Available online at www.sciencedirect.com
ScienceDirect
ELSEVIER
Desalination 234 (2008) 416–425
DESALINATION
www.elsevier.com/locate/desal

Factors affecting phenol transfer through polydimethylsiloxane composite membrane

Mao-Sung Lee[a,d], Chihpin Huang[a]*, Kueir-Rarn Lee[b], Jill R. Pan[c], Wang-Kuan Chang[d]

[a]*Institute of Environmental Engineering, National Chiao Tung University, Hsinchu, Taiwan*
Tel. +886-3 5726463; Fax +886-3 5725958; email: cphuang@mail.nctu.edu.tw
[b]*R&D Center for Membrane Technology and Department of Chemical Engineering, Chung Yuan University, Chungli, Taiwan*
[c]*Biotechnology Center, National Chung Hsing University, Taichung, Taiwan*
[d]*Energy and Environment Research Laboratories, Industrial Technology Research Institute, Hsinchu, Taiwan*

Received 15 August 2007; accepted revised 28 September 2007

Abstract

Polydimethylsiloxane composite membrane was employed for the separation of phenol and sodium chloride in synthetic wastewater. The major operational parameters affecting phenol transfer through this composite membrane were screened by the orthogonal array and range analysis. The results showed that the significance of parameters on the permeate flux followed the order of phenol concentration, membrane skin layer thickness, recirculation rate, and sodium chloride concentration after 6 and 48 h operations. Optimal operation range was determined by the response surface methodology coupled with central composite design. The higher was the phenol concentration in the influent or the thicker was the membrane skin layer thickness, the higher was the permeate flux through membrane. Also, the higher was the recirculation rate, the higher was the permeate flux through membrane.

Keywords: Wet-phase inversion; Extractive membrane; Phenol; Permeation; Range analysis

1. Introduction

Industrial wastewaters frequently contain high concentration of acids, bases or salts. Biological treatment is generally a top priority for the removal of organic pollutant from wastewaters because of its low operation cost. However, the presence of high concentration of inorganic ions often suppresses the microbial activities and

*Corresponding author.

Presented at the Fourth Conference of Aseanian Membrane Society (AMS 4), 16–18 August 2007, Taipei, Taiwan.

doi:10.1016/j.desal.2007.09.112

inhibits the degradation of organic pollutants in biological treatment. Industries such as pharmaceutical, chemical and biotechnology usually face with these problems. Extractive membrane bioreactor (EMB) is an effective way to biodegrade organic pollutants with the separation of high-strength inorganic ions beforehand [1]. The membrane used in the EMB is similar to that used in pervaporation process except that the vacuum phase is replaced by a biological medium [2]. The concentration gradient across membrane allowing the transfer of phenol from the wastewater side to the biological phase is maintained by the degradation of phenol [3]. Excessive biofilm growth on membrane also played a role to hinder the mass and oxygen transfer through the membrane [4].

Previous studies with the EMB [5] showed that addition with the biocarrier could retain the suspended solids and prevent biofilm growth from membrane and transfer of phenol was the rate determining step in the process of degradation of phenol.

An innovative approach by using a wet phase inversion process was improved polydimethylsiloxane (PDMS) composite membrane was employed to enhance the transfer of phenol through membrane. The skin layer thickness of the asymmetric membrane was controlled by changing the membrane formation condition. The sorption and desorption potentials for these membranes were examined. The reproducibility of the permeation tests were also carried out. Major parameters screened by the orthogonal array and range analysis, were used to determine the optimal operation range by Response Surface Methodology (RSM) [6] coupled with Central Composite Design (CCD). Biological tests were also conducted to verify the effectiveness of membrane permeation.

