



## Studies on the extraction of phenol in wastewater

Hong Jiang<sup>1</sup>, Ying Fang<sup>2</sup>, Yao Fu<sup>2</sup>, Qing-Xiang Guo\*

*Department of Chemistry, University of Science and Technology of China,  
96 Jinzhai Road, Hefei 230026, China*

Received 16 August 2002; received in revised form 27 May 2003; accepted 29 May 2003

---

### Abstract

A novel extraction procedure has been developed for treating phenolic wastewater. Alcohols, amines, and organic acids were applied as extractants in separation of phenol from the wastewater containing 6000 mg/l phenol and 5% salts discharged by chemical plants, >99% phenol was recovered by extracting with octanol. The interactions of phenol with alcohols, amines, and organic acids were studied by a theoretical calculation with GAUSSIAN 98. The extraction efficiency is strongly dependent on the intermolecular interactions between the phenol and extractants. Based on the experimental and theoretical studies, a pilot-scale LLES was set-up and worked well. © 2003 Elsevier B.V. All rights reserved.

*Keywords:* Phenol; Extraction; Wastewater; Theoretical calculation; Recycle

---

### 1. Introduction

Phenol is a common pollutant discharged by polymeric resin production, chemical industries, oil refineries and coking plants. Phenol is lethal to fish at low concentrations (5–25 mg/l) and brings objectionable tastes to drinking water at about 0.5 mg/l. Phenol was listed as a priority pollutant by the US Environmental Protection Agency (EPA). The European Union (EU) also regards several phenols as priority pollutants and the 80/778/EC directive regulates total phenols in drinking water to <0.0005 mg/l [1].

Phenolic wastewaters are usually treated by biodegradation, thermal decomposition and absorption. Under aerobic or anaerobic conditions, phenols can be degraded to harmless compounds by microorganisms. Some aerobic bacteria and fungi utilize phenols as a source

---

\* Corresponding author. Tel.: +86-551-3607466; fax: +86-551-3606689.

*E-mail addresses:* jhong@ustc.edu.cn (H. Jiang), fangying@mail.ustc.edu.cn (Y. Fang), fangying@mail.ustc.edu.cn (Y. Fu), qxguo@ustc.edu.cn (Q.-X. Guo).

<sup>1</sup> Tel.: +86-551-3607482; fax: +86-551-3606689.

<sup>2</sup> Tel.: +86-551-3606640; fax: +86-551-3606689.

of carbon and energy, and degrade it [2]. However, the major disadvantage of biological treatment is that the microorganisms cannot survive in high concentrations of phenol, e.g. more than 3000 mg/l. Inhibition of microorganisms by high concentrations of phenol has been reported by many researchers [3,4]. The microorganisms are also difficult to survive in the wastewater containing 5% salt. Most kinds of phenolic wastewater discharged by chemical plants contain high concentrations of phenol and salts. Furthermore, long time is needed usually for degrading the phenol, e.g. more than 7 days.

Thermal decomposition can be used to treat wastewater with concentrations of phenol as high as 15,000 mg/l, but it is only used in small scale for the high energy demand. Wet air oxidation, a typical thermal decomposition method, is usually operated at temperatures ranging from 200 to 330 °C and pressures ranging from 2–20 MPa [5–8]. In order to keep the severely reactive conditions, a lot of energy should be supplied. Hence, thermal treatment is not an economical effective means to phenol degradation. Furthermore, some salts and acids, such as chloric ion dissolved in effluents can erode steel tanks severely, that is difficult for material selection.

Absorption is an effective method of treating dilute phenolic wastewater. However, for the relatively high cost of activated carbon or other sorbents, adsorption cannot be used to treat high concentrated phenolic wastewater [9–13].

Liquid–liquid extraction system (LLES) has advantages on treating high concentrated phenol (over 3000 mg/l) wastewater. Herein, we report a novel method to treat wastewater containing about 6000 mg/l phenol and 5% salt. In pilot-scale LLES, 99% of phenol in the wastewater was effectively recovered.

