The Effect of Supported Liquid Membrane and Liquid Membrane Phase on the Extraction Efficiency of Coal Gasification Wastewater

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Abstract: The extraction and recovery of phenol from high concentration coal gasification wastewater has been investigated using polypropylene (PP) hollow fiber membranes and polyvinylidene fluoride (PVDF) hollow fiber membranes as supported liquid membrane and the mixture of extraction agent and paraffin as liquid membrane phase, with sodium hydroxide as stripping agent. The effect of the composition of the liquid membrane phase made of N-503-kerosene, tributyl phosphate (TBP)-kerosene or trialkyl phosphine oxide (TRPO)-kerosene on extraction efficiency has been studied. The supported liquid membrane give novel extraction result for the extraction of phenol from high concentration coal gasification wastewater when proper liquid membrane phases and liquid membrane support body materials are used in supported liquid membrane system. Under the operating conditions of waste water temperature at 20 ˚C pH at 8.4, waste water and stripping phase flow rate at 5 L/h, the supported liquid membrane using PP as supported liquid membrane and the extraction agent of TBP with volume proportion of 20% could operate continuously and stablely more than 24 hours and the extraction efficiency be 4% higher than that of PVDF-TBP supported liquid membrane systems.

Keywords: Supported liquid membrane, extracting agent, coal gasification wastewater, phenol recovery.

INTRODUCTION

Hollow fiber supported liquid membranes, with large mass transfer area per unit volume and good stability, is used to investigate the extraction and recovery of phenol from high concentration coal gasification wastewater, which mainly contains the membrane support body, membrane solvent and mobile carrier (extractant). Among them, the liquid membrane phase is composed of a solvent together with mobile carrier phase, which make supported liquid membrane system has the characteristics of selective and mass transfer against a concentration gradient. The membrane support bodies provide attachment points for the liquid membrane phase and isolate the feed phase and the membrane phase. Therefore, the membrane support bodies as well as the composition of the liquid membrane phase have an important effect on the mass transfer efficiency and continuous and stable operation of the supported liquid membrane [1, 2]. The relationship between the membrane support body and the composition of liquid membrane phase with the extraction efficiency and stable operation of supported liquid membrane system is experimentally studied for wastewater containing phenols from one coal gasification plant.

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1. EXPERIMENT

1.1. Experimental Materials

Trialkyl phosphine oxide (93%, Shanghai LaiYashi Chemical Co., Ltd.); tributyl phosphate (98%, Shanghai LaiYashi Chemical Co., Ltd.); N, N-bis (1-methyl-heptyl) amide (Shanghai LaiYashi Chemical Co., Ltd.); bis (2 - ethylhexyl phosphoric acid) (Shanghai LaiYashi Chemical Co., Ltd.); sodium hydroxide and kerosene were analytical grade; and magnetic stirrer (Jintan Shuangjie Instruments Plant); GC-MS (Model: 6890 (GC)/5975 (MS), Agilent); T6-UV-Vis spectrophotometer (Beijing Puxi General Instrument Co., Ltd.); peristaltic pump (Model: BT100-2J, Baoding Lange Constant Flow Pump Co., Ltd.) are used.

Membrane module from Institute of Biological and Chemistry, Tianjin Polytechnic University: diameter 4.0 mm, effective length 21 cm, effective mass transfer

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Table 1: Parameters of the Hollow Fiber Membrane Materials

Membrane material	Diameter (mm)	Thickness (mm)	Open porosity (%)	Membrane pore size (μm)
PVDF	0.8	0.3	85	0.16
PP	0.4	0.1	72	0.1

area of 0.28 m^2 and membrane silk parameters shown in Table **1**.

1.2. Analysis of Wastewater from Coal Gasification Plant

The coal gasification wastewater, with COD 13000-15000 mg/L; total phenols 1600-1800 mg/L; pH 7.5-8.6, from Qitaihe Baotailong Coal Chemical Co., Ltd., was analyzed with GC-MS, pretreated by bromide derivatization, then extracted by methyl tertiary butyl ether, as shown in Figure **1**. GC-MS spectra showed that components of coal gas wastewater includes: phenol, binary phenols (catechol, resorcinol, hydroquinone), methyl phenol (p-methyl phenol, m-cresol, o-cresol), multiple diphenol methyl (2- methyl-1, 3-dihydroxybenzene, 3,4-dimethylphenol, 2, 3,5-trimethylphenol, 4,5-dimethyl-, 3-dihydroxybenzene, 3-methyl-1, 2-dihydroxybenzene), etc.

