Pilot Investigation of Coal Chemical Wastewater Containing Phenol by Pervaporation Process

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Abstract: Coal chemical wastewater contains a large number of industrial raw materials, such as phenol, resulting in difficulty as target to be treated and the resource waste as industrial raw materials. A pilot pervaporation process is investigated to separate and recycle phenols from coal chemical wastewater to reduce the follow-up biochemical processing load. Operation parameters which affect removing and recovering efficiency are studied, such as temperature, flow rate and downstream pressure. Phenol removal efficiency could reach 50% under the conditions of 70° C, 210 L/h and 3000 Pa. The system could continuously run for 20 cycles. Furthermore, the pervaporation procedure could be enhanced when pumped with gas which made the removal efficiency up to 66%.

Keywords: Coal chemical wastewater, pervaporation, pilot scale.

INTRODUCTION

China is the world's second largest energy producer and consumer, and its rich coal source and relatively poor petroleum provide a development space for China's coal chemical industry. But the coal chemical industry is a high energy-consuming and high polluting industry. It is very difficult to treat phenols and other chemicals biologically from coal chemical wastewater, increasing the processing load and resulting in waste of resources. Pervaporation, a membrane separation with low energy consuming and high performance selectivity [1] gives up a unique advantage in the recovery of phenol substances from coal chemical wastewater [2], chosen as pre-treatment process.

METHODS

The Experimental Setup

As shown in Figure 1, pilot setup consists of three main systems: material circulation system, membrane separation system, the vacuum condensate system. Heated liquid in the liquid tank was delivered to the membrane separation system through metering pump, some of which pass through the membrane under vacuum conditions and the retentate back into the

liquid tank. The vacuum condensate system supply vacuum conditions for permeate to pass the membrane and condensed to be collected as phenolic mixtures.

The Membrane Material

PDMS pervaporation membrane used in this experiment purchased from Dalian Physiochemical Institute is complex membrane with selective penetration feature, composed of separating layers and supporting layer [3]. For separating layers with film thickness of 10µm, propcyanide group was grafted into PDMS pervaporation membrane, and the addition of propcyanide group would strengthen pervaporation membrane affinity for phenol and enhance the mass flux of volatile phenol substances and further improving the separation factor [4]. Support layer, with film thickness of 100µm PVDF micro porous membrane from MOTIMO, enhance the mechanical strength of the composite membrane [5].

Experimental Materials

Experimental wastewater was supplied by a comprehensive coal chemical enterprise from Heilongjiang, its quality given in Table **1**.

The Experimental Procedure

120L coal chemical wastewater was pump into the liquid tank, the temperature control system switched on for sewage heating, and then the material circulation

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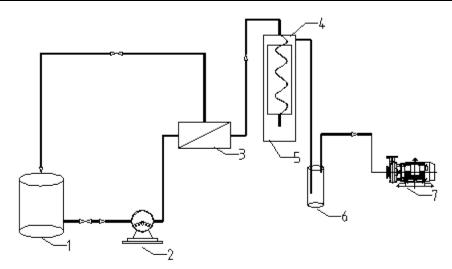


Figure 1: Pilot scale pervaporation setup.

1 liquid tank, 2 feeding pump, 3 membrane module, 4 condenser 5 permeate, 6 vacuum buffer tank, 7 vacuum pump.

Table 1: Characteristics of Coal Chemical Wastewate

Items	values	Items	values
COD	13400mg/L	SS	890mg/L
PH	7.5-8.1	color	Brown Yellow
Volatile phenol	1960mg/L	temperature	70°C-80°C

system and vacuum condensate system turned on. The run cycle is 10 hours, and for every two hours, liquid flow rate, liquid tank level and membrane lateral pressure, and wastewater temperature were recorded.

RESULTS AND DISCUSSION

Traditional Pervaporation

The Effect of Flow Rate on Phenol Removal Efficiency

100L coal chemical wastewater was added to the setup, circulation flow rate fixed at 210L/h.t, pressure under membrane 3000Pa to 4000Pa and temperature was regulated to 60°C, 70°C, and 80°C respectively, volatile phenol removal efficiency recorded in Figure 2. From Figure 2, it could be found that the enhance of temperature from 60°C to 70°C would roughly increase in removal efficiency of each cycle by 10%. And in cycle 1 to 3, under 80°C, the removal efficiency of volatile phenols could reach 70%. However, the removal efficiency of the reaction in the third cycle of 80°C appeared substantial decline, even worse than that under 60°C. Observation on the membrane surface after seven cycles run for at 80°C illustrate that surface layer of graft modified composite PDMS

membrane shown cracking, some areas separated, and even film edge burns, indicating that the very high temperature is not suitable for the existing experimental pervaporation composite membrane [6].

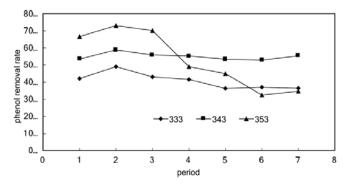


Figure 2: Effect of temperature on removal efficiency.