## 2. Principles and materials

### 2.1. Principles

LLES can be used for phenol separation. The main principles for phenol extraction are following:

- (1) Phenol has different solubility in extractants and water, so we can select some extractants in which the solubility of phenol is much higher than that in water in order to separate the phenol from wastewater. Herein, for a wastewater (W) and an extractant (R), a competing equilibrium of phenol concentration exists between phase W and phase R after being mixed and separated completely (Eq. (1) and Fig. 1).

$$Ph_W \rightleftharpoons Ph_R \quad (1)$$

where  $Ph_W$  is the phenol concentration in wastewater and  $Ph_R$  the phenol concentration in extractant.

The phenol concentrations  $Ph_w$  and  $Ph_R$  will become unchanged at the equilibrium. Distribution ratio is defined as the phenol concentration in wastewater to that in extractant, as shown in Eq. (2).

$$D_r = \frac{Ph_R}{Ph_W} \quad (2)$$

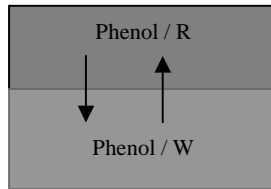


Fig. 1. Schematic of liquid–liquid extraction.

So, the key to promote the extraction efficiency is to enhance the distribution ratio ( $D_r$ ) [14].  $D_r$  is determined by intrinsic characters of extractants and wastewater which is not able to be changed. However, some suitable extractants with high value of  $D_r$  are able to be found by means of analysis of solubility data of extractants in water.

- (2) Extractants and water can form complexes by hydrogen bond between them or by other kinds of intermolecular interactions. The hydrogen bond may have a main effect on the  $D_r$ . In this work, the calculations of hydrogen bonding were performed using GAUSSIAN 98 software.
- (3) Although extractive conditions such as stirred intensity and separated factor cannot change the  $D_r$  of extractants, the recovery efficiency of phenol from wastewater are effected directly by them. In order to accelerate the process of mass transfer between extractant and wastewater, a beater is needed to mix two liquid phases. The stirred intensity is important to mass transfer. Lower stirred intensity makes mass transfer between two phases slowly which increased the cost of wastewater treatment, and high stirred intensity makes them emulsified which make the following separation difficult. So, optimal stirred speed and length of oars should be determined at first in the experiment.

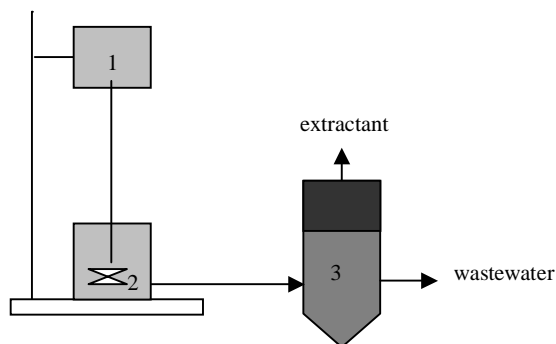
When the extractant and wastewater are mixed sufficiently, the extractant containing high concentrations of phenol was separated from wastewater containing low concentrations of phenol. Separation by eccentricity is more effective than by gravity only. The separated factor is defined as the ratio of eccentricity to gravity which is shown as following in Eq. (3).

$$S_f = \frac{F}{G} \quad (3)$$

where  $S_f$ ,  $F$  and  $G$  stand for separated factor, eccentricity and gravity, respectively. High value of  $S_f$  is benefit to separation of extractant from wastewater, but it is not notable when  $S_f$  is big enough.

## 2.2. Materials

- (1) Extraction experiments were performed with a dc digital display stepless speed regulating beater (SXJQ-1, Zhengzhou Great Wall Scientific, Industrial and Trading Co. Ltd.) and a centrifugal extraction machine (Beijing Centrifugal Machine Co. Ltd.). The lab scale LLES was shown in Fig. 2.



1. digital display 2. oar of beater 3. centrifugal machine

Fig. 2. A lab-scale LLES.