1.3. Experimental Setup

Flow chart of supported liquid membrane extraction to treat coal gasification wastewater was shown in Figure **2**. Before the start of the experiment, the liquid membrane phase flowed inside the tube of membrane system for 8-10 min, to form liquid membrane phase in the pores of the membrane which plays an extracted role in the extraction process. The aqueous phase flowed in circulation inside the tube of the supported liquid membrane system and at the same time, the stripping phase sodium salt flowed countercurrent in shell of the supported liquid membrane system. Temperature of experimental water was 20 ˚C, pH 8.4, the flow rate of aqueous phase 5 L/h, and the flow rate of stripping phase 5L/h. In order to reduce effluent contamination on the supported liquid membrane, backwash of deionized water with flow rate of 10L/h was carried out for support film 10min [3] after the experiments. Water samples were analyzed using UV-visible spectrophotometry pretreated with 4-amino antipyrine at the wavelength at 510 nm.

2. RESULT AND DISCUSSION

2.1. Effect of N-503 Volume Proportion in Liquid Membrane Phase on Extraction Efficiency

The mobile carrier in hollow fiber supported liquid membrane system has an important impact on the extraction efficiency of phenol, therefore, the effects of the different mobile carriers volume proportion in the membrane phase on the extraction efficiency of coal gasification wastewater were studied. In this test, the

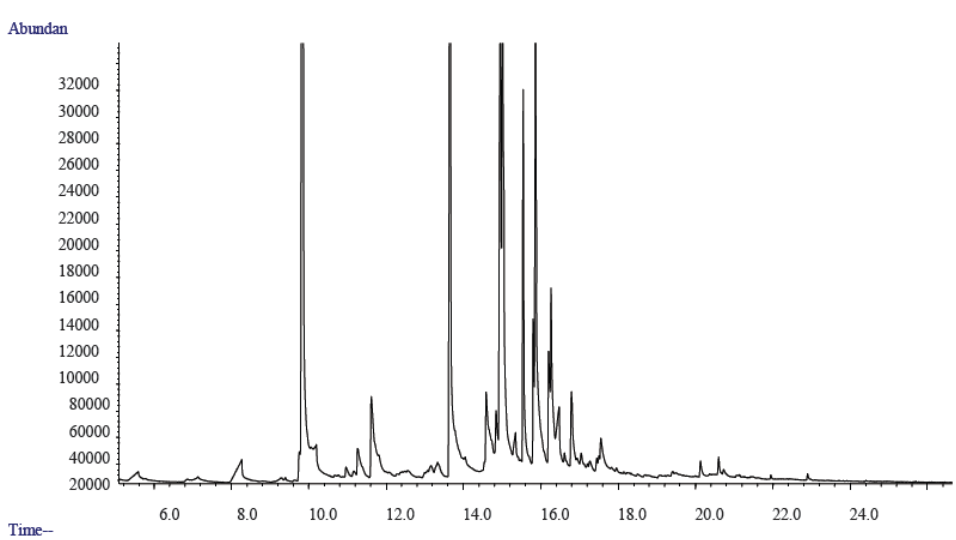


Figure 1: The GC-MS spectra of coal gasification wastewater.

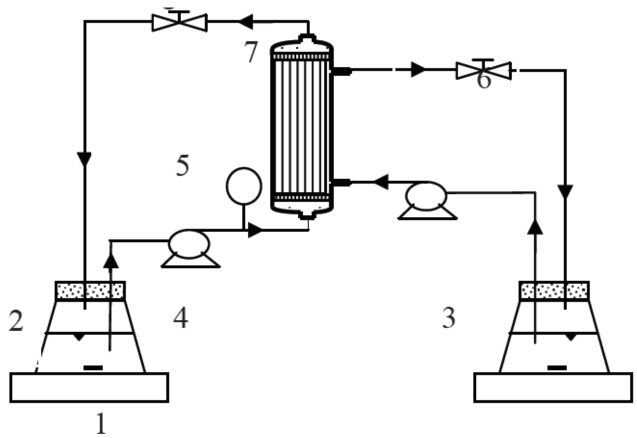


Figure 2: Flow chart of supported liquid membrane extraction to treat coal gasification wastewater. 1 -Stirrer; 2 -Feed tank; 3-NaOH solvent tank; 4 -Peristaltic pump; 5 -Gauges; 6 -Valves; 7 –supported liquid membrane module.

