Pilot Scale Hollow Fiber Pervaporation System for Phenol Recycling from Coal to Chemical Wastewater

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Abstract: Polydimethylsiloxane (PDMS)/Polyvinylidene fluoride (PVDF) hollow fiber composite membrane was prepared by dynamic negative pressure method to treat coal to chemical wastewater containing high concentration of phenol, in which PVDF hollow fiber membrane acts as base membrane and PDMS as modified membrane. In the pilot scale experiment, the influence of aeration rate, temperature, flow rate, pressure under membrane on phenol removal efficiency were investigated and operating parameter optimized. At temperature 70℃, flow rate of 150 L/h, pressure under membrane 5 KPa, gas-water ratio 0.3, 75 L coal to chemical wastewater containing phenol fluctuated between 1600 and 1800 mg/L was treated for 6h, and phenol removal efficiency reached 72%. The system ran stably for 120 h and performed well, phenol removal efficiency being kept more than 60%.

Keywords: Hollow fiber composite membrane, dynamic negative pressure method, pilot scale pervaporation system, coal to chemical wastewater.

1. INTRODUCTION

Coal to chemical industries result in a large amount of high concentration organic wastewater, mainly containing phenolic compounds [1], alkane, aromatic hydrocarbons, heterocyclic, ammonia nitrogen and cyanide, hard to be treated by traditional biological treatment [2]. As the unit of preliminary treatment, pervaporation process, with low energy consumption and being environmental friendly, was introduced to recycle phenolic compounds and reduce the biochemical treatment difficulty to achieve resource recycling and improving performance of wastewater treatment .

In comparison with plate-and-frame module, hollow fiber membrane [3-5] illustrates the advantages of high-packing density, self-contained mechanical support, self-contained vacuum channel and economical superiority. In the pilot scale experiment, PDMS/PVDF composite membrane was made by dynamic negative pressure method, and the influence of aeration rate, temperature, flow rate, and pressure under membrane were investigated and optimized.

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2. EXPERIMENTAL

2.1. Materials and Reagents

PVDF hollow fiber membrane module (pure water flux 1000 L/m^2·h, work pressure 0.1-0.25 Mpa, membrane area 0.46 m^2), from SENUO Filtration Technology Co. Ltd.; polydimethylsiloxane (PDMS, molecular weight 6000), from Heowns Biochem Technologies Co. Ltd.; (3-cyanide propyl) triethoxy silane, from Heowns Biochem Technologies Co. Ltd.; dibutyltin dilaurate, from Heowns Biochem Technologies Co. Ltd.; n-hexane, analytically pure, from National Medicine Group Chemical Reagent Co. Ltd. were used.

2.2. Preparation of Composite Membrane

PDMS casting solution was prepared by dissolving PDMS, cross-linking agent and catalyst (dibutyltin dilaurate) with mass ratio of 20:3:1 in n-hexane with continuous adding of n-hexane till concentration of PDMS reaching 20 *wt* %, stirred, centrifuged, and deaerated. PVDF membrane was activated by pumping heated NaOH solution (65°℃, 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, shown in Figure **1**, in which peristaltic pump

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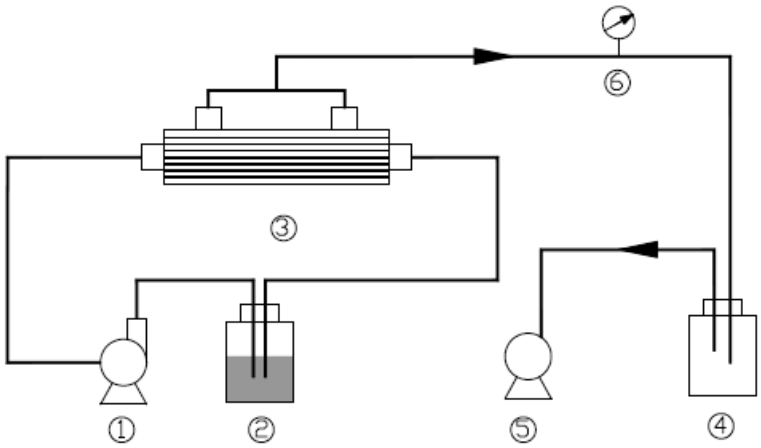

Figure 1: Coating process diagram.
1. Peristaltic pump; 2. Liquid material tank; 3. Hollow fiber membrane module; 4. Buffer bottle; 5. Vacuum pump; 6. Vacuum gauge.

was used to pump PDMS casting solution into hollow fiber module, and the flow direction of casting solution varied every 10min. Certain negative pressure (0.06 MPa) inside hollow fiber membrane shell was generated with vacuum pump to form a composite layer after 40 min and cross-link last for 48 h in 30℃ till the membrane dried.