2. Material and methods

Polysulfone and nonwoven were used as the support material for the asymmetric membrane. The polydimethylsiloxane (PDMS) thickness on the support material was controlled by changing the membrane formation condition to form PDMS/polysulfone composite membranes. Before the experiment, membranes of different skin layers thicknesses were prepared in the laboratory. The thickness of the composite membranes is listed in Table 1. The SEM micrograph for the cross-section is displayed in Fig. 1. The layer of this hydrophobic composite membrane is one of the important factors to influence the transfer of pollutants through the membrane. To measure the extent of phenol sorbed on membrane, the PDMS membranes were immersed in 1 wt.% aqueous phenol solution for 24 h at room temperature. They were subsequently blotted between tissue paper to remove excess solvent and placed in the left tube of a twin tube set-up. The system was evacuated while the left tube was heated with hot water and the right tube was cooled in liquid nitrogen. The composition of the condensed liquid in the right tube was determined by G.C.

This study has selected phenol as a model organic pollutant because of its general application in the process of chemical industry. Three test conditions were listed as following: (1) permeation test: 400 mg/L of phenol and 20 g/L of sodium chloride [7]; (2) determining the major parameters: 100–1000 mg/L of phenol concentration, 30–150 mL/min of recirculation rate,

Table 1
Skin layer thickness of PDMS membranes

Membrane[a]	Skin layer thickness (μm)
PH-22100	26.2
PH-2275	14.4
PH-2250	9.6
PH-0350	1.0
PH-0320	0.4

[a]Thickness of PSf/nonwoven supporting layer is 130 ± 5 μm.

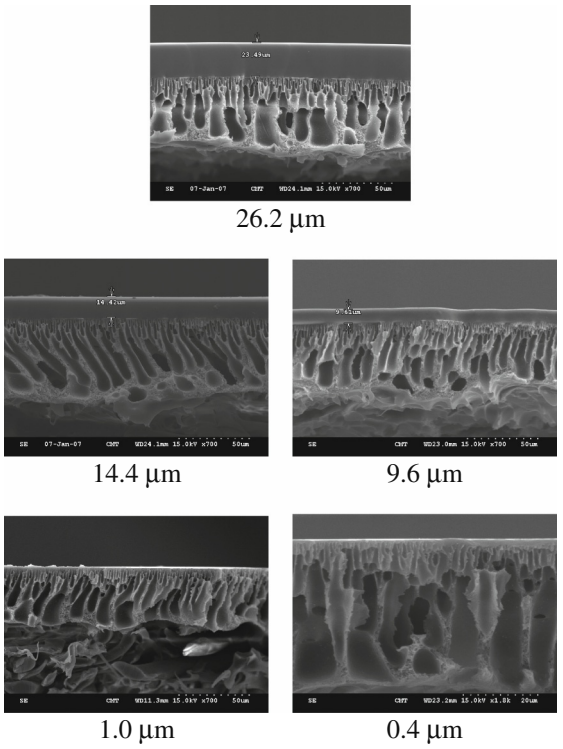

Fig. 1. SEM micrograph for the cross-section of PDMS/PSf composite membrane.

9.6–26.2 μm of membrane skin layer thickness and 10–50 g/L of sodium chloride; (3) RSM analysis: 9.6–26.2 μm of membrane skin layer thickness and 35–205 mL/min of recirculation rate. The Reynolds number for flow past the membranes were within 7–43.

Operational parameters including phenol concentration, sodium chloride concentration, recirculation rate and membrane thickness were evaluated by the methods of orthogonal array and range analysis. And then the optimal operation range were determined by RSM according to the major parameters with the permeate flux as an index.

Biological experiments were conducted to show the effect of salt concentration on the rate of biodegradation. The acclimated sludge was seeded to wastewater with different salt concentrations. Sufficient nutrients were also supplied in each experiment. At the same time, the air was supplied to each beaker by pump. Six one-liter samples were prepared with equal initial phenol concentration. Four of these samples were added with different concentration of sodium chloride (1%, 3%, 5% and 10%). All samples were seeded with acclimated sludge except the one without sodium chloride (blank test). The initial condition was VSS of 2500 mg/L, SS of 3300 mg/L, phenol of 373 mg/L, COD of 889 mg/L, and F/M of 0.36.