liquid membrane phase of hollow fiber supported liquid membrane system was made of kerosene (membrane solvent) and N-503(mobile carrier), and the operating conditions were the flow rate of aqueous phase and stripping phase 5 L/h, 0.1 mol/L NaOH as stripping phase, aqueous phase volume *Vaq* = 1.0 L, and stripping phase volume V_R = 0.3L. The concentration change of phenols in the aqueous phase was detected with the volume proportion of N-503 in the membrane phase as the controlling variable. The PVDF membrane was used in the experiments and the results were shown in Figure **3**.

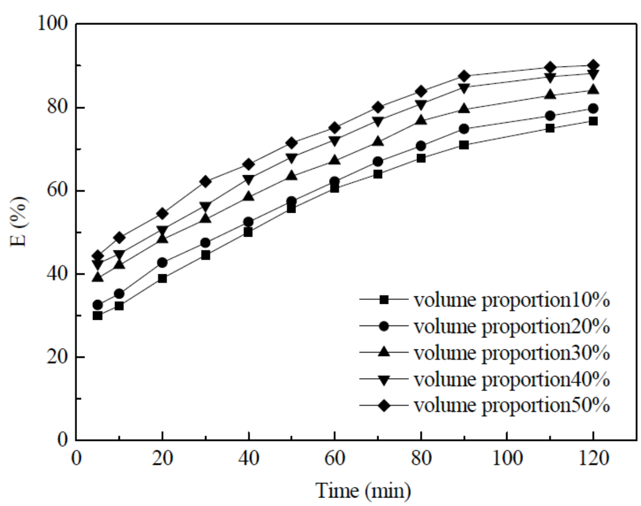


Figure 3: Effect of N-503 volume proportion on extraction with PVDF membranes.

As shown in Figure **3**, with the increase of volume proportion of N-503 in the membrane phase, the extraction efficiency gradually increases. When the volume proportion of 3 N-503 in the liquid membrane phase was 30% or more, the extraction efficiency of phenols by the supported liquid membrane system had reached more than 39% in 5min. and supported liquid membrane system gradually reached extraction equilibrium after 90 min. However, when the volume proportion of N -503 in the liquid membrane phase was more than 30%, increasing the volume proportion of N-503 had little effect on the final extraction efficiency. Thus, when the concentration of the extractant in the liquid membrane phase reached a certain level, it would be difficult by simply increasing the concentration of extractant to make the extraction efficiency achieve a higher level.

At the same extraction conditions, PP membrane was used in the experiments, shown in Figure **4**.

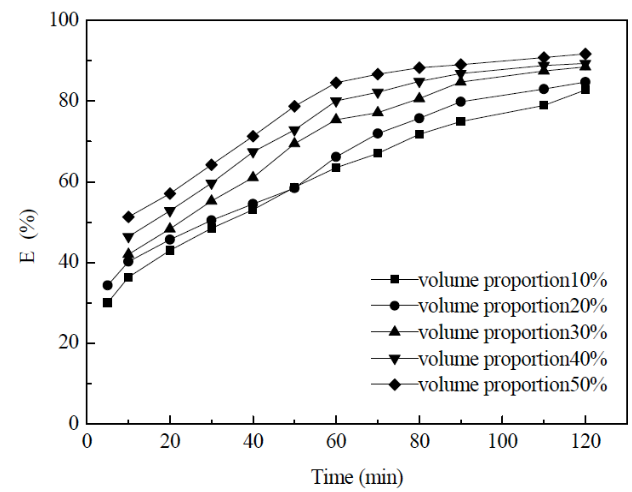


Figure 4: Effect of N-503 volume proportion on extraction with PP membranes.

It could be found that increasing the volume proportion of N-503 in the liquid membrane phase, the extraction efficiency gradually increases. In Figure **4**, it is apparent that the extraction efficiency with more than 30% volume proportion of N-503 in the liquid membrane phase was higher than that with the volume proportion less than 20%. Compared with Figures **3**, **4** showed that the extraction efficiency of the PP membrane modules was superior to the PVDF membrane modules under the same operating conditions. When the volume proportion of N-503 in the liquid membrane phase was 30%, the E_{5min} and E_{120min} of PP membrane module were 42% and 88% respectively, the E_{5min} and E_{120min} of PVDF membrane were 38% and 85% respectively. The mass transfer resistance of the membranes can be indicated by formula (1).

$$\frac{1}{k_m} = \frac{\tau_m t_m}{D_0 \varepsilon_m} \qquad (1)$$

In which:

k_m: mass transfer coefficient in membrane phase;

D_0 : diffusion coefficient of phenols in the membrane phase;

ε_m: membrane wire open porosity;

τ_m: curvature factor (>1);

t_m: membrane wire thickness.

