highly developed porosity and smooth fracture surface and the roughness was significantly increased after activation and fracture surface show a jagged edges. The highly developed pores were filled and the jagged edges were coated by PDMS membrane material, which prove that PDMS membrane materials had been combined with PVDF internal structure through pores and formed a PDMS/PVDF composite structure.

Synthesis and pervaporation test illustrate that PDMS/PVDF composite membrane made by dynamic

negative pressure coating method was perfect, solid and tight, PDMS dense endodermis being formed on the inner surface.

3.2. Effect of Cross-Linking Modification on PDMS Composite Membrane Pervaporation Performance

(3-cyanide propyl) triethoxy silane was used as cross-linking agent to introduce $-\text{CN}$ into PDMS material and in order to guarantee same degree of cross-linking, formula and preparation conditions of two kinds of membrane were given in Table 2, including pervaporation performance of membranes. Two membranes were tested by infrared absorption spectrum for confirming the introduction of $-\text{CN}$, and the membrane infrared image was shown in Figure 5.

The infrared spectrograms show 2963 cm^{-1} peak (C-H stretching vibration $3000\text{-}2843\text{ cm}^{-1}$), 1391 cm^{-1}

Table 2: PDMS Composite Membrane Preparation Conditions & Pervaporation Performance

Membrane	Mass ratio	PDMS concentration	Coating time (min)	Phenol flux $\text{g}/(\text{m}^2 \cdot \text{h})$	Water flux $\text{kg}/(\text{m}^2 \cdot \text{h})$	Separate factor
Original PDMS	PDMS: tetraethoxysilane:DBTL=20:2:1	20 wt %	20	13.74	2.321	4.496
Modified PDMS	PDMS: (3-cyanide propyl) triethoxy silane:DBTL=20:3:1	20 wt %	20	17.52	2.737	5.793

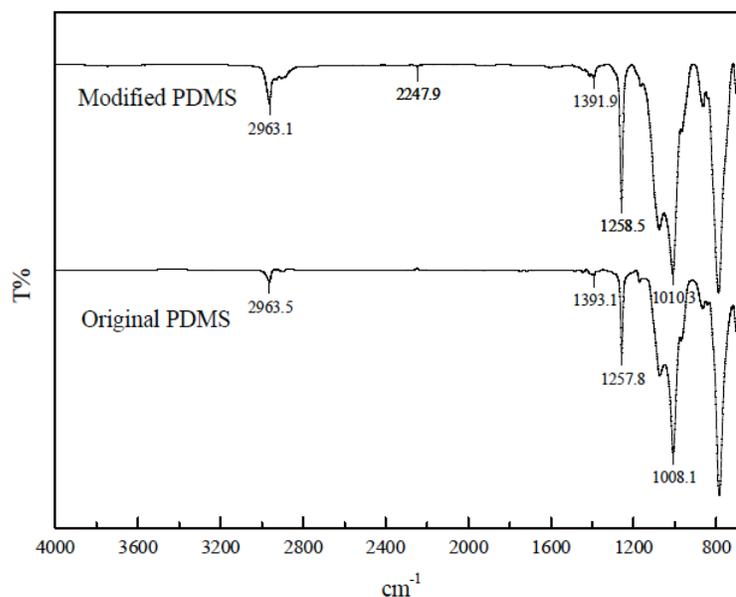


Figure 5: PDMS composite membrane infrared image.

12 (C-H bending vibration 1490-1350 cm^{-1}), 1258 cm^{-1} (C-O stretching vibration 1260-1000 cm^{-1}), 1010 cm^{-1} (Si-O characteristic absorption 1100-1000 cm^{-1}). It also tells that cross-linking modified membrane had an absorption peak of 2247.9 cm^{-1} (C≡N characteristic absorption 2260-2240 cm^{-1}), which means cross-linking modification was successful to introduce -CN into PDMS.

Pervaporation performance in Table 2 reveals that cross-linking modification raised the phenol flux, water flux and separation factor at the same time. Cross-linking modification by using (3-cyanide propyl) triethoxy silane and the introduction of -CN in the membrane material would reduce the tightness of membrane, and increase the water flux. Introduction of -CN may enhance membrane materials selectivity for phenol and significantly increase the flux of phenol, so phenol flux improvement was more remarkable than water flux improvement, and so as to increase the separation factor from 4.496 to 5.793 and improve pervaporation performance, more suitable for the treatment and recycle of phenolic wastewater.

3.3. Effect of Concentration of Cross-Linking Agent on PDMS Composite Membrane Pervaporation Performance

To study the effect of concentration of cross-linking agent on PDMS composite membrane pervaporation performance, preparation conditions of four kinds of membrane were given in Table 3, and the pervaporation performance of membranes were given in Figure 6.