Membrane extraction incorporated with biodegradation was conducted to evaluate the feasibility for the biodegradation of organic wastewater with high intensity of salt in EMB. The rectangle reactor was made of acrylic material with equivalent volume (400 mL) of two chambers divided by the membrane. Feed chamber was for influent input and permeate chamber for permeate liquid deposition. The phenol solution was circulated in the feed chamber and permeate was also circulated in permeate chamber by pump. Before biological testing, acclimated sludge was seeded directly to shorten the startup time and the MLSS concentration were controlled around 200–600 mg/L. The seeding sludge was also supplied with nutrients regularly. At the same time, the air was transferred to the permeate chamber by the compressor. The mixing intensity of feed solution was enhanced in the feed chamber (3500 mL) by installing five partition barriers. The experimental setup is displayed in Fig. 2.

To search for the suitable amount of biocarrier for the reactor, various amounts of biocarrier, namely, 2.25, 4.5, 6.75, 9.0, 13.5 and 18 g, made of nonwoven material were added into the permeate chamber. The wastewater contained 400 mg phenol/L and 20 g NaCl/L. The wastewater was treated by a batch mode while the nutrients were routinely added. The degradation of the phenol was determined by high performance liquid chromatography (HPLC, detector: Waters 490E, Column: Hypersil BDS C18). Conductivity was

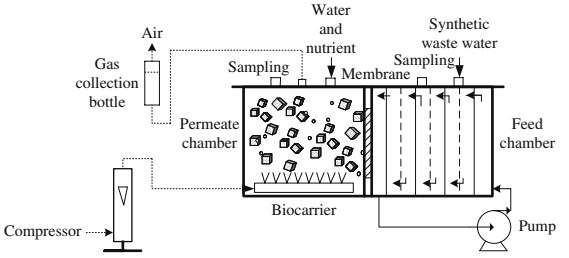

Fig. 2. Set-up of extractive membrane bioreactor system.

measured by a conductivity meter (SUNTEX SC-170). The permeate flux of phenol was determined after the EMB was run for 72 h.

3. Results and discussion

3.1. Permeation test

Permeate test have been repeated three times under the same operating condition. The test results with 95% confidence interval are shown in Fig. 3. The 9.6 μm membrane with the largest PDMS thickness showed the highest reduction of phenol in feed chamber and lowest increase of phenol in permeate chamber. However, the reduction of phenol was lower for membranes of 1.0 and 0.4 μm because of small thickness of PDMS and short-term testing.

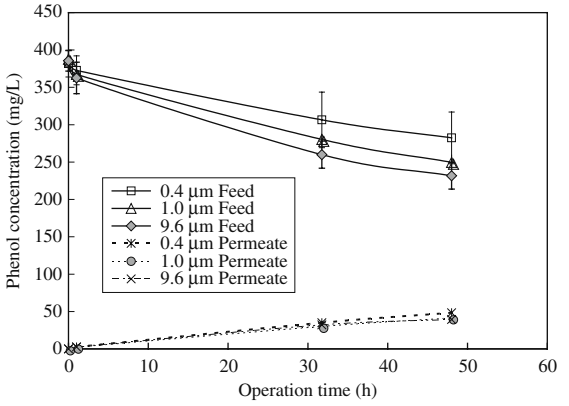

Fig. 3. The short-term changes of phenol concentrations with time in two chambers (triplicate).