Effect of Pressure Under Membrane on Phenol Removal Efficiency

At system temperature 70°C, pressure under membrane 3000Pa-4000Pa, circulation flow rate was fixed at 150L/h, 180L/h, 210L/h, and 240L/h, volatile phenol removal efficiency is shown in Figure **3**.

Figure **3** tells that, at a flow rate of 90L/h, the removal efficiency is about 30%, and when flow rate significantly upgraded to 150L/h and 210L/h, removal

efficiencies were raised to 45% and 55% respectively, indicating that the increase of flow rate would strengthen the separation of pervaporation process [7]. But when the flow rate was upgraded from 210L/h to 240L/h the removal efficiency of volatile phenols in the process changed little, the enhancement of convective mass transfer with the flow rate is limited [8].

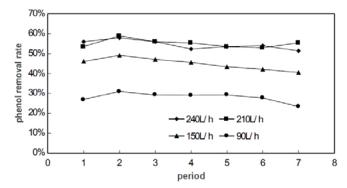


Figure 3: Effect of flow rate on removal efficiency.

Effect of Pressure Under Membrane on Phenol Removal Efficiency

At temperature 70°C, the circulation flow rate 210L/h, pressure under membrane is changed from 4000Pa to 10000Pa to examine the effect of pressure under membrane on volatile phenol removal efficiency. Figure **4** shows that at pressure under membrane 4000Pa the removal efficiency of volatile phenols by pervaporation system was about 55%, when at the pressure 7000Pa, removal efficiency decreased by 15% and when then pressure under membrane in 10000Pa, the removal efficiency appears been less than 30%. The lower the pressure under membrane, the better of the separation process is [9].

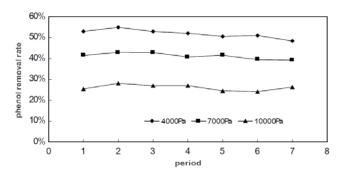


Figure 4: Effect of pressure under membrane on removal efficiency.

The System Separation Performance at Continuous Operation

Carried out for 20 cycles at the above optimal control conditions: temperature 70°C, the flow rate of 210L/h, pressure under membrane 3000Kpa to

4000Kpa, removal efficiencies are shown in Figure **5**. It is obvious that the influent water quality shown a certain degree of fluctuation [10]. As the amount of volatile phenols in the wastewater was changed from original 1700mg/L to 800mg/L after four cycles, and mostly lower than 900mg/L, it could be guaranteed that phenol removal efficiency is above 50% for coal chemical wastewater by the pervaporation systems, flat membrane and limited membrane surface, 593.7cm².

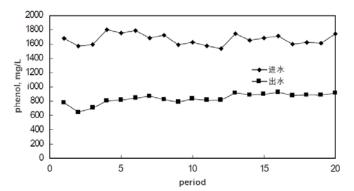


Figure 5: The system separation performance at continuous operation.

Aeration Pervaporation

Compared to traditional pervaporation setup, feeding air to the solution with pump would strengthen the passing rate of phenol through membrane.

The Effect of Aeration Intensity on Removal Efficiency

As system circulation flow rate controlled at 150L/h, the temperature 70°C, pressure under membrane 3000Pa, volume ratio of gas over water (g/l)were changed 0, 0.1, 0.2, 0.3, 0.4, and 0.5 respectively, the phenol removal efficiencies with actual wastewater by gassing pervaporation experiments are given in Figure **6**.

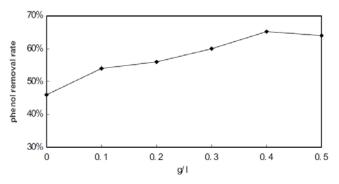


Figure 6: Effect of aeration intensity on removal efficiency.

It could be concluded from the data above that with the aeration increased, the removal efficiency of the whole system has improved when the stability of the other conditions ensured, and as volume ratio of gas over water 0.4, the removal efficiency of volatile phenols was raised to 65%, compared removal efficiency of only 46% without aeration. The main reasons should the presence of bubbles in the water enhance the turbulence of the membrane surface of the liquid which increases the shear force of the membrane surface, and promotes the pervaporation membrane mass transfer.

The Effect of Temperature on Removal Efficiency

As volume ratio of gas over water fixed 0 and 0.4 respectively, temperature was raised from 50°C to 70°C, it could be observed that temperature of the system would increase the removing efficiency, as shown in Figure 7. As volume ratio of gas over water is traditional pervaporation membrane namely 0, separation system, enhancement of the temperature from 50°C to 70°C resulted in volatile phenol removal efficiency from 27% to 47%. When volume ratio of gas over water is 0.4, aeration pervaporation system, the temperature enhancement made volatile phenol removal efficiency from 31% to 64%, indicating an apparent temperature effect than conventional separation.