The Figure 6 showed that the separation factor presented a trend of decrease after the first increase with increase of the concentration of cross-linking agent. When the concentration of cross-linking agent was in low proportion (mass ratio 20:2:1), increase of cross-linking agent dosage made water flux decrease, phenol flux increase, and separate factor rise. Because the cross-linking agent could improve the tightness of membrane and enhanced phenol selectivity, when the mass ratio was 20:3:1, phenol flux and separate factor reached the peak, 17.52 $\text{g}/(\text{m}^2\cdot\text{h})$ and 5.793, respectively. Then continuous addition of cross-linking agent make membranes more dense, water flux

Table 3: PDMS Composite Membrane Preparation Conditions

Membrane number	Mass ratio (PDMS:Cross-linking agent:DBTL)	PDMS Concentration	Coating time (min)
M1	20:2:1	20 wt %	20
M2	20:3:1	20 wt %	20
M3	20:4:1	20 wt %	20
M4	20:5:1	20 wt %	20

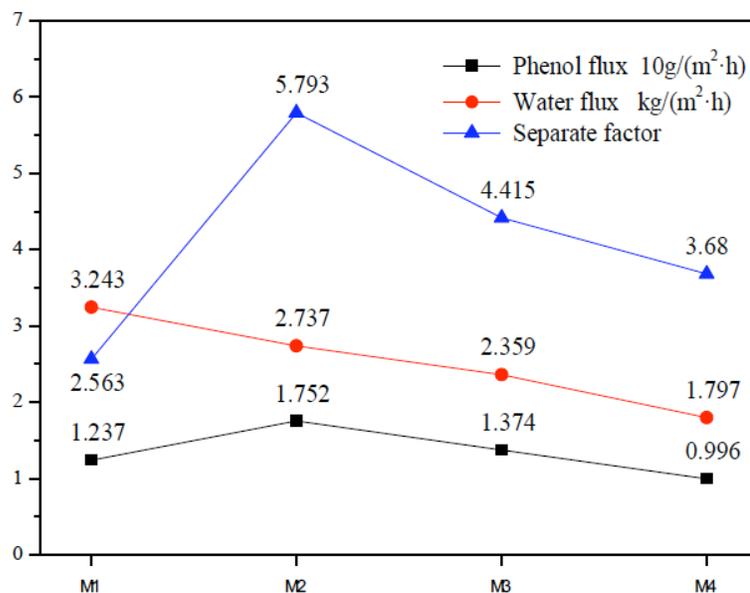


Figure 6: Effect of concentration of cross-linking agent on PDMS composite membrane pervaporation performance.

continues to decline. The resistance of phenol molecules through membrane increased, the phenol flux decreased, and the separation factor presented downward trend.

3.4. Effect of Concentration of PDMS on PDMS Composite Membrane Pervaporation Performance

To study the effect of concentration of PDMS on PDMS composite membrane pervaporation performance, preparation conditions of four kinds of membrane were given in Table 4 and the pervaporation performance of membranes were given in Figure 7.

The Figure 7 showed that with the increase of PDMS concentration, phenol flux and water flux were both decreased, whereas the separation factor presented a trend of decrease after the first increase. Because PDMS concentration would determine casting solution viscosity, so the greater the concentration, the higher the viscosity. When PDMS concentration was too low, the viscosity was low, the formation of separate layer was thin, and resistance of phenol and water through membrane was low which made the

separation factor low. At the same time, if the PDMS concentration was too high, viscosity was high which made separation layer dense, resistance of phenol and water through membrane was high, so phenol flux and water flux were at low levels, and the separation factor was low. In addition high viscosity was not conducive to dynamic coating process; high viscosity solution was easy to make the hollow fiber membrane obstruction and internal coating uneven. Therefore, appropriate PDMS concentration was very important for high quality coating.

3.5. Effect of Coating Time on PDMS Composite Membrane Pervaporation Performance

Preparation conditions of four kinds of membrane were given in Table 5 and the pervaporation performance of membranes were given in Figure 8.

The Figure 8 showed that with the increase of PDMS concentration, phenol flux and water flux were both decreased, whereas the separation factor presented a trend of decrease after the first increase. Coating time extended from 20min to 40 min, water flux

Table 4: PDMS Composite Membrane Preparation Conditions

Membrane number	Mass ratio (PDMS:Cross-linking agent:DBTL)	PDMS Concentration	Coating time (min)
M1	20:3:1	15 wt %	20
M2	20:3:1	20 wt %	20
M3	20:3:1	25 wt %	20
M4	20:3:1	30 wt %	20