- (2) Absorption spectra were measured with a UV-Vis spectrophotometer (Shanghai Analysis Instrument Co. Ltd.).
- (3) Chemical oxygen demand with potassium dichromate oxidation ( $\text{COD}_{\text{Cr}}$ ) was determined with  $\text{COD}_{\text{Cr}}$  analyzer (Spectralab Company, USA).

#### 2.2.1. Determination of phenol index

The 4-aminoantipyrene spectrometric method was used to measure phenol concentration after distillation. In alkali solution, phenol interacts with 4-aminoantipyrene and ferricyanide to produce red 4-aminoantipyrene dye. A spectrophotometer at wavelength of 460 nm was used to determine phenol concentration.

#### 2.2.2. Determination of $\text{COD}_{\text{Cr}}$

The potassium dichromate oxidation method (EPA410.4) was used. The sample must be chloride ion free using this method to determine the  $\text{COD}_{\text{Cr}}$ , since chloride ion influence the determination of  $\text{COD}_{\text{Cr}}$ . The sample including 5% salts was prepared by adding  $\text{HgSO}_4$  to the wastewater in which the mass ratio of  $\text{HgSO}_4$  to  $\text{Cl}^-$  is about 2, or by adding equal molar  $\text{AgNO}_3$  to the sample in order to separate the  $\text{Cl}^-$  from the wastewater.

### 3. Results and discussion

#### 3.1. Experimental separation

A phenolic wastewater discharged from a chemical plant located in southern China was used in this study. The wastewater contained 6000 mg/l phenol, 5% sodium chloride, and had a  $\text{COD}_{\text{Cr}}$  of 18,200 mg/l. The phenolic wastewater and extractant were mixed by the beater (Fig. 2). Under the conditions of 1 atm, ambient temperature, pH 3.0 and  $S_f = 700$ , experiments were carried out using  $\text{C}_8\text{H}_{17}\text{OH}$  as extractant to determine the suitable rotary

Table 1  
The concentration of phenol in different rotary speeds and diameters of oar at  $S_f = 700$

Diameter of oar $d$ (cm)	Rotary speed $n$ (rpm)									
	100	200	400	800	900	1000	1200	1300	1400	1500
	Phenol concentration (mg/l)									
2	5248	4815	4097	2409	1813	1220	654	410	320	1460
3	4482	3687	2542	1227	670	384	330	1287	1356	1279
4	4128	2875	1453	784	720	1572	1839	1920	1727	1743

speed ( $N$ ) and diameter ( $d$ ) of oar. Results were listed in Table 1 and shown in Fig. 3. From Fig. 3,  $d = 2$  cm, in the ranges of 0–1200 rotates per minute (rpm), the concentration of phenol in water phase was in inverse proportion with the rotary speed, but when rotary speed is more than 1400 rpm, wastewater and extractant were not separated completely because of the emulsification. When  $d = 3$  and 4 cm, the optimal rotary speed were about 1200 and 900 rpm, respectively. In later experiments, the wastewater and extractant were mixed by an oar at 1300 rpm and  $d = 2$  cm considering the cost of energy.

Separated factor ( $S_f$ ) had an important influence on extractive efficiency. Theoretically, higher  $S_f$  was advantageous on separation of two phases. Table 2 and Fig. 4 showed this trend. The data were obtained under the conditions of  $d = 2$  cm and  $n = 1300$ . Extractant and wastewater were separated almost completely when  $S_f = 750$ .