Through the formula (1), the mass transfer resistance of the PVDF membrane was triple of the mass transfer resistance of PP membrane; therefore, the extraction effect of the support liquid membrane with PP membranes is naturally superior to that with PVDF membranes under the same extraction conditions.

2.2. Effect of TBP Volume Proportion in Liquid Membrane Phase on Extraction Efficiency

The liquid membrane phase of hollow fiber supported liquid membrane system was made of kerosene (membrane solvent) and TBP (mobile carrier). The concentration change of phenols in the aqueous phase with the volume proportion of TBP in the membrane phase as the control variable was detected, with PP membrane, as shown in Figure **5**.

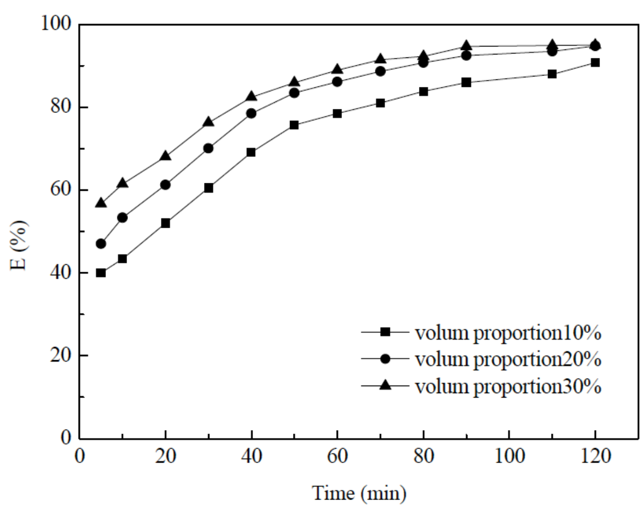


Figure 5: Effect of TBP volume proportion on extraction efficiency with PP membranes.

As shown in the Figure **5**, increasing the volume proportion of TBP in the liquid membrane phase, the extraction efficiency gradually increases. The extraction efficiency when the volume proportion of TBP in the liquid membrane phase was 30% were very close to that when the volume proportion of TBP in the liquid membrane phase was 20% and the final extraction efficiencies were 95% and 94.8%. So the maximum volume proportion of TBP in the membrane phase was fixed at 30% on the extraction experiments to study the effect of TBP volume proportion in the liquid membrane phase on extraction efficiency. At the same extraction conditions, PVDF membrane was used in the experiments, shown in Figure **6**.

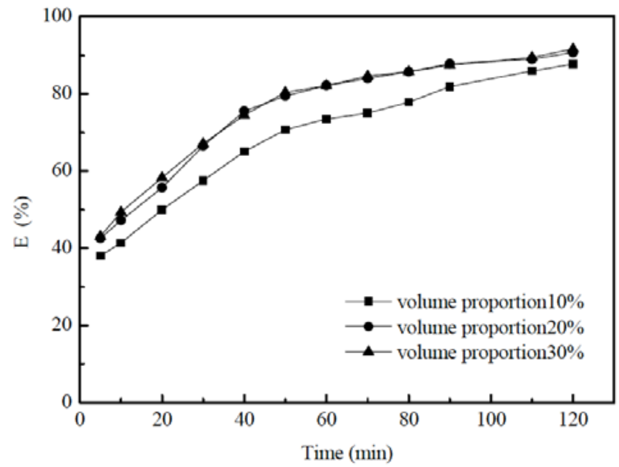


Figure 6: Effect of TBP volume proportion on extraction efficiency with PVDF membranes.