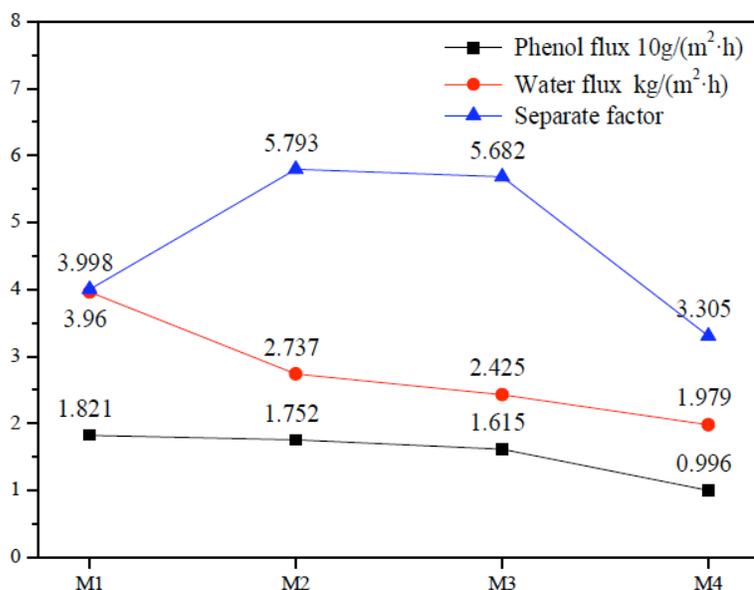


Figure 7: Effect of concentration of PDMS on PDMS composite membrane pervaporation performance.

Table 5: PDMS Composite Membrane Preparation Conditions

Membrane number	Mass ratio (PDMS:Cross-linking agent:DBTL)	PDMS Concentration	Coating time (min)
M1	20:3:1	20 wt %	20
M2	20:3:1	20 wt %	40
M3	20:3:1	20 wt %	60
M4	20:3:1	20 wt %	80

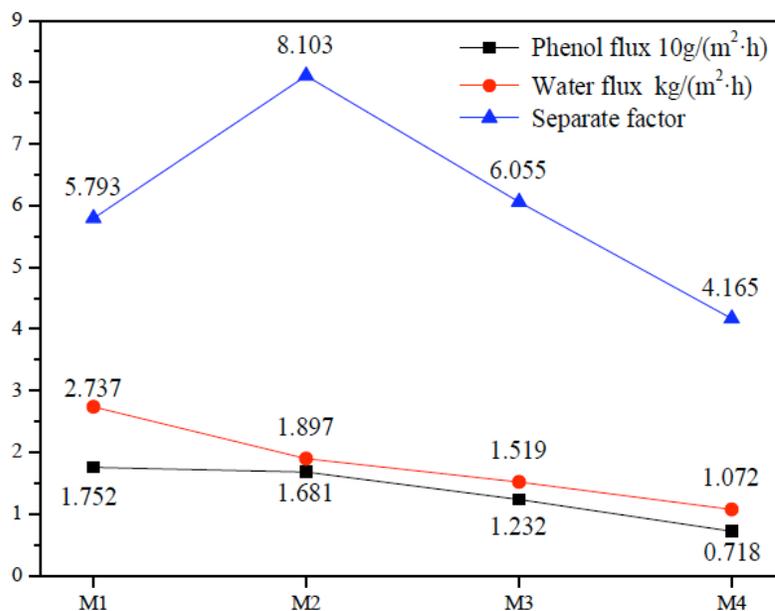


Figure 8: Effect of concentration of coating time on PDMS composite membrane pervaporation performance.

decreased significantly, phenol flux decreased from 17.52 $g/(m^2 \cdot h)$ to 16.81 $g/(m^2 \cdot h)$, separate factor increased from 5.793 to 8.103, and membrane

pervaporation performance was the best at this time. Then extended coating time, phenol flux, water flux and separate factor all decreased. Because the coating

time determined the thickness of separate layer, long coating time would result in thicker separate layer, and furthermore greater resistant of phenol and water.

4. CONCLUSION

PDMS/PVDF hollow fiber pervaporation composite membrane was made by dynamic negative pressure coating method, used to treat coal gasification wastewater containing phenol. PDMS membrane materials form perfect dense endodermis on the inner surface and combine with PVDF internal structure and construct a composite structure.

PDMS material was cross-linking modified by (3-cyanide propyl) triethoxy silane and the introduction of -CN in membrane which could enhance selectivity for phenol and separate factor, more suitable for treating phenolic wastewater.

The influence of cross-linking agent, PDMS concentration, coating time on the pervaporation performance of the composite membrane was investigated. The membrane, mass ratio as PDMS: (3-cyanide propyl) triethoxy silane: DBTL=20:3:1, concentration of PDMS 20 wt %, coated 40min, pervaporation performed the best. Actual coal chemical industry wastewater with phenol concentration 1600-

1800 mg/L, COD 13000-15000 mg/L was treated by the obtained PDMS/PVDF composite membrane, at temperature 70 °C, the flow rate of 10 L/h, pressure under membrane 3KPa, phenol flux was 16.81 g/(m²·h), separation factor reached 8.103.

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