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# Membrane aromatic recovery system (MARS) — a new membrane process for the recovery of phenols from wastewaters

Shejiao Han, Frederico Castelo Ferreira, Andrew Livingston\*

*Department of Chemical Engineering and Chemical Technology, Imperial College of Science, Technology and Medicine, Prince Consort Road, London SW7 2BY, UK*

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## Abstract

This paper describes a new process for recovery of aromatic acids and bases, the membrane aromatic recovery system (MARS). The process comprises a stripping vessel, where phenols are extracted through nonporous membranes and concentrated into a NaOH solution as phenolate, and a two-phase separator in which the solution collected from the stripping vessel is separated into a phenolic phase and an aqueous phase by adjusting pH to acidic conditions with the addition of HCl. Silicone rubber tubing was used as a membrane in this study. The temperature in the stripping vessel and NaOH concentration in the solution fed into the stripping vessel are two important operating parameters. In this study the temperature was 50°C and NaOH concentration 12.5 wt.%. At steady-state, the total phenol concentration in the stripping solution can be orders of magnitude higher than in the wastewater, ensuring a high phenol recovery efficiency. The work found phenol recovery efficiencies of over 94%, with a recovered organic-rich phase comprising 86.5 wt.% phenol, and the balance water.

The overall mass transfer coefficients (OMTCs) for other phenols were investigated to demonstrate the wide potential applications of MARS technology. Insights into OMTCs and permeabilities of phenols include the effect of Reynolds number in the tube side on OMTC, and the effect of temperature on the permeabilities of phenolic compounds in the membrane. The membrane resistance dominates the OMTCs of phenols in this study. The van't Hoff–Arrhenius relationship for the temperature dependence of the permeability of the penetrant through the polymer gave excellent agreement with our experimental data. © 2001 Elsevier Science B.V. All rights reserved.

*Keywords:* Phenol recovery; Membrane separation; Mass transfer rate

## 1. Introduction

Phenols, i.e. hydroxy compounds of aromatic hydrocarbons, are common pollutants of wastewater streams from petroleum refineries, petrochemical industries, the production of phenolic resins, dyes, pesticides, etc. [1]. Since phenols are highly toxic and at high concentration (>200 mg/l) are inhibitory to

biological treatment, the recovery of phenols from industrial wastewater streams has generated significant interest [2,3].

Methods for the recovery of phenols include solvent extraction [2,4], activated carbon and polymer adsorption [5–7], and membrane processes [8–13]. Among these recovery processes solvent extraction is widely reported since good inter-phase contact can result in high mass transfer rates. In general, solvent extraction consists of two stages, i.e. dispersion of one phase into another phase, and separation of the two phases to extract compounds of interest from the continuous

\* Corresponding author. Tel.: +44-20-75945582;  
fax: +44-20-75945629.  
E-mail address: a.livingston@ic.ac.uk (A. Livingston).

**Nomenclature**

$C_f$	concentration in the feed side ( $\text{g l}^{-1}$ )
$C_{f,\text{in}}$	inlet concentration in the feed side ( $\text{g l}^{-1}$ )
$C_{f,\text{out}}$	outlet concentration in the feed side ( $\text{g l}^{-1}$ )
$C_s$	concentration in the stripping solution ( $\text{g l}^{-1}$ )
$C_t$	total concentration in the stripping solution ( $\text{g l}^{-1}$ )
$D$	diffusion coefficient ( $\text{m}^2 \text{s}^{-1}$ )
$E_p$	apparent activation energy (J)
$F$	flow rate ( $\text{m}^3 \text{s}^{-1}$ )
$k_{\text{ov}}$	overall mass transfer coefficient ( $\text{m s}^{-1}$ )
$k_s$	mass transfer coefficient in the shell side ( $\text{m s}^{-1}$ )
$k_t$	mass transfer coefficient in the tube side ( $\text{m s}^{-1}$ )
$K$	partition coefficient
$K_a$	dissociation constant
$L$	membrane length (m)
$N$	mass transfer rate per length unit ( $\text{g m}^{-1} \text{s}^{-1}$ )
$P$	permeability ( $\text{m s}^{-1}$ )
$P_0$	pre-exponential factor in Eq. (9) ( $\text{m s}^{-1}$ )
$r_i$	internal radius of the tube (m)
$r_o$	outer radius of the tube (m)
$R$	molar gas constant ( $\text{J mol}^{-1} \text{K}^{-1}$ )
$Re$	Reynolds number, $du\rho/\mu$
$T$	absolute temperature (K)
$u$	velocity of liquid in the tube side ( $\text{m s}^{-1}$ )
$x$	position in the membrane (m)

*Greek symbols*

$\mu$	viscosity ( $\text{kg m s}^{-1}$ )
$\rho$	density of liquid ( $\text{kg m}^{-3}$ )

phase. Unfortunately, problems can arise in the phase separation due to a tendency to form stable emulsions in the system [14]. In solvent extraction, there are two kinds of solvent often used, i.e. non-polar and polar solvents. Non-polar solvents have low distribution coefficients for phenols in the solvent phase, resulting in the low recovery efficiency in the process. Polar solvents have better distribution coefficients than non-polar solvents. However, in the extraction

processes with polar solvents, the wastewater often needs to be re-treated to remove the dissolved solvents before discharge, due to the higher solubility of polar solvents in water [2]. To overcome the shortcomings in solvent extraction, activated carbon and polymeric adsorption processes were developed. In adsorption processes, phase separation is quite easy to realise in liquid–solid two-phase systems, and the aqueous phase is not easily re-contaminated. However, there is the requirement for the elution of phenols from the loaded carbons or the resins, usually via solvents. In some cases, it is difficult to effectively regenerate activated carbons [7].

Membrane technologies have attracted attention for removal of low-volatility organics from wastewaters. Porous membranes have been used for membrane solvent extraction by Kiani et al. [15], Uramoto et al. [8], and Netke and Pangarkar [14] for the recovery of organics from aqueous solutions. However, porous membranes have a major shortcoming due to their instability [16], i.e. breakthrough of the immobilised phase in the pores can occur unless a high breakthrough pressure through the membrane is maintained. Nonporous membranes were proposed for carrying out extraction by Lee et al. [17], which led to some related later work done by Netke and Pangarkar [14], Ray et al. [9], Wehtje et al. [18] and Doig et al. [16]. Compared to porous membranes, the breakthrough pressure is much higher through nonporous membranes; however, this is at the expense of a lower mass transfer rate in the membrane extraction.

Pervaporation processes have also been applied for the recovery of phenol from wastewaters [10–13]. Since phenol has a relatively low vapour pressure (0.055 kPa at 25°C), the driving force for phenol transport is low in pervaporation, resulting in low mass transfer rates. Membranes with high affinity for phenol were pursued to improve the phenol permeability such as polyether-block-polyamides (PEBA) [10] and polyurethane [11]. A hybrid process has recently been proposed to achieve low phenol discharge concentration and phenol recovery, through a combination of pervaporation, adsorption and liquid–liquid phase separation [13]. However, in spite of more than 10 years of research, the use of organophilic pervaporation systems for recovery of low volatility organics in waste streams has not been adopted commercially [13].