As can be seen from Figure **6**, the two curves which show the extraction efficiency of 20% and 30% TBP volume proportion in the liquid membrane phase were almost coincident. When the concentration of extractant in the liquid membrane phase reached a certain level, the effect of increasing extractant concentration in the liquid membrane phase on the extraction efficiency was getting smaller and smaller. Considering the economic factors, the volume proportion of TBP in the liquid membrane phase was 20% in the subsequent stability experiments. Similarly, from the comparison with Figures **5** and **6**, the extraction efficiency of the PP membrane modules was better than that of the PVDF membrane modules under the same extraction conditions. When the volume proportion of TBP in the liquid membrane phase was 20%, the E_{5min} and E_{120min} of PP membrane module were 47% and 94.88% respectively, the E_{5min} and E_{120min} of PVDF membrane were 42.5% and 90.7% respectively. Thus, suitable support materials can lead to the final extraction efficiency be further improved.

2.3. Effect of TRPO Volume Proportion in Liquid Membrane Phase on Extraction Efficiency

The liquid membrane phase of hollow fiber supported liquid membrane system was made of kerosene (membrane solvent) and the extractant which containing TRPO and D_2EHPA (volume proportion 3:1). The concentration change of phenols in the aqueous phase with the volume proportion of TRPO in the membrane phase as the control variable was detected with PP membrane, as shown in Figure **7**.

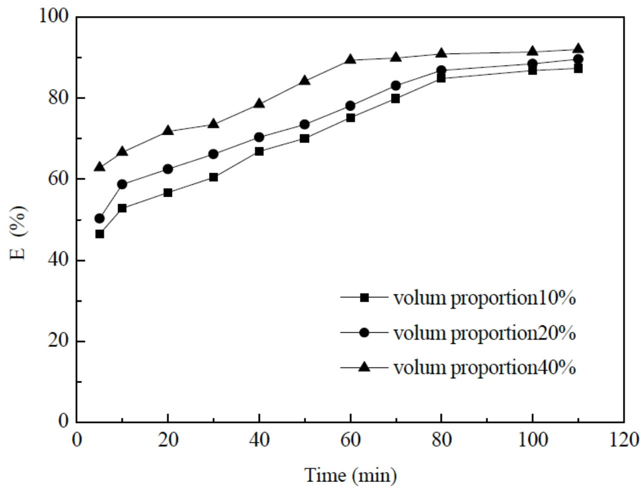


Figure 7: Effect of TRPO volume proportion on extraction efficiency with PP membranes.

As shown in the Figure **7**, increasing the volume proportion of TRPO in the liquid membrane phase, the extraction efficiency gradually increases. Especially when the volume proportion of extractant in the liquid membrane phase was 40%, E_{5min} and E_{120min} reached 62.8% and 92% respectively. Thus, the mixed extraction solvent can contribute to higher extraction efficiency of phenols and shorter time to reach the extraction equilibrium.

At the same extraction conditions, the results for PVDF membrane was were shown in Figure **8**.

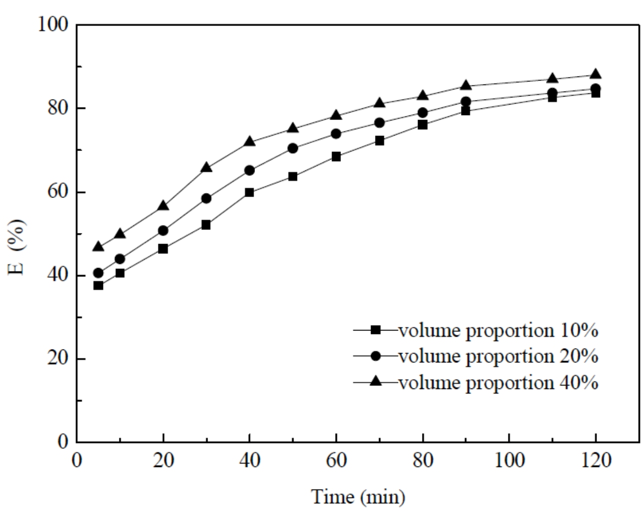


Figure 8: Effect of TRPO volume proportion on extraction with PVDF membranes.

From Figure **8**, the same regular pattern can be concluded that: increasing the volume proportion of TRPO in the liquid membrane phase, the extraction efficiency gradually increases. Because of its structural advantages, TRPO can contribute to more rapid extraction efficiency and greater equilibrium distribution coefficient. Compared with TBP, the phosphorus atom of TRPO connected with more alkyls which enhanced the ability of TRPO to form hydrogen bonds, a greater equilibrium partitioning coefficients than that of TBP.