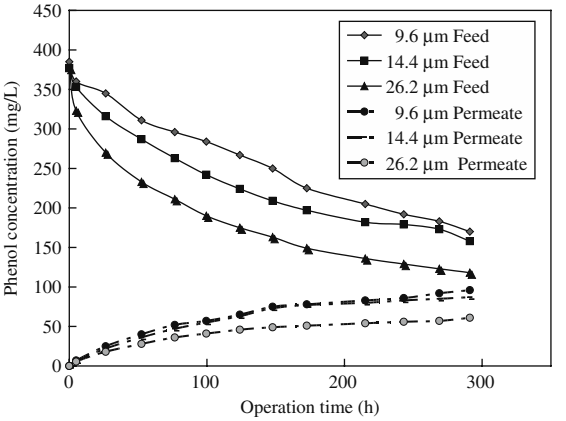

Fig. 4. Changes of phenol concentrations in two chambers with time (triplicate).

Similar results for larger PDMS thickness were observed in Fig. 4. These results revealed that phenol could be sorbed in PDMS before permeate through the membrane. The larger was the PDMS thickness, the more phenol was sorbed. The results for the 9.6 μm membrane are shown in Fig. 5.

The adsorption and desorption experiments were conducted to verify the above observation (Table 2). A sample of membrane was immersed in a 1 wt.% phenol solution for one day to adsorb phenol from the solution. The phenol concentration in membrane was concentrated

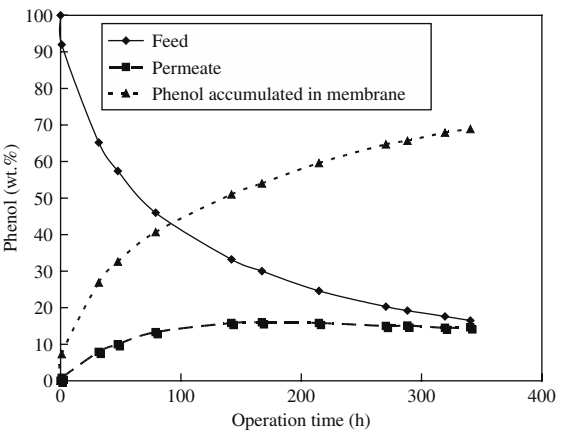

Fig. 5. Permeation of phenol for 9.6 μm membrane.

Table 2
Sorption experimental data

Materials	Solubility parameter (δ) $(J/cm^3)^{1/2}$	Difference of solubility parameters ($\Delta\delta_{polymer-solvent}$)
PDMS	14.9	
Phenol	24.1	9.2
Water	47.8	32.9

Note: Feed solution: 1 wt.% aqueous phenol solution; phenol in PDMS membrane: 32.3 wt.%.

from 1 wt.% up to 32.3 wt.%. The higher affinity PDMS membrane for phenol can be further illustrated by considering the difference in solubility parameters. The difference of solubility parameters between phenol and PDMS membrane ($\Delta\delta_{phenol}$–PDMS = 9.2 $(J/cm^3)^{1/2}$) is lower than that between water and PDMS membrane ($\Delta\delta_{water}$–PDMS = 32.9 $(J/cm^3)^{1/2}$). That is, phenol has a stronger interaction with PDMS than water.

The result also showed that the membrane with thickness of 9.6 μm retained 27% of phenol on the membrane leaving 8% of phenol passing through the membrane into the permeate chamber and 65% of phenol in the feed during 32 h permeation. If time extended to 340 h, the result showed that retained 69% of phenol on the membrane leaving 15% of phenol passing through the membrane into the permeate chamber and 16% of phenol in the feed. The result verified that the reduction of phenol in the feed chamber was higher than the increase of phenol in the permeate chamber for a period of time before enough phenol was released to the permeate chamber.

3.2. Determining the major parameters

The major parameters have been screened by the orthogonal array and range analysis. Four parameters and three levels shown in Table 3 have been used in the analysis. The four parameters, including phenol concentration in influent, recirculation rate, membrane skin layer thickness, and sodium chloride concentration in influent have been operated under different conditions (as shown in Table 3) to determine the permeate flux. The results of 6 and 48 h operations are listed in Table 4. It revealed that the higher was the phenol concentration in the influent, the higher was the permeate flux through the membrane. The R values of four parameters for 6 and 48 h operations were 2.86, 0.41, 0.62, 0.27 and 2.29, 0.11, 0.31, 0.10, respectively. The results showed that the significance of parameters on the permeate flux follows the order of phenol concentration, membrane skin layer thickness, recirculation rate, and sodium chloride concentration at 6 and 48 h operations.