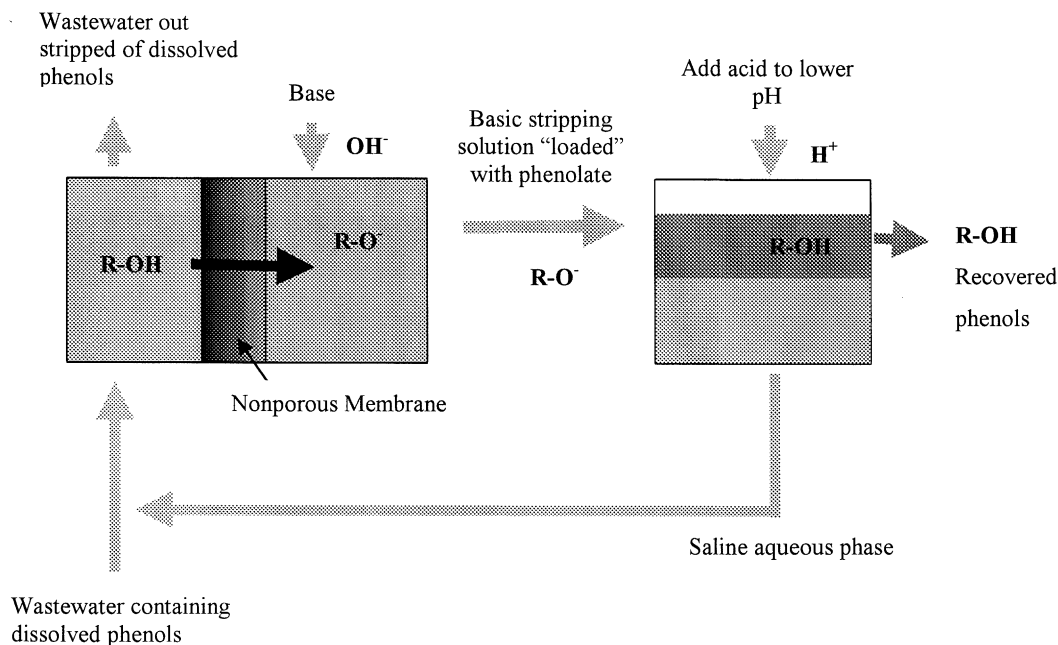


Fig. 1. A schematic diagram of MARS process.

The present paper describes a novel process, the membrane aromatic recovery system (MARS) process, for recovery of phenolic compounds. The process is shown schematically in Fig. 1. The coupling of separation with a reversible reaction to form phenolate salts has been applied to recover phenol. Phenolic compounds are weak acids and so dissociate in basic medium and associate in acidic medium, a process which is reversible upon adjustment of pH in the solution. A basic medium was maintained as a stripping solution to extract phenol from the wastewater. The stripping solution was collected and adjusted to acidic conditions to recover the phenol. Subsequently phenol was removed as a phenol-rich organic phase and the saline aqueous underlayer was returned to the wastewater feed. It should be noted that the process can also easily be applied to recovery of aromatic bases such as aniline and pyridine and their derivatives, by simply reversing the roles of acid and base in the process.

Silicone rubber membrane tubing was used, as it has a better phenol permeability than almost all other materials reported until now, due to the flexibility of the backbone  $-\text{Si}-\text{O}-$  in PDMS [19]. A temperature of  $50^{\circ}\text{C}$  was used to improve permeation rates. The

paper describes the extraction and recovery of phenols from a synthetic wastewater, including the purity of the recovered phenol phase, and provides mass transfer data to show that the process is applicable to a wide range of phenolic compounds as well as phenol.

## 2. Theoretical background

The rate of phenol permeation in this work has been characterised by the overall mass transfer coefficient based on concentration driving force,  $k_{\text{ov}}$ .

### 2.1. Resistances-in-series model

The resistances-in-series model has been widely used to describe the transport of penetrant through a membrane with liquid films in both sides [20]. Assuming no accumulation of the penetrant in the membrane and liquid films, one obtains the following:

$$N = k_{\text{ov}}(2\pi r_1)(C_f - C_s) \quad (1)$$

where  $N$  is mass transfer rate per length unit,  $k_{\text{ov}}$  the overall mass transfer coefficient,  $r_1$  the internal radius

of the membrane tube,  $C_f$  the phenol concentration in the wastewater, and  $C_s$  is the undissociated phenol concentration in the stripping solution. The overall mass transfer coefficient can be shown to be the sum of individual resistances in the fluid films and the membrane as follows:

$$\frac{1}{k_{ov}} = \frac{1}{k_t} + \frac{r_i \ln r_o/r_i}{DK} + \frac{r_i}{k_s r_o} \quad (2)$$

where  $k_t$  is the fluid film resistance in the wastewater,  $k_s$  the fluid film resistance on the stripping solution side,  $D$  and  $K$  the diffusivity and partition coefficients, respectively, for phenol in the membrane, and  $r_o$  is the outer radius of the membrane tube. When both fluid film resistances are negligible, Eq. (2) can be rewritten as

$$P = DK = \left( r_i \ln \frac{r_o}{r_i} \right) k_{ov} \quad (3)$$

where  $P$  is the membrane permeability. Since the overall mass transfer coefficient  $k_{ov}$  can be determined experimentally, the permeability of component  $i$  through the membrane can be obtained from Eq. (3).

## 2.2. Determination of $k_{ov}$ for wastewater inside membrane, stripping solution outside

At steady-state, when wastewater flows down the inside of a membrane tube and the stripping solution on the outside of the membrane tube can be considered to be well mixed at a uniform concentration, a mass balance on a differential element of membrane tube gives

$$-F \frac{dC_f}{dx} = k_{ov}(2\pi r_i)(C_f - C_s) \quad (4)$$

where  $F$  is wastewater flow rate and  $x$  the position along the membrane tube. Integrating the above equation yields

$$k_{ov} = \frac{F}{2\pi r_i L} \ln \frac{C_{f,in} - C_s}{C_{f,out} - C_s} \quad (5)$$

where  $L$  is the length of the membrane tube and  $C_{f,in}$  and  $C_{f,out}$  are the phenol concentrations at the inlet and outlet of the membrane tube, respectively. The equation for the dissociation of phenol and its corresponding acid dissociation constant,  $K_a$ , can be expressed as



and

$$K_a = \frac{[\text{Phenolate}][\text{H}^+]}{[\text{Phenol}]} \quad (6)$$

Eq. (6) yields

$$C_s = \frac{C_t}{1 + K_a/10^{-\text{pH}}} \quad (7)$$

where  $C_t$  is the total concentration of undissociated and dissociated phenol in the stripping solution. The  $K_a$  value will depend on the ionic strength in the stripping solution, and the temperature of operation. However, as a first approximation we have not considered these influences and  $K_a$  was chosen to be  $10^{-10}$  in this study [21].