2.3. Pervaporation Test

The characteristics of wastewater, from Qitaihe Baotailong Coal to Chemical Co. Ltd, were shown in Table **1**, which mainly contain phenol, cresol, benzodiazepines, and heterocyclic compounds. The pilot scale pervaporation setup was shown in Figure **2**, in which coal to chemical wastewater was pumped into the membrane reaction tank, and the treated water recycled back to wastewater storage tank. In membrane reaction tank, organic substance in wastewater was pervaporated into gas phase through membrane because of the negative pressure made by vacuum pump, then cooled and collected.

The operating parameter was shown in Table **2**, determined by Simple Variable Method, in which the

Table 1: Characteristics of Coal to 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

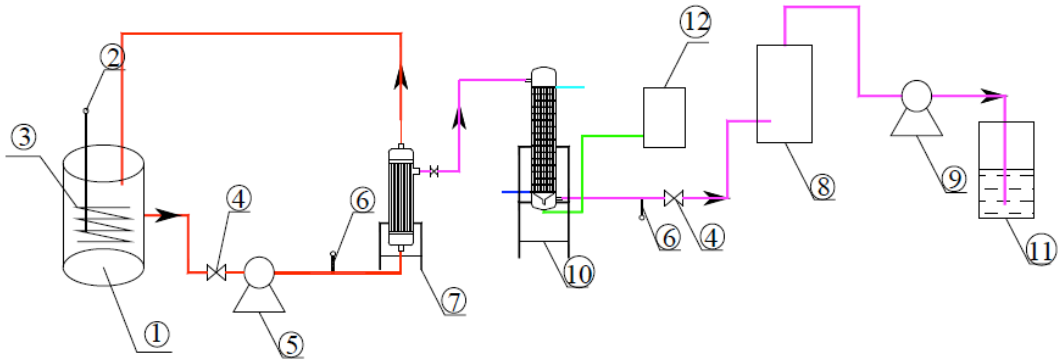

Figure 2: Pervaporation process.
1. Wastewater storage tank; 2.Thermometer; 3 Heater; 4. Valve; 5. Peristaltic pump; 6. Pressure gauge; 7. The membrane reaction tank; 8. Buffer tank; 9. Vacuum pump; 10. Condenser; 11. Absorption bottle; 12. Condensate collecting bottles.

Table 2: Operating Parameters

Operating parameter		Operating parameter	
Feed volume	75 L	Cycle length	6h
Aeration rate	0.3(gas-water ratio)	Temperature	70℃
Flow rate	150 L/h	Pressure under membrane	5 KPa

operating condition of system was evaluated by phenol removal efficiency.

3. RESULTS AND DISCUSSION

3.1. Determination of Operation Parameter

3.1.1. Determination of Cycle Length

Figure **3** showed that with the increase of time, phenol removal efficiency increased while phenol flux decreased. Because the removal of phenol resulted in smaller concentration difference between two sides of the membrane, the mass transfer impetus weakened and phenol flux decreased. After 6h, the phenol concentration reached 476 mg/L and phenol removal efficiency 72%; and while 10h, the phenol concentration 380 mg/L, the efficiency reached 78%. And it could be found that the operation from 6h to 10 h only enhances phenol removal efficiency 6%, so from the view of economics, the operation time was fixed at 6h.