The above experiments showed that the effect of TRPO and TBP on the extraction and recovery of phenols was better than that of N-503. The effect of TRPO was slightly better than TBP. Considering the actual situation with the huge amount of coal gasification wastewater, TBP had more practical value because of its lower price than that of TRPO.

2.4. Continuous and Stable Operation of Supported Liquid Membrane System

Liquid drain is the main reason of unstable operation [4] of supported liquid membrane system, but suitable support material can reduce the drain of the membrane phase in the operation, so continuous experiments on PVDF membrane module and membrane PP module examining were carried out to determine the nature of the two kind materials in the continuous operation.

With kerosene and TBP (volume proportion of 20%) as liquid membrane phase, the flow rate of aqueous phase and stripping phase are 5 L/h, 0.1 mol/L NaOH as stripping phase, aqueous phase volume V_{aq} = 12 L, and stripping phase volume V_R=3L, 24h continuous extraction experiments were conducted and the

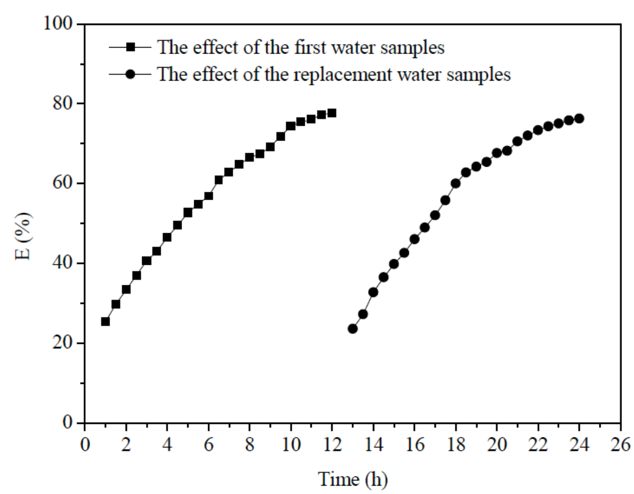
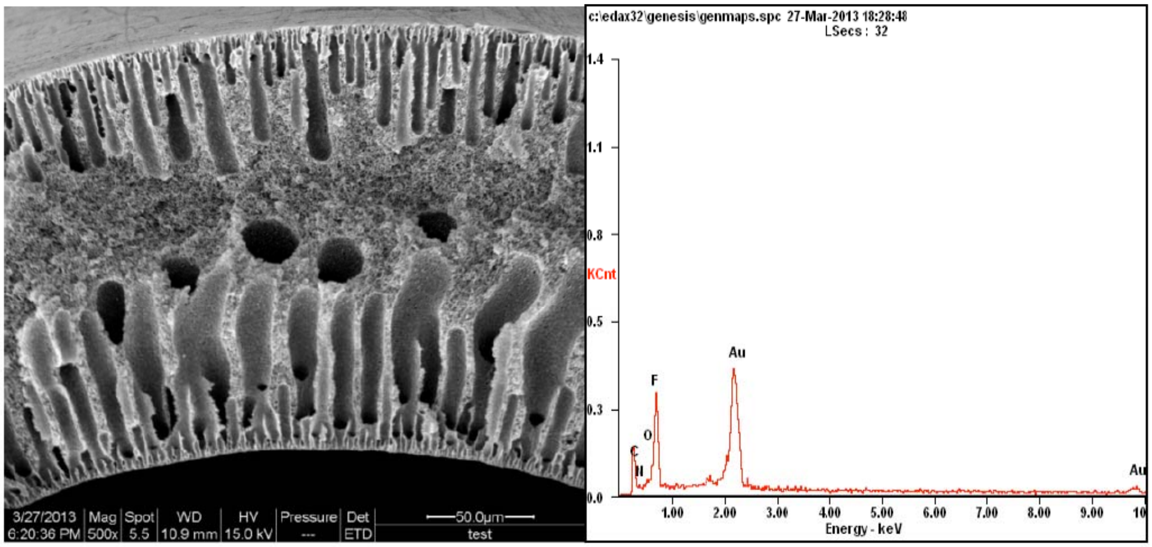


Figure 9: Continuous operation with PVDF membranes.