Substituting Eq. (7) into Eq. (5) gives

$$k_{ov} = \frac{F}{2\pi r_i L} \ln \frac{C_{f,in} - C_t/(1 + K_a/10^{-\text{pH}})}{C_{f,out} - C_t/(1 + K_a/10^{-\text{pH}})} \quad (8)$$

All parameters in the above equation are measurable or known, therefore, the total mass transfer coefficient can be determined.

## 3. Experimental

### 3.1. Chemicals and analytical techniques

A range of phenols was investigated in this study, and their physical properties are shown in Table 1. All chemicals were supplied by Lancaster Synthesis Ltd., UK.

A GC (Autosystem XL) (Perkin-Elmer, USA) and a total organic carbon (TOC) machine (Shimadzu Corporation, Japan) were used to analyse the concentrations of all samples involved in this study. For GC analysis, samples were extracted into dichloromethane solution containing chlorobenzene as an internal standard. A  $1 \mu\text{l}$  sample of this extract was injected into the GC to analyse its concentration. The coefficient of variation of this assay (over five measurements) was 5% at  $50 \text{ mg l}^{-1}$ .

The total organic carbon (TOC) of the samples was measured using a total organic carbon analyser model TOC-5050. The total carbon (TC) was first measured and the inorganic carbon (IC) was determined through the catalytic conversion of all carbon

Table 1  
Physical and chemical properties of phenols of interest

Compound	Molecular weight (g mol <sup>-1</sup> )	Molar volume (cm <sup>3</sup> mol <sup>-1</sup> ) <sup>a</sup>	Solubility in water (g l <sup>-1</sup> )	pK <sub>a</sub> [21]	Solubility parameter (MPa) <sup>1/2b</sup>
Phenol	94.11	85.5	82 at 25°C	9.89 at 20°C	25.3
4-Chlorophenol	128.56	99.0	27.1 at 20°C	9.18 at 25°C	25.4
2,4-Dichlorophenol	163.00	112.5	4.5 at 20°C	–	23.3
4-Nitrophenol	139.11	111.5	16 at 25°C	7.15 at 25°C	24.9
<i>p</i> -Cresol	108.14	101.1	25 at 50°C	10.17 at 50°C	24.0
Hydroquinone	110.11	92.0	72 at 25°C	10.35 at 25°C	28.9

<sup>a</sup> Obtained by the method of group contributions proposed by Hoy [22].

<sup>b</sup> Obtained by the method of group contributions proposed by Hoftyzer and Van Krevelen [22].

to carbon dioxide followed by detection of CO<sub>2</sub> in an i.r. analyser. The TOC was determined by subtracting IC from TC. The machine repeats the assay until a coefficient of variation of less than 2% is obtained.

### 3.2. Membrane

The membrane used in this study was silicone rubber tubing, composed of 30 wt.% fumed silica and 70 wt.% poly(dimethylsiloxane) or PDMS, supplied by Silex Ltd., UK. The dimensions of the membrane tubes used in our experiments are given in Table 2.

### 3.3. Description of the MARS process

A schematic diagram of the MARS is shown in Fig. 2. The membrane tube was rolled around a support, and immersed into the stripping solution in the stripping vessel, which seated on the top of a magnetic stirrer hot-plate. The temperature of the stripping solution was controlled by a feedback loop with a probe

installed in the stripping solution. The pH of the stripping solution was kept constant by another feedback loop with a probe installed in the stripping solution and a pump which added 12.5 wt.% NaOH solution into the stripping solution on demand. The aqueous solution was pumped through the membrane tube side by a peristaltic pump.

The stripping solution overflowed from the vessel was collected in a flask equipped with a condenser at the top to prevent vaporisation. Samples of the stripping solution were removed from the flask periodically for pH adjustment and phenol recovery. For recovery, the pH was adjusted to around 1, the resulting two phase mixture created upon springing of the phenol allowed to stand until two phase separation occurred, and the phenol phase was then collected. The main operating parameters in the system are shown in Table 2.

### 3.4. Overall mass transfer coefficients for phenols

The MARS process should be suitable for all other phenols with an acceptable mass transfer rate through the membrane, which may be the most important parameter in the industrial application of the MARS process. Thus, we used an experimental rig to measure OMTCs of a range of phenols. The rig is similar to the stripping vessel as mentioned above. The same membrane tubing with a length of 18 m was used in this cell.

In order to ensure undissociated phenol concentration in the stripping solution was negligible for these experiments, the pH was controlled to be around 14. The effect of the temperature on the OMTC was further investigated for selected compounds.

Table 2  
Operating parameters in this study

Parameter	Value
Wastewater flow rate	2 l/day
Phenol concentration in the wastewater	10 g l <sup>-1</sup>
Membrane length	28 m
Membrane dimensions	3 mm i.d. × 0.5 mm wall 3 mm i.d. × 0.35 mm wall
Volume of the stripping vessel	1.5 l
Temperature in the stripping solution	50°C
pH in the stripping solution	11–14
NaOH solution	12.5 wt.%