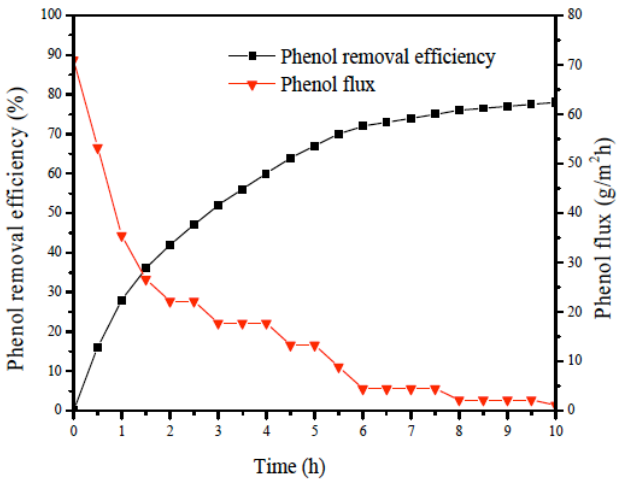

Figure 3: Relationship of phenol removal efficiency and phenol flux with time.

3.1.2. Determination of Aeration Rate

The Figure **4** showed that with the enhancement of gas-water ratio, phenol removal efficiency increased, because the aeration created bubbles in the water, which could improve the degree of turbulence in the liquid phase, compress boundary layer on the surface of the membrane, weaken the concentration polarization phenomenon, and reduce the mass transfer resistance. At the same time, aeration could reduce the solubility of phenol in wastewater and make phenol easy to escape from wastewater. When the gas water ratio reaches 0.3, continuous aeration could not improve removal efficiency effectively, and so gas water ratio of 0.3 be fixed.

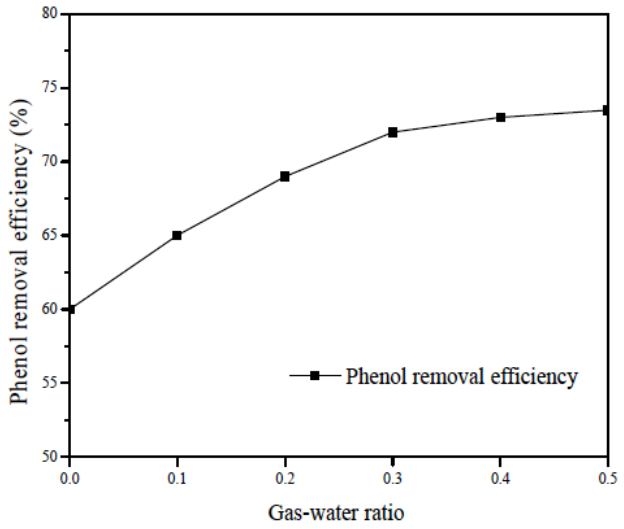

Figure 4: Relationship of phenol removal efficiency with aeration rate.

3.1.3. Determination of Temperature

The Figure **5** tells that the elevation of temperature from 55℃ to 70℃, phenol removal efficiency increased from 49% to 72%, because the higher the temperature, the higher phenol molecular energy, which make phenol easy to permeate the membrane and improve phenol removal efficiency. When temperature was 75℃, the removal efficiency reached 78%, but long time operation at high temperature would cause inconvertible damage for composite membrane, as surface breakage which result in membrane life shorted.

3.1.4. Determination of Flow Rate

The Figure **6** showed that with the increase of flow rate, phenol removal efficiency increased, and it is

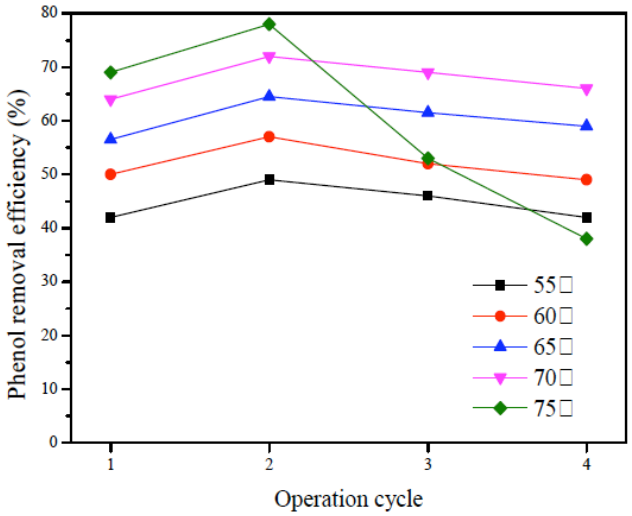

Figure 5: Relationship of phenol removal efficiency with temperature.

found that the influence on phenol removal efficiency is same as aeration, high flow rate accelerate the degree of turbulence in the liquid phase, compressed boundary layer on the surface of the membrane, weakened the concentration polarization phenomenon, reduced the mass transfer resistance. High flow rate had inhibitory effect on membrane fouling, high speed wastewater scour separation membrane surface and made SS, oil hard to adhere membrane surface. While flow rate increased from 150 L/h to 210 L/h, there is limited phenol removal efficiency increase.