The target of this work was not only to find the extractive conditions, but also to find better extractants for phenol recovery. So, a series of experiments were performed under the same conditions with different extractants, such as alcohols, amines and acids. Their

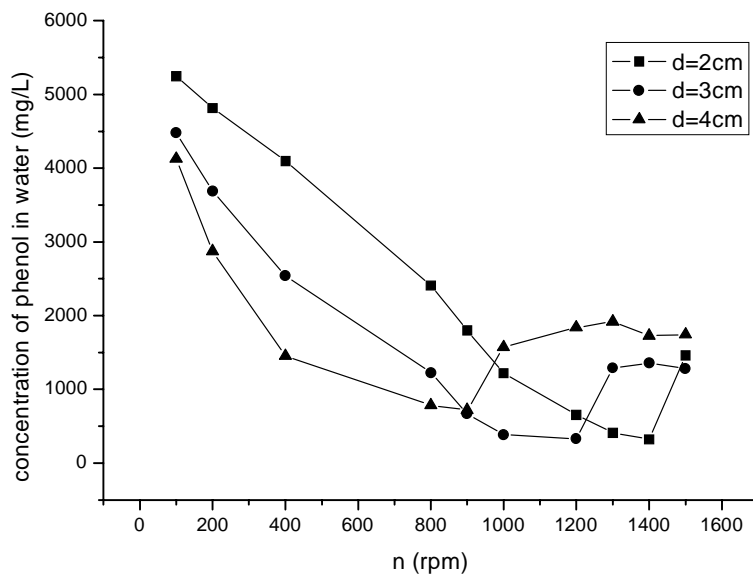


Fig. 3. The concentration of phenol in wastewater after extraction with different rotary speed and diameters of oar.

Table 2  
The concentration of phenol in wastewater after separation with different  $S_f$

$S_f$	Concentration of phenol (mg/l)
400	2472
500	565
600	157
750	93
900	91
1200	90

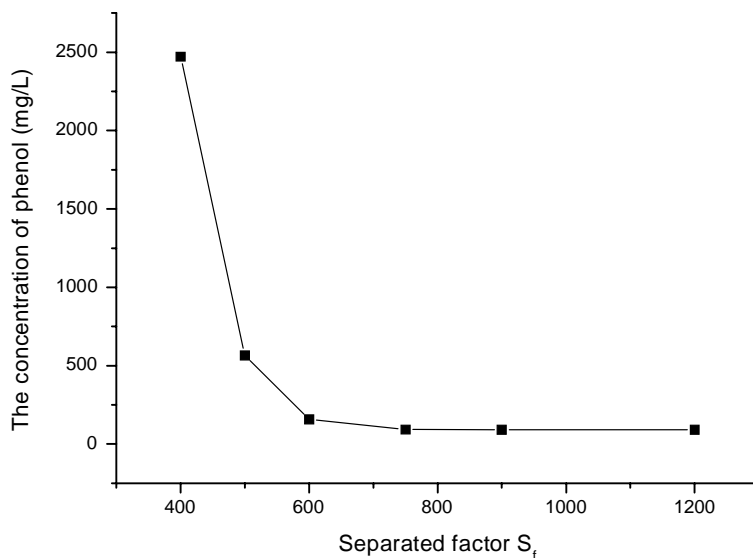


Fig. 4. The concentration of phenol in wastewater after separation with different  $S_f$ .

extractive efficiencies were compared. The extractive and separated times were 3 min and 2 h, respectively, so that the mass transfer and phases separation were complete. The bulk ratio of wastewater and extractant was 1:3. The equilibrium 1 was reached under these conditions. The experimental results are shown in Tables 3–5.

Table 3  
Extraction efficiency for phenol using different amines ( $RNH_2$ )

R	Phenol (%)	COD
$C_9H_{19}$	73.5	69.4
$C_{10}H_{21}$	74.8	72.6
$C_{11}H_{23}$	78.3	76.4
$C_{12}H_{25}$	82.5	81.4
$C_{13}H_{27}$	88.0	87.8
$C_{14}H_{29}$	92.4	92.3

Table 4  
Extraction efficiency for phenol using different acids (RCOOH)

R	Phenol (%)	COD
C <sub>4</sub> H <sub>9</sub>	48.2	44.8
C <sub>5</sub> H <sub>11</sub>	45.2	44.1
C <sub>6</sub> H <sub>11</sub>	44.7	42.3
C <sub>7</sub> H <sub>15</sub>	43.9	43.5
C <sub>8</sub> H <sub>17</sub>	44.0	42.5
C <sub>10</sub> H <sub>21</sub>	43.4	42

From Table 3 it can be seen that the extractive efficiency using alcohols with longer hydrocarbon chains is higher than those with shorter ones. The extractive efficiency of amines has the same trend as alcohols (Table 4). Contrary to the results of alcohols and amines, the extractive efficiency of acids with shorter hydrocarbon chains is higher than that with longer ones (Table 5). Alcohols are more effective for phenol extraction than amines and acids from Fig. 5.