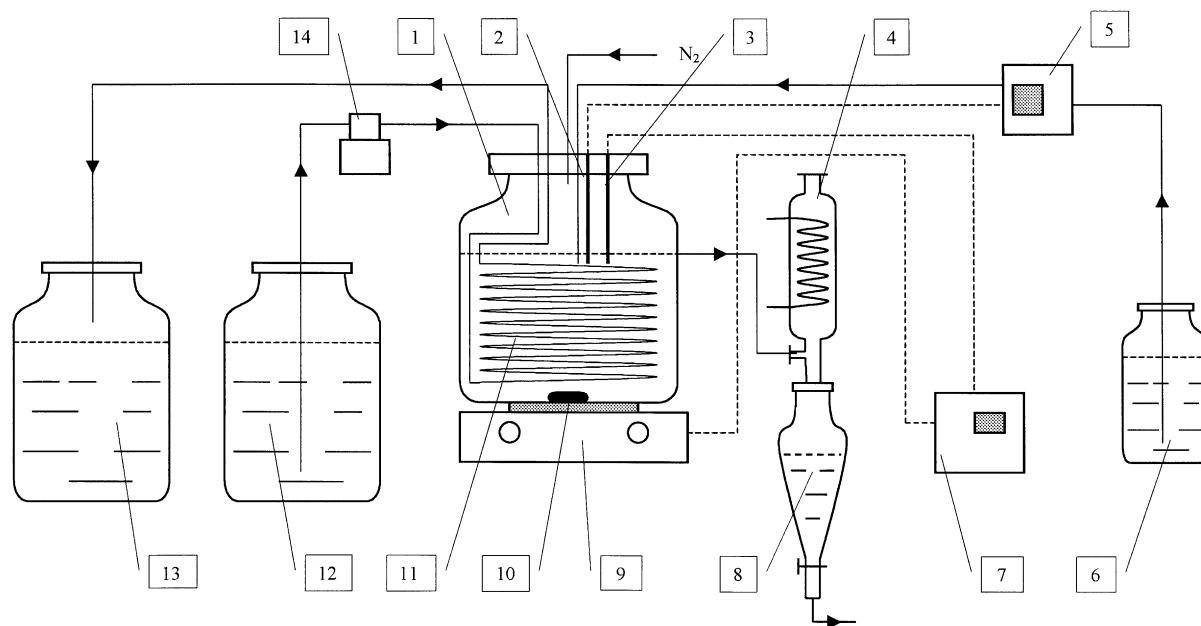


Fig. 2. Diagram of the experimental set-up. 1: The stripping solution vessel; 2: pH probe; 3: temperature probe; 4: condenser; 5: pH controller; 6: NaOH solution tank; 7: temperature controller; 8: collector; 9: magnetic stirrer hotplate; 10: stirrer; 11: membrane tube; 12: phenol solution tank; 13: cleaned water tank; 14: pump.

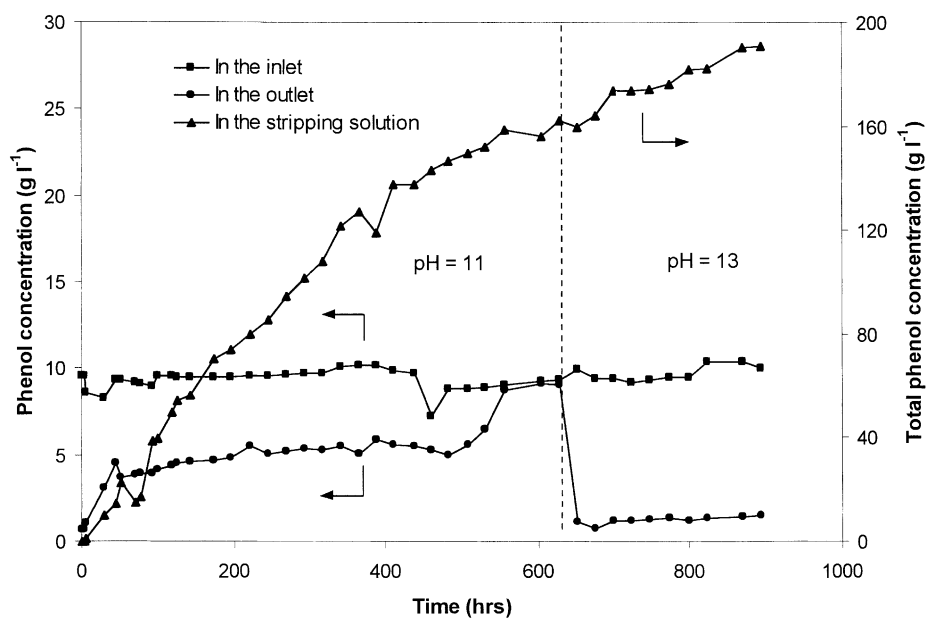


Fig. 3. Phenol concentration profiles in the inlet, the outlet and the stripping solution at different pH values with time: membrane tubing: 3.0 mm i.d.  $\times$  0.35 mm wall.

## 4. Results and discussion

### 4.1. Operation of MARS process

Fig. 3 shows the inlet and outlet phenol concentrations in the membrane tube, and the phenol concentration in the stripping solution, over a period of 40 days. It is clear that the pH in the stripping solution had a significant effect on the phenol outlet concentration, i.e. mass transfer rate through the membrane, and is a key adjustable operating parameter in MARS process — with pH = 13 phenol removals of over 90% were obtained. It is also shown in Fig. 3 that the total phenol concentration in the stripping solution can be orders of magnitude higher than in wastewater ( $200 \text{ g l}^{-1}$  versus  $10 \text{ g l}^{-1}$ ), ensuring high phenol recovery efficiency.

The stripping solution collection vessel was periodically drained for phenol recovery. For each period, we recorded the volume collected from the stripping vessel and its concentration. A mass balance can then be made each period between phenol removed from the wastewater versus the phenol in the collected stripping solution, Fig. 4, which shows good agreement with an average deviation of  $\pm 8\%$ .

The collected stripping solution was then neutralised in four batches using 37 wt.% HCl, and the results are shown in Fig. 5. Here, we define the recovery efficiency as the ratio of the mass of recovered phenol

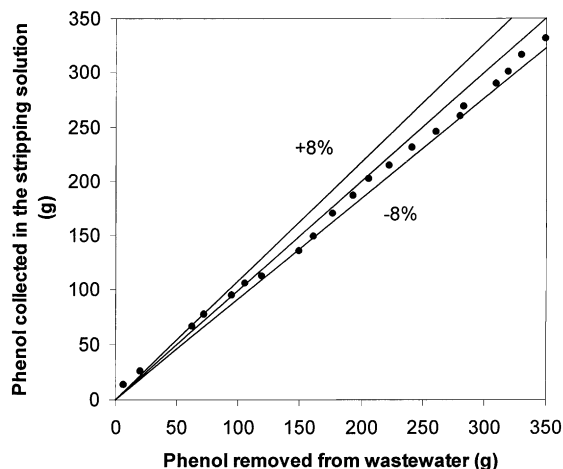


Fig. 4. The mass balance between phenol weight removed from wastewater vs. the value in the collector.

over the mass of phenol removed from the wastewater. The recovery efficiencies of phenol are all over 94%. The organic phase from recovery comprised of phenol and water — no other organic compound was detected by GC. The mass of phenol in this recovered phenol-rich phase is 86.5 wt.% with an average deviation of less than 1% over the four batches.

From these results, the MARS process appears promising for industrial application since besides high recovery efficiency, the operation of the system

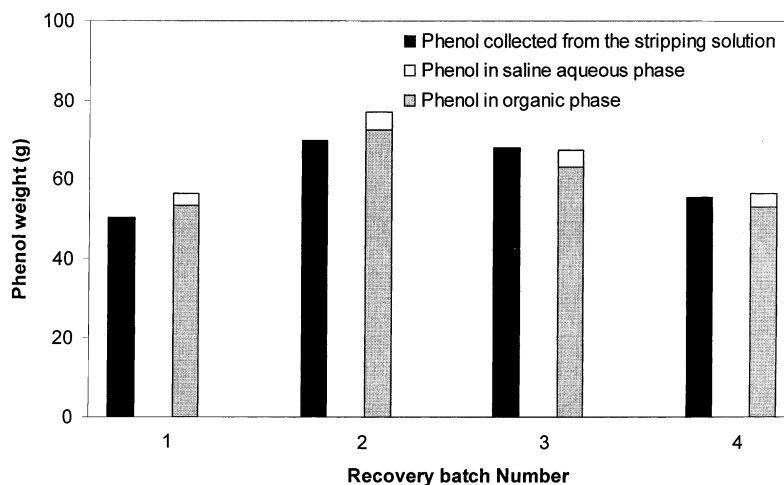


Fig. 5. Phenol recovery efficiencies for recovery batches 1–4.

is simple, as shown in Fig. 1, and stable because of the application of nonporous membranes.