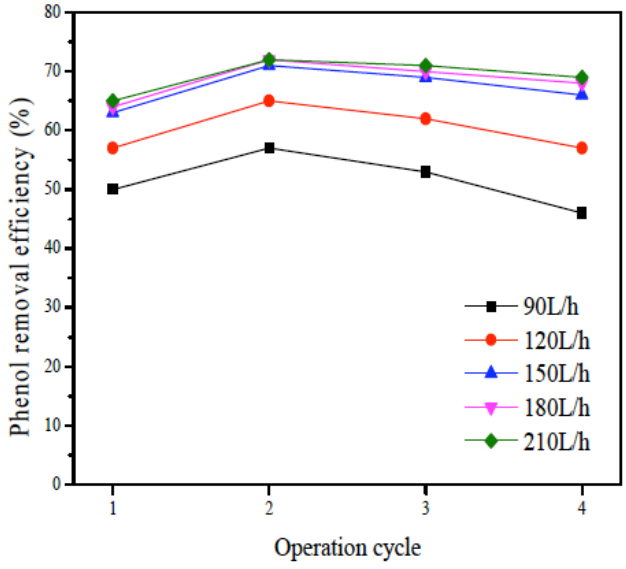

Figure 6: Relationship of phenol removal efficiency with flow rate.

3.1.5. Determination of Pressure Under Membrane

From Figure **7** it is found that with the decrease of pressure under membrane, phenol removal efficiency increased, because the lower pressure under membrane, the bigger steam partial pressure concentration difference between two sides of the membrane. The mass transfer impetus increased and promoted phenol permeation, and at low pressure under membrane there is an acceleration for membrane fouling, because whenever pressure is lower, contaminating substance is more inclined to axial movement and adhere to membrane surface. It's important to ensure system sealing and keep pressure under 5 kpa for stable operation.

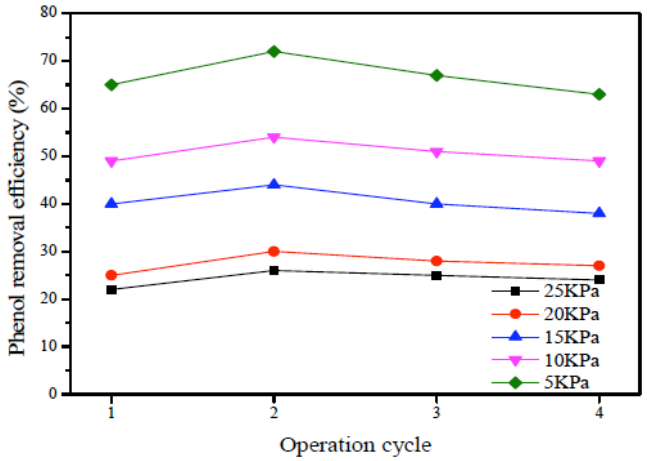

Figure 7: Relationship of phenol removal efficiency with pressure under membrane.

3.2. Membrane Clean

Whenever the pervaporation membrane system appear the following situations, such as phenol flux less than 15%; phenol removal efficiency less than 15%; or obvious membrane fouling, membrane clean is required to restore performance. Membrane cleaning steps includes the following: pumping deionized water to flush the membrane module for 10 min; pumping 4 kinds of liquid, such as deionized water, 0.5 *wt* % HCl solutions, 0.5 *wt* % NaOH solutions, and 0.5 *wt* % surfactant solution, to flush the membrane module for 15 min, and pumping deionized water to rinse the residual liquid. The performance of membrane clean method was evaluated by phenol removal efficiency, as shown in Table **3**.