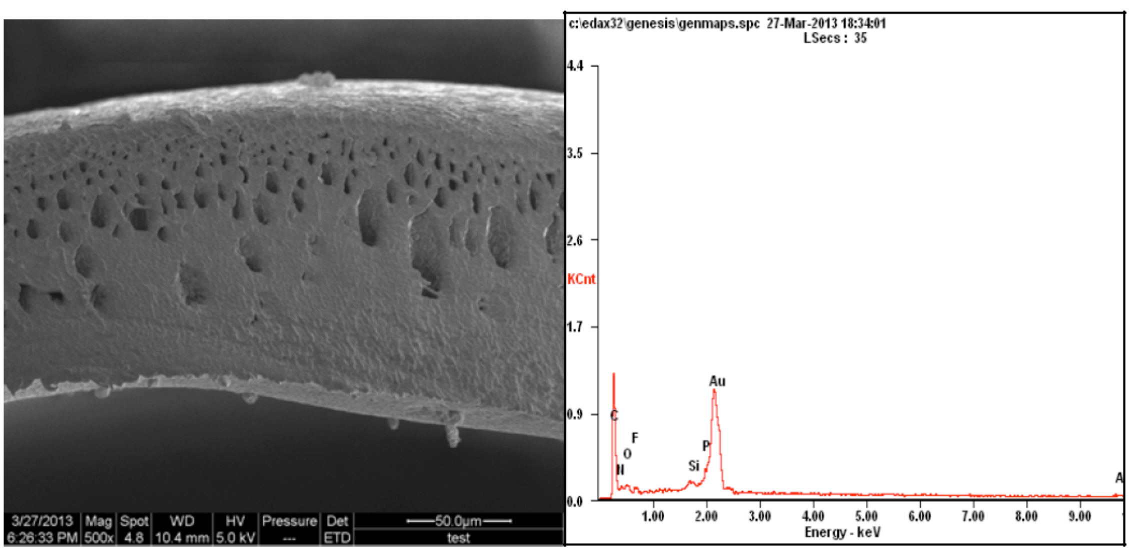
a) SEM picture b) EDS picture

Figure 10: SEM and EDS pictures of unused PVDF membranes cross-section.

concentration change of phenols in the aqueous phase detected. The PVDF membrane was used in the experiments and the results were shown in Figure **9**.

12L wastewater sample was used in the first experiments, then replaced after12 hours and new replacement 12L water samples continued to run 12 hours. Figure **9** showed that the extraction efficiency of the replacement water samples and the extraction efficiency of the first water samples were basically the same. SEM and EDS pictures of unused PVDF membranes cross-section were showed in Figure **10** and the SEM and EDS pictures of the membranes cross-section which were used continuously 24 hours were shown in Figure **11**.

From the comparison with Figures **10a** and **11a**, it could be seen that a lot of the liquid membrane phase retained in the membrane holes after 24 hours continuous operation, which ensure sustained stable operation of supported liquid membrane system. The comparison with Figures **10b** and **11b** showed that the content of element C, O, and F in unused membrane module, and the content of element C, Si and P in the used membrane module improved significantly, reason of this phenomenon being that TBP (extractant used in



a) SEM picture b) EDS picture

Figure 11: SEM and EDS picture of used PVDF membranes cross section.

the experiment) occupy majority of residues in the hollow fiber membrane. The EDS pictures directly revealed that the oily residue in membrane wire holes were liquid membrane phase containing TBP. Also in the same extraction conditions, the same experiments on the PP membrane modules were conducted and the same experimental results obtained. The support liquid membrane system with PP membrane modules and the kerosene-TBP (volume proportion of 20%) liquid membrane phase can steadily run for 24 hours.

CONCLUSION

Through the above extraction experiments on the coal gasification wastewater containing phenol, the following conclusions could be obtained.

When the concentration of the extractant in the liquid membrane phase reached a certain level, the effect of increasing extractant concentration in the liquid membrane phase on the extraction efficiency was getting smaller and smaller. Compared with TBP, TRPO can contribute to more rapid extraction efficiency and greater equilibrium distribution coefficient because of its structural advantages.

The extraction efficiency of the supported liquid membrane system has been affected by the nature of membrane support materials. Under the same extraction conditions, the extraction effect of the supported liquid membrane system with PP membranes (membrane wire thickness 0.1mm) on the coal gasification wastewater is superior to that with PVDF membranes (membrane wire thickness is 0.3mm).

The supported liquid membrane system with PP membrane modules and the kerosene-TBP (volume proportion of 20%) liquid membrane phase can steadily run for 24 hours and the extraction efficiency of this supported liquid membrane system for coal gasification wastewater can reach up to more than 92%.

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