#### 4.2. Effect of pH in the stripping solution on phenol concentrations

As shown in Fig. 3, the phenol outlet concentration continued increasing over time when the pH value in the stripping solution was controlled at 11, and the phenol inlet and outlet concentrations were almost equal after around 630 h running. This suggests that the mass transport of phenol through the membrane had stopped, since the undissociated phenol concentration at this point was high enough to create a negligible mass transfer driving force. With the increase in pH up to 13, the phenol outlet concentration sharply decreased from around 5 down to  $1 \text{ g l}^{-1}$ . This data shows that the pH is a very important parameter controlling mass transport through the membrane.

As theoretically discussed in Section 2, the undissociated phenol concentration in the stripping solution depends on the pH. From Eq. (7), one can predict concentration percentages of dissociated and undissociated phenol with pH, as shown in Fig. 6. Fig. 6 shows that the percentage of undissociated phenol sharply decreases with increasing in pH above pH 8 till it goes reaches nearly zero after pH 12. Therefore, the driving force for mass transport through the membrane,

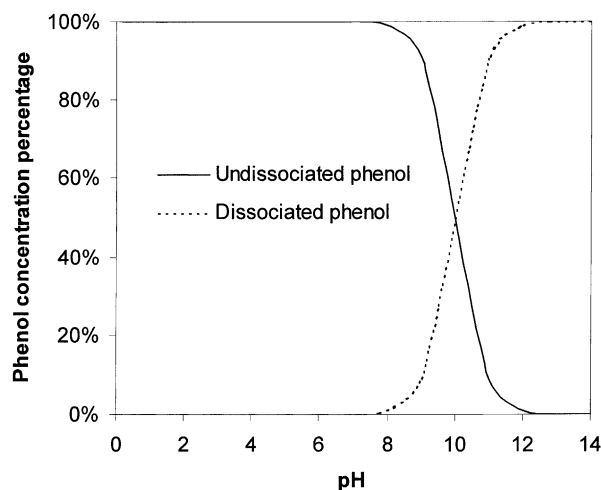
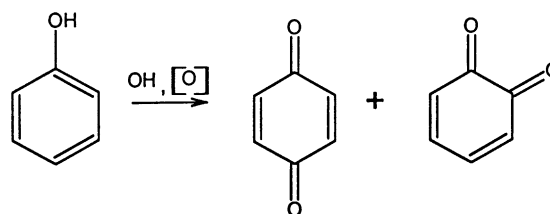


Fig. 6. Theoretical prediction of percentage of dissociated and undissociated phenol which is a function of pH.

as shown in Eq. (1), increases with increasing pH for  $\text{pH} > 8$ , and the mass transfer rate of phenol through the membrane increases, resulting in lower phenol outlet concentration. The change of phenol outlet concentrations shown in Fig. 3 is consistent with this theoretical prediction, since we calculate from the data in Figs. 3 and 6 that undissociated phenol concentration in the stripping solution was  $9.1 \text{ g l}^{-1}$  at pH 11 and 630 h, much higher than the  $0.1 \text{ g l}^{-1}$  we predict at pH 13.

#### 4.3. Oxidation

Ge and Jin [4] reported that phenol can be oxidised into quinones in an open basic medium at room temperature. The oxidation of phenol is as follows:



The occurrence of oxidation would reduce the recovery efficiency of phenol and contaminate the recovered material. To prevent oxidation in the stripping solution, nitrogen gas was introduced to completely remove oxygen from the stripping vessel before the experiments, and kept covering the free space during the experiments.

Total phenol concentration in the stripping solution can be directly measured by acidification, and then extraction into solvent followed by GC. The organic carbon (OC) in the stripping solution was determined by TOC machine, and a calculated total phenol concentration can be obtained by multiplying the OC value by  $1.3 \text{ g (phenol) g}^{-1}$  (organic carbon). If no oxidation occurs in the stripping solution, and no other organic compounds are present, the ratio between these two measurements should be 1.0. The experimental data is shown in Fig. 7, and it can be seen that these two measured values are quite comparable, with deviations at random around the parity line. If the concentration was systematically smaller from GC than from TOC machine, it would suggest that oxidation could have occurred in the stripping vessel. We conclude that in



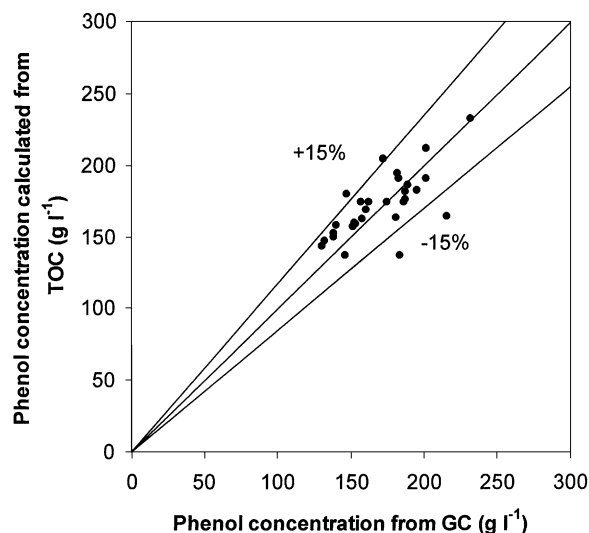


Fig. 7. Comparison of phenol concentrations measured by GC and calculated phenol concentrations from TOC.

fact the nitrogen blanket prevented the oxidation of phenol in the present system.

#### 4.4. Effect of the concentration of NaOH solution

In the MARS process, the NaOH used for extracting the phenol is neutralised and ultimately ends up as NaCl in the saline aqueous underlayer from phenol recovery (see Fig. 1). The solubility of phenol in this aqueous underlayer has an effect on the phenol recovery efficiency (see Fig. 5).