3.3. Optimal operation range

From the orthogonal array and range analysis on the four selected parameters, phenol

Table 3
L_9 parameter and level values of permeation test

Parameters	Level 1	Level 2	Level 3
A: phenol concentration in influent (mg/L)	100	550	1000
B: recirculation rate (mL/min)	30	90	150
C: membrane skin layer thickness (μm)	26.2	9.6	0.4
D: sodium chloride concentration in influent (%)	1	3	5

Table 4
Results of L_9 orthogonal array analysis in permeate test

Concentration					Results	
No.	Phenol conc. in influent (mg/L)	Recirculation rate (mL/min)	Membrane skin layer thickness (μm)	Conc. of NaCl in influent (%)	Permeate flux of phenol after 6 h ($g/m^2 \cdot d$)	Permeate flux of phenol after 48 h ($g/m^2 \cdot d$)
1	100	30	26.2	1	0.93	0.38
2	100	90	9.6	3	0.60	0.25
3	100	150	0.4	5	0.35	0.18
4	550	30	9.6	5	1.21	1.14
5	550	90	0.4	1	1.11	1.07
6	550	150	26.2	3	1.40	1.29
7	1000	30	0.4	3	3.25	2.35
8	1000	90	26.2	5	4.24	2.87
9	1000	150	9.6	1	2.96	2.46

concentration in influent and membrane skin layer thickness have been determined to be the major variables on the permeate flux. Nine groups of experiments have been conducted to find the optimal operation range according to the Response Surface Methodology (RSM). The test conditions and results are listed in Table 5. All the experiments have been operated with the influent containing 3% sodium chloride and at the recirculation rate of 90 mL/min. The results revealed that the highest phenol permeate flux for 13 and 48 h operations were 15.5 and

Table 5
The conditions and results of response surface methodology coupled with central composite design

Conditions[a]			Results			
			Permeate		Feed	
No.	Phenol conc. in influent (mg/L)	Membrane skin layer thickness (μm)	Phenol after 13 h operation ($g/m^2 \cdot d$)	Phenol after 48 h operation ($g/m^2 \cdot d$)	Phenol after 13 h operation ($g/m^2 \cdot d$)	Phenol after 48 h ($g/m^2 \cdot d$)
1	200	1.0	0.86	0.58	0.90	0.90
2	200	14.4	1.62	0.92	0.34	0.69
3	1100	1.0	3.45	3.18	6.49	4.97
4	1100	14.4	3.00	2.24	15.5	8.63
5	650	9.6	1.48	1.48	5.45	4.23
6	650	0.40	1.70	1.58	4.65	3.78
7	650	26.2	3.40	2.40	9.58	5.68
8	14	9.6	0.17	0.05	0.07	0.32
9	1286	9.6	3.54	3.08	8.35	6.56

[a]All the experiments have been operated with 3% sodium chloride at influent and recirculation rate of 90 mL/min.

8.63 g/m^2 · d, respectively when phenol concentration and skin layer thickness of the membrane were 1100 mg/L and 14.4 μm. Based on the results of response surface (Fig. 6), it revealed that the higher was the phenol concentration in the influent or the thicker was the membrane skin layer thickness, the higher was the permeate flux through the membrane.

At the operating conditions for practices, membrane skin layer thickness and recirculation rate were considered to be the major variables on the permeate flux. Nine groups of experiments have been conducted as well. The test conditions and results are listed in Table 6. All the experiments have been operated with 3% sodium chloride concentration and 922 mg/L phenol concentration in influent. The results revealed that the highest phenol permeate flux for 6 h operation was 26.47 g/m^2 · d when skin layer thickness of the membrane and recirculation rate were 0.4 μm and 120 mL/min, respectively. Based on the results of response surface (Fig. 7), it revealed that the higher was the recirculation rate, the higher was the permeate flux through the membrane.