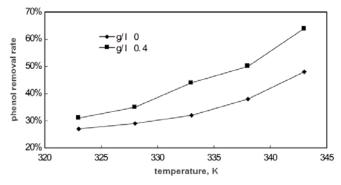


Figure 7: Effect of temperature on removal efficiency.

Effect of Flow Rate on Removal Efficiency

As temperature 70°C, pressure under membrane 3000Pa, the flow rate is changed from 120L/h to240L/h, effect of flow rate on removal efficiency is given in Figure 8. From the Figure 8, it could be concluded that for traditional pervaporation systems, volatile phenol removal efficiency increased with the increase of flow rate and when the flow rate is 210L/h, the removal efficiency reached 61% of the maximum value. Nevertheless continuous enhance of flow rate will not improve the system removal efficiency [11]. As volume ratio of gas over water is 0.4, when flow rate achieves 150L/h, the system removal efficiency

reached 66%. From the above it could be generated that aeration and enhancement of flow rate can enhance the convective mass transfer rate outside the boundary layer of pervaporation membrane, and for aeration pervaporation system optimal flow rate is much less than traditional pervaporation systems.

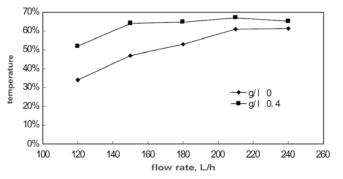


Figure 8: Effect of flow rate on removal efficiency.

CONCLUSIONS

Pervaporation system is dominated by kinetics and thermodynamics process, so enhancing flow rate and temperature will contribute to improve mass transfer process and enhance membrane separation efficiency. For pervaporation without aeration, as temperature 70°C, the flow of 210L/h, pressure under membrane 3000Pa to 4000Pa the removal efficiency of volatile phenols appear more than 50%. And for aeration pervaporation system when the controlled conditions are temperature 70°C, flow rate of 150L / h, volume ratio of gas over water 0.4, the system removal efficiency for volatile phenol will reach 66 %, a higher membrane separation efficiency.

REFERENCE

- [1] László H, Edit M, Snezana K. Recovery of aroma compounds from model solution using pervaporation membrane. 5th International Technical Symposium on Food Processing, Monitoring Technology in Bioprocesses and Food Quality Management 2009; pp. 1233-1236.
- [2] Garcia M, Sanz MT, Beltran S. Separation by pervaporation of ethanol from aqueous solutions and effect of other components present in fermentation broths. J Chem Technol Biotechnol 2009; 84: 1873-82. <u>http://dx.doi.org/10.1002/jctb.2259</u>
- [3] Iqbal A, Che PNF, Mohd NMG. Modifiedpolydimethylsiloxane/polystyrene blended IPN pervaporation membrane for ethanol/water separation. J Appl Polym Sci 2011; 122(4): 2666-79.

http://dx.doi.org/10.1002/app.34319

- [4] Offeman RD, Ludvik CN. Poisoning of mixed matrix membranes by fermentation components in pervaporation of ethanol. J Membr Sci 2011; 367: 288-95. <u>http://dx.doi.org/10.1016/j.memsci.2010.11.005</u>
- [5] Liu G, Wei W, Wu H. Pervaporation performance of PDMS/ceramic composite membrane in acetone butanol

ethanol (ABE) fermentation-PV coupled process. J Membr Sci 2011; 373: 121-29. http://dx.doi.org/10.1016/j.memsci.2011.02.042

- [6] Gupta T, Pradham NC, Adhikan B. Separation of phenol from aqueous solution by pervaporation using HTPB-based polyurethaneuera membrane. J Membr Sci 2009; 217(1-2): 43-53. http://dx.doi.org/10.1016/S0376-7388(03)00069-3
- Sadao A, Satoshi I, Shunsuke T. Pervaporation of [7] organic/water mixtures with hydrophobic silica membranes functionalized by phenyl groups. J Membr Sci 2011; 380(1-2): 41-47. http://dx.doi.org/10.1016/j.memsci.2011.06.026
- [8] Shirazi Y, Ghadimi A, Mohammadi T. Recovery of Alcohols Water Polydimethylsiloxane-Silica from Using Nanocomposite Membranes: Characterization and

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Pervaporation Performance. J Appl Polym Sci 2012; 124: 2871-82. http://dx.doi.org/10.1002/app.35313

Prabhat G, Singh RP, Veena C. Pervaporation separation of [9] organic azeotrope using poly(dimethyl siloxane)/clay nanocomposite membranes. Separation Purification Technol 2011; 80(3): 435-44.

http://dx.doi.org/10.1016/j.seppur.2011.05.020

- Hao X, Pritzker M, Feng X. Use of pervaporation for the [10] separation of phenol from dilute aqueous solutions. J Membr Sci 2009; 96: 96-102. http://dx.doi.org/10.1016/j.memsci.2009.02.036
- Overington AR, Marie W, Harrison JA. Estimation of mass [11] transfer rates through hydrophobic pervaporation membranes. J Separation Sci Technol 2009; 44(4): 787-16. http://dx.doi.org/10.1080/01496390802697106