The “salting-out” effect was investigated for the saline–phenol–aqueous system. Equilibrium composition solutions were prepared by mixing together 20 g phenol, 100 ml water NaCl as required, and then allowing two-phase separation to occur. Water concentration in the phenol-rich layer was measured using Karl Fisher titration, and  $\text{Na}^+$  and  $\text{Cl}^-$  in the aqueous layer were measured by ion chromatography. The experimental results are shown in Fig. 8, which shows data for 30°C. The solubility of phenol in water sharply decreases from 83 to  $15.7 \text{ g l}^{-1}$  with an increase in NaCl concentration from 0 to  $200 \text{ g l}^{-1}$ , then stays almost constant with further increases in NaCl concentration. The concentration of phenol in the phenol-rich layer increases from 70.5 to 87 wt.% over the same NaCl concentration range. These results show that a

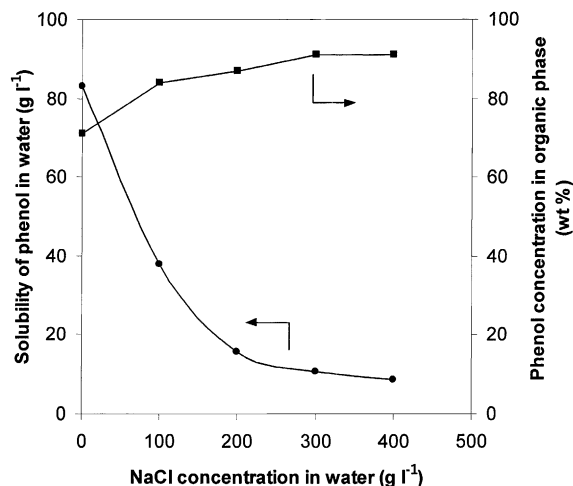


Fig. 8. Solubilities of phenol in aqueous solution and phenol concentrations in the phenol-rich layer as a function of NaCl concentration.

low NaCl concentration leads to both a higher concentration of phenol in the aqueous saline underlayer recycled to the wastewater feed, and a lower phenol content of the phenol rich layer.

Undissociated phenol concentration is negligible compared to the dissociated phenol concentration in the stripping solution at pH greater than 12, as shown in Fig. 6. Therefore, at steady-state, 1 mole of phenol removed from the wastewater requires one mole of NaOH to be added to the stripping solution to maintain pH at the set-point. Hence, increasing NaOH concentrations leads to higher steady-state total phenol concentrations in the stripping solution. Based on Eq. (7) and a mass balance in the stripping vessel, we can predict the relationships of total and undissociated phenol concentrations at steady-state in the stripping solution as a function of NaOH concentration at pH 13. The predicted results are shown in Fig. 9. It can be seen that if 50 wt.% NaOH were used, this would result in an undissociated phenol concentration of around  $0.7 \text{ g l}^{-1}$  in the stripping solution, compared to a concentration of around  $0.2 \text{ g l}^{-1}$  when using 12.5 wt.% NaOH. The outlet phenol concentration at pH 13 is around  $1 \text{ g l}^{-1}$ , corresponding to 90% phenol removal. A 50 wt.% NaOH concentration would lead to an equilibrium undissociated phenol concentration of  $0.7 \text{ g l}^{-1}$ , which is significant compared to the

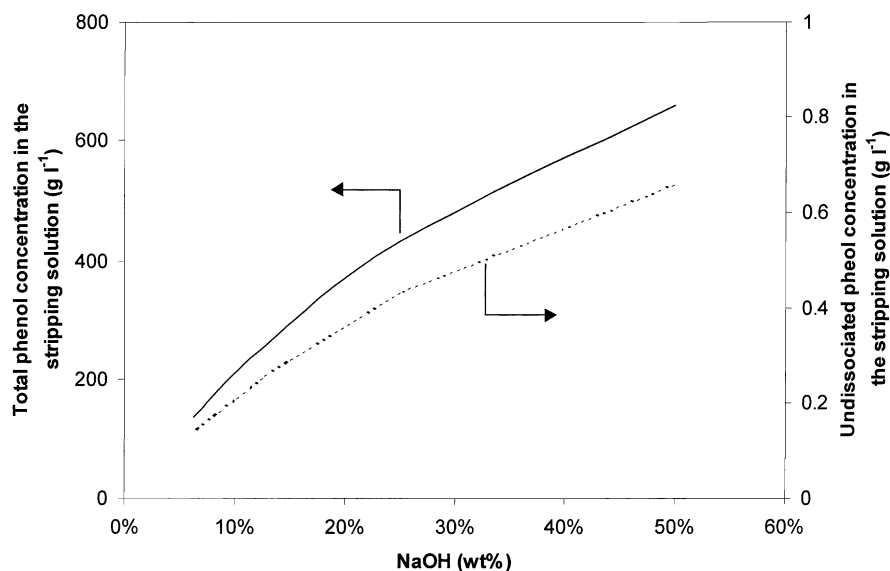


Fig. 9. Theoretical calculation of total and undissociated phenol concentrations in the stripping solution at steady-state as a function of the concentration of NaOH used for stripping.

outlet wastewater concentration, and so would reduce mass transfer driving force and increase membrane area requirements.

However, the use of NaOH solution with low concentrations, i.e. below 5 wt.% would create a larger volume of the salt layer after recovery than 50 wt.% (roughly 10 times), which would also have a higher phenol concentration due to lower NaCl levels, creating the need for re-treatment of a large amount of saline aqueous underlayer solution after two-phase separation.

A 12.5 wt.% NaOH concentration by addition of water was used in this first study of the MARS system, but clearly further work is required to optimise this parameter.

#### 4.5. Steady-state and overall mass transfer coefficients (OMTCs)

With a caustic concentration of 12.5 wt.%, from Fig. 9, the theoretical steady-state total phenol concentration in the stripping solution is 251 g l<sup>-1</sup>. We had not reached this value after 900 h, and so to save time and investigate the performance of the stripping vessel at steady-state, a synthetic stripping solution was prepared in which total phenol concentration was

at the steady-state value from the outset. The experimental data in Fig. 10 shows that the inlet and outlet concentrations on the tube side, and the concentration in the stripping solution, remained constant during steady-state operation. The average total phenol

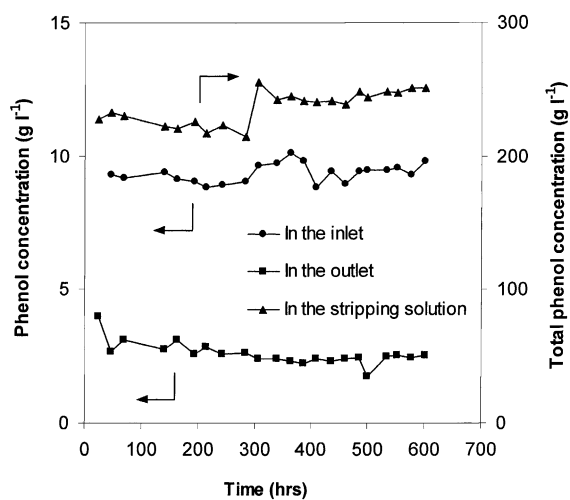


Fig. 10. Phenol concentration profiles in the inlet, the outlet and the stripping solution at steady-state with time: pH = 13 and membrane tube of 3.0 mm i.d. × 0.5 mm wall.