3.4. Biological test

The results showed that no significant effect of sodium chloride on phenol biodegradation was observed for sodium chloride concentration below 1%. Phenol degradation rate was reduced significantly for sodium chloride concentration over 3% (Fig. 8).

The effect of biocarrier concentration on the flux is shown in Fig. 9. The flux increased with biocarrier dose until it reached a maximum. The peak flux of PDMS membrane is 9.54 g/m^2 · d. The biofouling of the membrane surface was expected to be significant due to high density of suspended solids. It shows that the biofouling could be reduced by biocarrier. This reduction was enhanced with the increasing of biocarrier dose until that the optimum dosage was reached. After the optimal dosage, the flux dropped because over-packing of biocarrier interfered the free movement of biocarriers and reduced the permeation flux.

The conductivity and the concentration of phenol in the biological chamber were monitored along with the permeate flux. The results,

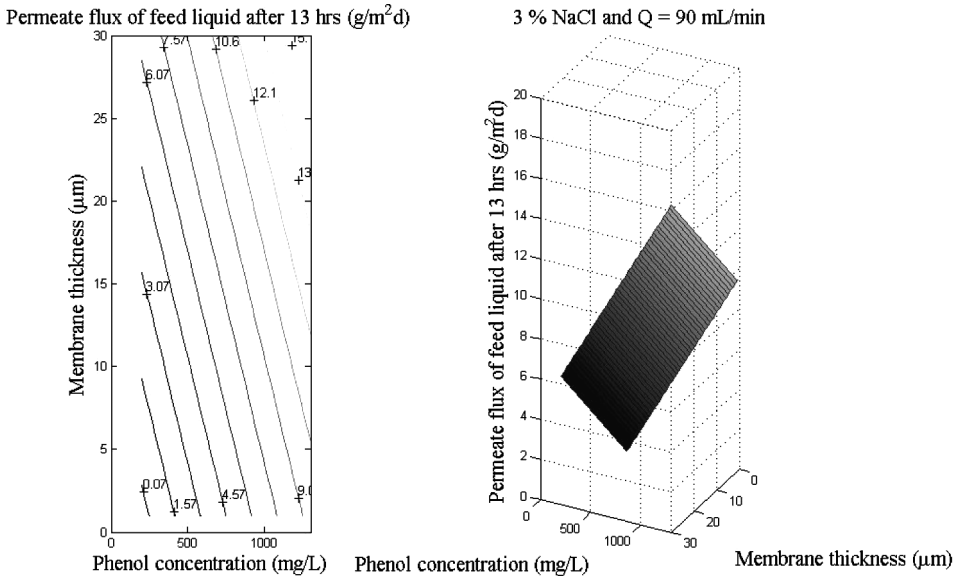

Fig. 6. Response surface of permeate flux corresponding to phenol concentration and membrane thickness.

Table 6
The conditions and results of response surface methodology coupled with central composite design

Conditions[a]			Results	
			Permeate	Feed
No.	Membrane skin layer thickness (μm)	Recirculation rate (mL/min)	Phenol after 6 h operation ($g/m^2 \cdot d$)	Phenol after 6 h operation ($g/m^2 \cdot d$)
1	1.0	60	5.15	8.49
2	1.0	180	4.58	15.58
3	14.4	60	7.64	18.04
4	14.4	180	7.17	17.86
5	9.6	120	3.89	4.67
6	9.6	35	4.10	13.38
7	9.6	205	3.73	14.80
8	0.4	120	8.36	26.47
9	26.2	120	3.47	13.33

[a]All the experiments have been operated with 3% sodium chloride and 922 mg/L phenol concentration in influent.