From Table **3**, the performance of system was recovered after membrane clean, in which surfactant clean performed the best, because PDMS material had a strong affinity for organic pollutant and so oil contamination adhered to membrane and blocked, which could be removed by surfactant clean, and at the same time, surfactant brought bubbles into liquid, flushed SS which adhere to membrane surface.

Table 3: Membrane Clean and Performance

Membrane clean method	Before clean	After clean	Performance improvement
Deionized water clean	57.8%	60.2%	4.2%
HCl clean	57.2%	63.5%	11.0%
NaOH clean	56.8%	62.7%	10.4%
Surfactant clean	57.3%	69.6%	21.5%

3.3. Continuous Operation Stability of Pervaporation System

Figures **8** and **9** illustrate that the pervaporation system need about 2 cycles (12 h) to adjust new coal to chemical wastewater and after 2 cycles, system pervaporation performance appears the best, the phenol removal efficiency reaching 72%, then phenol removal efficiency beginning to decrease because of membrane fouling, and after 10 cycles (60h), phenol removal efficiency dropped to 57%, system needing to be cleaned to recover performance. When feed phenol concentration fluctuated between 1600 and 1800 mg/L, the system ran stably for 120 h and performed well, effluent phenol concentration ranging from 400 to 600 mg/L, phenol removal efficiency kept more than 60%.

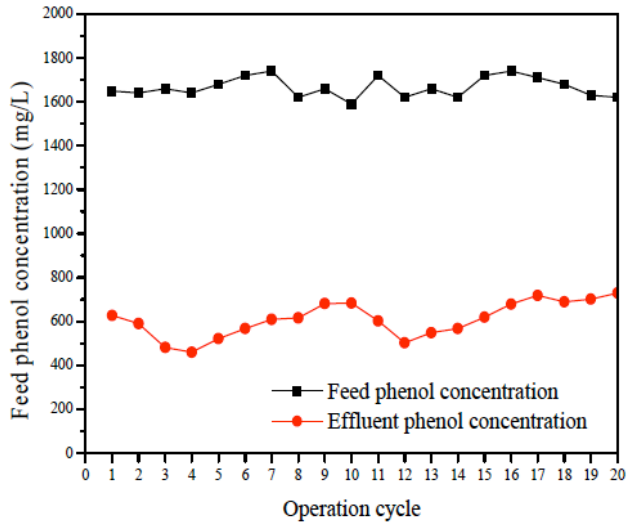

Figure 8: Relationship of phenol feed/effluent concentration with operation cycle.

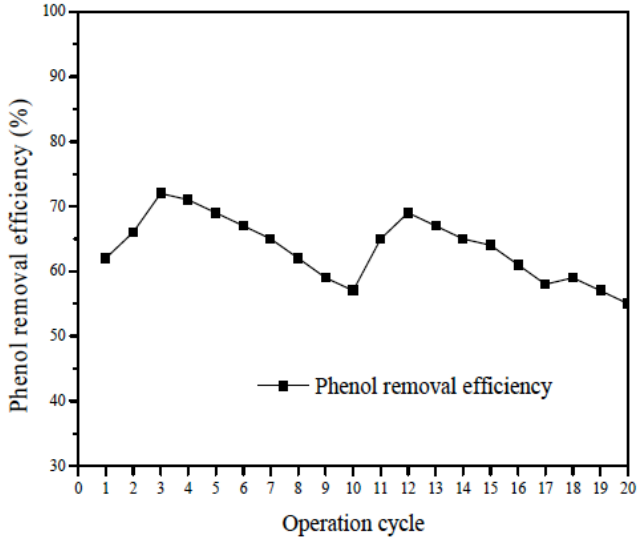

Figure 9: Relationship of phenol removal efficiency with operation cycle.

4. CONCLUSIONS

It could be generated that at temperature 70℃, the flow rate of 150 L/h, pressure under membrane 5 KPa, gas-water ratio 0.3, 75 L coal to chemical wastewater was treated for 6h, phenol removal efficiency reached 72%. The performance of system recovered after membrane clean, in which surfactant clean performed best, and performance improvement reach 21.5%. The system ran stably for 120 h and performed well, as feed phenol concentration fluctuated between 1600 and 1800 mg/L, effluent phenol concentration ranging from 400 to 600 mg/L, and phenol removal efficiency kept more than 60%.

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