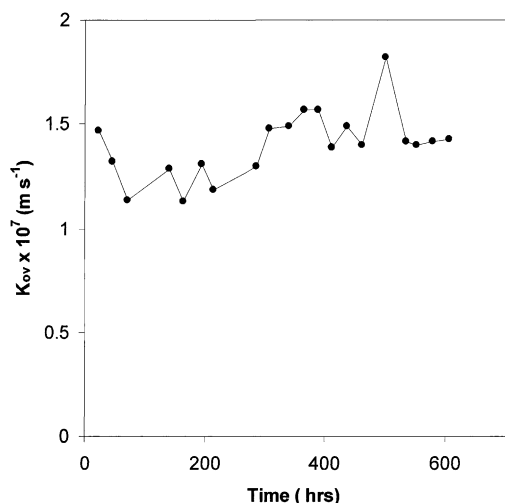


Fig. 11. OMTCs of phenol with time: pH = 13 and membrane tube of 3.0 mm i.d.  $\times$  0.5 mm wall.

concentration in the stripping solution was  $242 \text{ g l}^{-1}$ , close to the calculated value of  $251 \text{ g l}^{-1}$  from Fig. 9.

Using Eq. (8), OMTCs were calculated, and the data is shown in Fig. 11. The OMTCs of phenol fluctuated slightly, probably due to the errors of experimental measurements since no system parameters were changed. The average value of the OMTC is  $1.4 \times 10^{-7} \text{ m s}^{-1}$  with an average deviation of  $\pm 8\%$ . This is relatively low compared to other values we have obtained, and the reasons are discussed below. It is also interesting to note that the concentration of phenol in the membrane outlet in Fig. 10 is higher than we observed in Fig. 3, under equivalent conditions of wastewater concentration and flow. We ascribe this to the higher phenol concentration in the stripping solution and the consequently higher concentration of undissociated phenols present in the strip, at steady-state.

#### 4.6. OMTCs of a range of phenolic compounds

Table 3 shows the data of OMTCs of a range of phenolic compounds, which were obtained with pH 14 in the stripping solution. The OMTC of phenol shown in Table 3 is around two times higher than the average value obtained in the MARS process. The deviation may be mainly due to the fact that the effective membrane–solution interfacial area in the stripping vessel could be lower than the value calculated on the basis of membrane dimensions, since the 28 m of membrane tubing used in the MARS process was tightly rolled around a support to allow it to be held in the vessel, whereas the 18 m membrane tubing used for mass transfer tests was loosely arranged.

In these mass transfer tests, pH was controlled at 14 in the stripping solution, so undissociated phenol concentration in the stripping solution was nearly zero, and it can be assumed that phenol dissociates in the stripping solution as soon as it reaches the membrane–stripping solution interface. Therefore, the stripping solution film resistance can be assumed negligible. The film resistance in the wastewater side was investigated with phenol and 2,4-dichlorophenol. Fig. 12 shows the effect of Reynolds number in the wastewater on the OMTCs of phenol and 2,4-dichlorophenol. It can be seen that the changes in flowrate on the tube side had little effect on the OMTCs in the range studied, and so we conclude that the membrane resistance dominated the fluxes of phenols through the membrane. This high membrane resistance for phenols is mainly due to the fact that hydrophilic phenols have relatively low partition coefficients between the hydrophobic silicone rubber membrane and aqueous solution.

Assuming that liquid film resistances on both sides of the membrane are negligible, Eq. (3) has been

Table 3  
Overall mass transfer coefficients and permeabilities of phenols at  $50^\circ\text{C}$

Compound	$k_{ov} \times 10^7$ (m s <sup>-1</sup> )	$D_{mem}K \times 10^{10}$ (m <sup>2</sup> s <sup>-1</sup> )	$K$	$D_{mem} \times 10^{10}$ (m <sup>2</sup> s <sup>-1</sup> )
Phenol	3.10	1.34	0.25	5.36
4-Chlorophenol	9.30	4.02	1.79	2.25
2,4-Dichlorophenol	14.70	6.35	6.40	0.99
4-Nitrophenol	0.48	0.21	0.13	1.62
<i>p</i> -Cresol	7.04	3.04	1.25	2.43
Hydroquinone	2.37	1.02	0.11	9.27

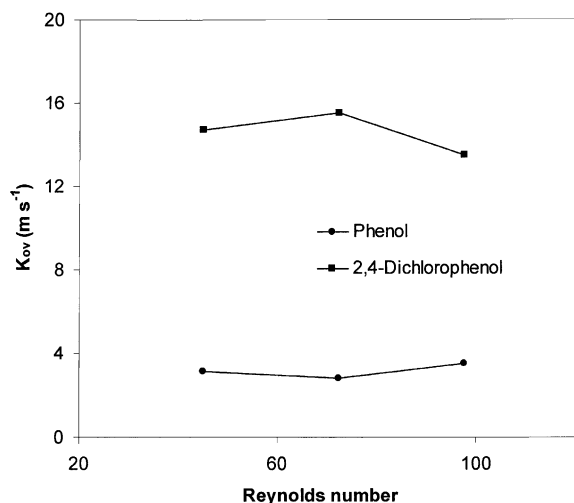


Fig. 12. Effect of tube side Reynolds number on the overall mass transfer coefficient: membrane tube of 3.0 mm i.d.  $\times$  0.5 mm wall.

used to calculate the permeabilities shown in Table 3. It can be seen that permeability decreases in the order 2,4-dichlorophenol > 4-chlorophenol > *p*-cresol > phenol > hydroquinone > 4-nitrophenol, which means that 2,4-dichlorophenol could be most economically recovered from a wastewater using the MARS process, while 4-nitrophenol would be more challenging.

The comparison of permeabilities of phenols in Table 3 with their corresponding solubilities in Table 1 indicates that there is an approximate relationship between permeabilities of phenols and their solubilities in water, i.e. the higher the solubility in water, the lower the permeability in the membrane. Solubility in water reflects the partition coefficient between water and the membrane. Since the permeability in the membrane is the product of the partition coefficient and the diffusion coefficient of the compound, for hydrophobic membranes such as silicone rubber materials higher permeabilities are usually obtained for the compound with a lower solubility in water. Therefore, it is interesting to quantitatively study partition coefficients and diffusion coefficients of phenols.

The procedure described by Brookes and Livingston [20] was used to obtain the partition coefficients also shown in Table 3 at 50°C. Comparing the solubilities in water in Table 1 and partition coefficients of

phenols in Table 3, it is clear that compounds with higher solubilities in water have lower membrane-aqueous partition coefficients. Taking solubility parameters of 36.6 (MPa)<sup>1/2</sup> for water [20] and 15.7 (MPa)<sup>1/2</sup> for silicone rubber membrane [23], we used the model proposed by Brookes and Livingston [20] to predict partition coefficients of the phenols from this study. Unfortunately, the predicted values are lower than our experimental data by two or three orders of magnitude. This may be because of the limitations of the Hildebrand and Scatchard equation which have been highlighted by Barton [24]; also the data of Brookes and Livingston was all collected at 30°C and was used to obtain their correlation; perhaps the effect of temperature is less significant than the model suggests.