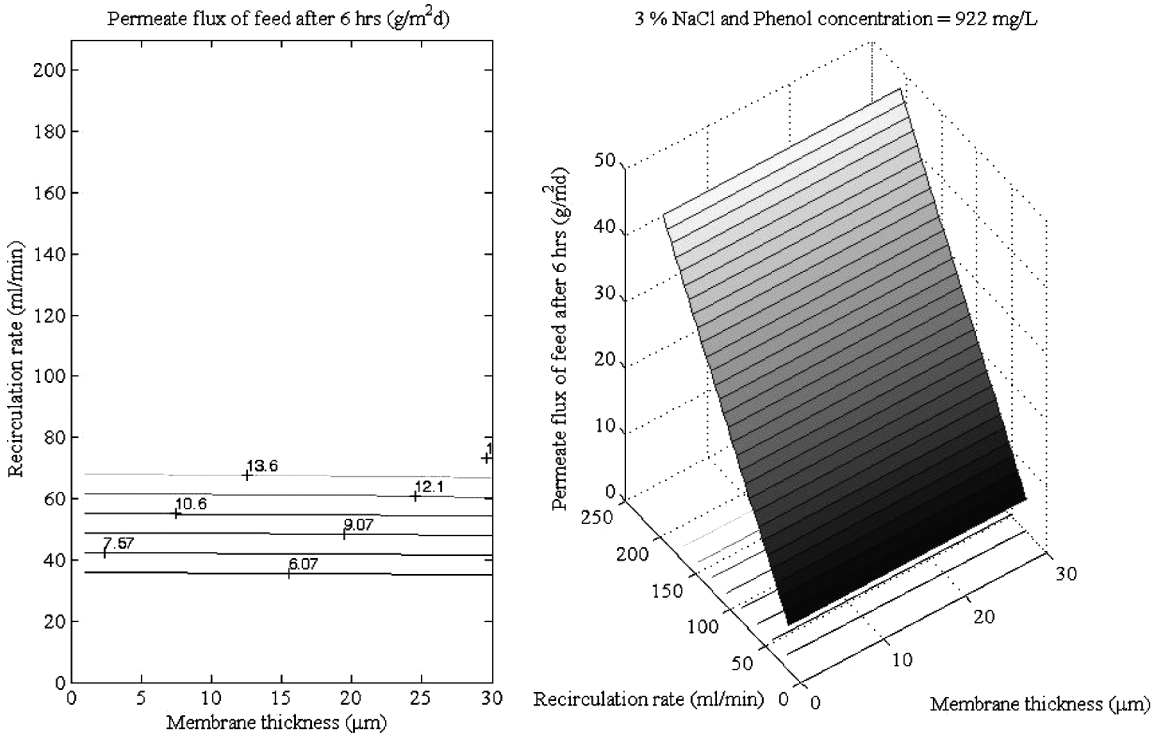

Fig. 7. Response surface of permeate flux corresponding to membrane thickness and recirculation rate.

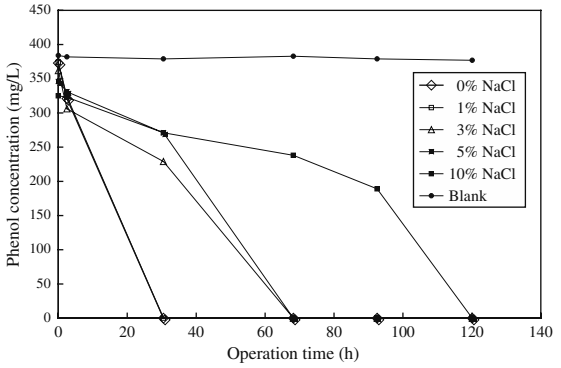

Fig. 8. Effect of sodium chloride concentration on biodegradation of phenol.

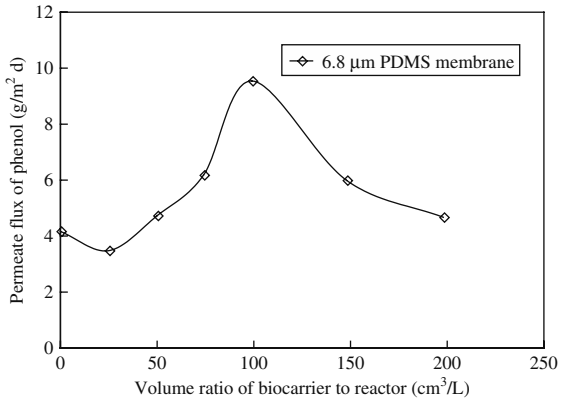

Fig. 9. Effects of biocarrier amount on permeate flux.

as shown in Table 7, indicated that the membrane could successfully extract the phenol from the high concentration salt and the biological phase could break down the permeated phenol completely.

4. Conclusion

Treatment of organic wastewater containing high concentration of salts is needed in many applications. Membrane transferring organics coupling biological degradation was studied in this paper. Factors affecting phenol transfer through PDMS composite membrane have been investigated. Experimental results showed that the significance of parameters on the permeate flux followed the order of phenol concentration, membrane skin layer thickness, recirculation rate, and sodium chloride concentration after 6 and 48 h operations. The higher was the phenol concentration in the influent or the thicker was the membrane skin layer thickness, the higher was the permeate flux through membrane. Also, the recirculation rate had the positive effect on the permeate flux through membrane. The results demonstrated that PDMS composite membranes could separate phenol from the high inorganic wastewater effectively and biological phase degraded the permeated phenol completely through optimum addition of biocarriers.

Table 7
Changes of conductivity and phenol concentration through EMB operation

PDMS membrane (thickness = 6.8 μm)	Start of operation		End of operation	
No. of run/operation time (h)	1/141	2/161	1/141	2/161
Feed chamber				
Conductivity (mho/cm)	31.5	31.3	31.4	31.4
Phenol concentration (mg/L)	401	404	362	323
Permeate chamber				
Conductivity (mho/cm)	0.35	0.62	1.01	1.28
Phenol concentration (mg/L)	ND	ND	ND	ND
Volume ratio of biocarrier to reactor (cm^3/L)	24.6	147	24.6	147

Acknowledgements

The authors would like to thank the Department of Industrial Technology, Ministry of Economic Affairs, R.O.C., for financially supporting this research.

References

[1] A.G. Livingston, J.P. Arcangeli, A.T. Boam, S. Zhang, M. Marangon and L.M. Freitas dos Santos, Extractive membrane bioreactor for detoxification of chemical industry wastes: process development, J. Membr. Sci., 151 (1998) 29–41.

[2] C. Lipski and P. Cote, The use of pervaporation for the removal of organic contaminants from water, Environ. Progr., 9 (1990) 254.

[3] A.G. Livingston, L.M. Freitas dos Santos, P. Pavasant, E.N. Pistikopoulos and L.F. Strachan, Detoxification of industrial wastewaters in an extractive membrane bioreactor, Water Sci. Technol., 33 (3) (1996) 1–8.

[4] E.A.C. Emanuelsson and A.G. Livingston, Overcoming oxygen limitations in membrane-attached biofilms — investigation of flux and diffusivity in an anoxic biofilm, Water Res., 38 (2004) 1530–1541.

[5] M.S. Lee, C.P. Huang, J.R. Pan, B.L. Shiau and W.K. Chang, Combination of extractive membrane and bio-carriers to treat wastewater containing phenol and high-strength NaCl, Proc. of Membrane Science and Technology Symposium, April 27–28, Singapore, 2006.

[6] R.H. Myers and D.C. Montgomery, Response Surface Methodology — Process and Product Optimization using Designed Experiments, 2nd edn., John Wiley and Sons, Inc, USA, 2002.

[7] M.F. Hamoda and I.M.S. AI-Attar, Effects of high sodium chloride concentrations on activated sludge treatment, Water Sci. Technol., 31 (9) (1995) 61–72.