From the permeability data and partition coefficients of phenol in Table 3, the diffusion coefficients of phenols were calculated, also shown in Table 3. Fig. 13 shows the relationship of diffusion coefficients with molar volumes for phenols involved in this study. It can be seen that the diffusion coefficient decreases with increasing molar volume, consistent with the result obtained by Harogoppad and Aminabhavi [25].

The diffusion-retention ( $D-k$ ) model proposed by LaPack et al. [23] was used to predict diffusion coefficients of phenols at 50°C, since the membrane used by LaPack et al. [23], which is composed of 69 wt.% of poly(dimethylsiloxane) and 31 wt.% fumed silica, has the almost same compositions as ours. However, almost all the predicted values are lower than our experimental data by an order of magnitude. These

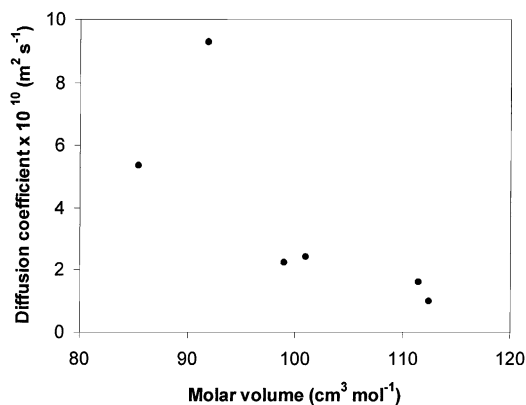


Fig. 13. The relationship of diffusion coefficients and molar volumes for phenols involved.

deviations may be due to the fact the adjustable parameters in the  $D$ - $k$  model were determined by fitting the model to the limited experimental data of LaPack et al. [23]. Moreover, although the effect of temperature was included in their model, all their experimental data was obtained at 25°C. We suspect that the effect of temperature is more important than is suggested by LaPack et al. [23] and this is why there is such a large deviation.

#### 4.7. The effect of temperature on OMTCs

According to the molecular models for rubbery polymers above their glass transition temperatures, the temperature dependence of the permeability of the penetrant through polymers follows the well known van't Hoff–Arrhenius relationship:

$$P = P_0 \exp\left(\frac{-E_p}{RT}\right) \quad (9)$$

where  $P_0$  is a pre-exponential factor,  $R$  the molar gas constant,  $T$  the absolute temperature and  $E_p$  is the apparent activation energy of permeation required for the sorption of the penetrant into polymers and the opening between polymer chains large enough to allow the penetrant to diffuse. Higher  $E_p$  suggests that more energy is needed for the penetrant to permeate through polymers. It can also be seen from Eq. (9) that for a given polymer and a penetrant,  $P$  increases with the increasing temperature. This is mainly due to the fact that the increasing temperature enhances the mobility of polymer chains for the penetrant to more easily diffuse.

Fig. 14 shows a plot of  $\log P$  versus  $1/T$ . The values of  $E_p$  obtained were 17 and 24 kJ mol<sup>-1</sup> for phenol and 2,4-dichlorophenol, respectively. The correlation coefficient values in the estimation of  $E_p$  are more than 0.99. We conclude that the permeabilities of phenols at different temperatures can be accurately predicted from Eq. (9) when  $P_0$  and  $E_p$  are known.

Although only two phenols were tested in the experiments, it can be seen that  $E_p$  increases with the increasing molecular size of phenols. This suggests that the larger molecules require more energy to pass through the polymer matrix, consistent with previous work [26].

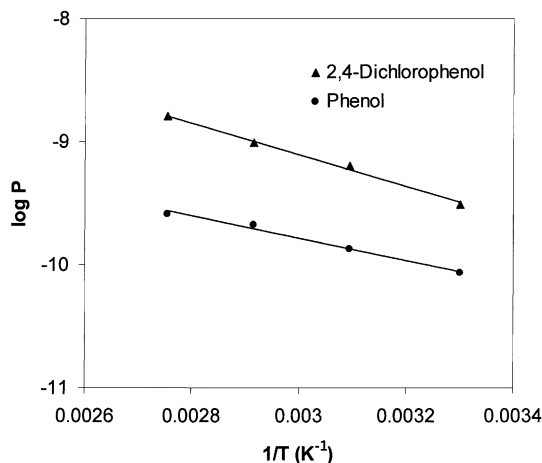


Fig. 14. van't Hoff–Arrhenius plots of  $\log P$  vs.  $1/T$  for phenol and 2,4-dichlorophenol.

## 5. Conclusions

The MARS process has been proved to achieve effective phenol removal and recovery. The recovery efficiency of phenol in the MARS process is over 94% and the phenol purity is 86.5 wt.%. The following main conclusions can be drawn:

- The pH in the stripping vessel is an important parameter controlling the mass transfer rate through the membrane. The undissociated phenol concentration in the stripping solution increases with decreasing pH, so that the driving force for mass transport through the membrane decreases. To overcome this problem, pH greater than 12 is preferred in the MARS process.
- The concentration of NaOH solution added into the stripping vessel affects the recovery efficiency of phenol in the MARS process. The undissociated phenol concentration increases with increase in the NaOH concentration, resulting in the reduction of the mass transfer rate through the membrane. On the other hand, the use of a solution with a low NaOH concentration creates the large volume of the solution collected from the stripping solution to be recovered, causing the re-treatment of a large amount of aqueous solution after two-phase separation. Moreover, the “salting-out” effect is weak with a low NaOH concentration, so that a higher

phenol concentration will be held in the saline aqueous underlayer after phase separation.

- At steady-state, the total phenol concentration can be much higher in the stripping solution than in the wastewater by two or three orders of magnitude, ensuring the high recovery efficiency of phenol.
- Oxidation of phenol can be prevented by the introduction of nitrogen gas to remove oxygen from the stripping vessel and keep covering the free space during the period of the experimental running.
- The permeabilities of phenols through the membrane can be improved by increasing the temperature in the stripping vessel. The van't Hoff–Arrhenius relationship gave excellent fittings to our experimental data.
- Membrane resistance dominates the overall mass transfer coefficient of phenols in our experimental system, since hydrophilic phenols have low partition coefficients between the hydrophobic silicone rubber membrane and aqueous solution.
- In the MARS process, the membrane is a key factor for the separation of organics from wastewaters, and alternative membranes necessarily need to be investigated to improve the mass transfer flux — nevertheless, we are encouraged by these initial results.
- The use of acid–base equilibria as a driving force removes the limitation on comparable membrane separations such as pervaporation, which requires a good volatility to be viable.
- This new process has shown promise for industrial application since it can achieve a high recovery efficiency, and its continuous operation is simple and stable due to the use of nonporous membranes. A range of phenolic compounds can be recovered as well as phenol, which is intermediate in difficulty relative to dichlorophenol (easy to recover) and nitrophenol (more difficult due to low mass transfer coefficient).

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