COD<sub>Cr</sub> value can denote the concentration of organic pollutant in wastewater. The original wastewater contains no other organic pollutants except for phenol, so the removal efficiency of COD<sub>Cr</sub> should be same as the extractive efficiency of phenol if no other organic compounds were added to this system. Tables 3–5 show that the former is less than the latter, for some extractants can be dissolved in wastewater and thereby the value of COD<sub>Cr</sub> value increased.

### 3.2. Theoretical calculations

In order to interpret the experimental results, the interaction energies between phenol and RNH<sub>2</sub>, ROH, and RCOOH were calculated with GAUSSIAN 98 (Gaussian, Inc. USA), a commercial software. The monomer H<sub>2</sub>O was studied with B3LYP/3–21g//B3LYP/6–31g\* method. The complexes and monomers RNH<sub>2</sub>, ROH, and RCOOH were optimized with B3LYP/3–21g. After geometry optimization, frequency calculation with the same method was performed to verify that the geometry was an energy minimum. For all the complexes, B3LYP/6–31g\* single-point calculations in water were performed on all the B3LYP/3–21g optimized structures. The solvation effect was taken into account by using the Onsager solvation model 9 [15] based on the self-consistent reaction field method. The results

Table 5  
Extraction efficiency for phenol using different alcohols (ROH)

R	Phenol (%)	COD
C <sub>5</sub> H <sub>11</sub>	75.2	69.3
C <sub>6</sub> H <sub>13</sub>	77.0	72.5
C <sub>7</sub> H <sub>15</sub>	85.3	78.9
C <sub>8</sub> H <sub>17</sub>	93.8	92.5
C <sub>11</sub> H <sub>23</sub>	92.4	91.3
C <sub>12</sub> H <sub>25</sub>	91.4	89.0

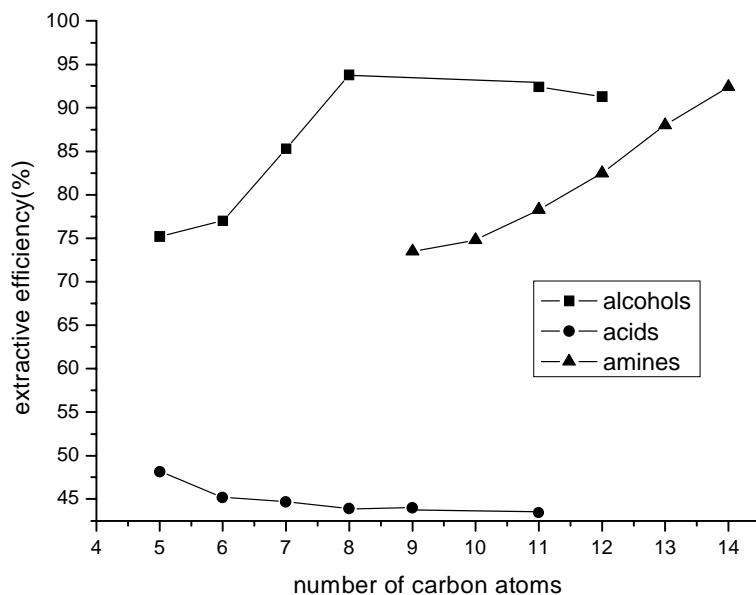


Fig. 5. Extractive efficiency of alcohols, amines and acids with different carbon chains.

were summarized in Tables 6–8 and Fig. 6. Greater interaction energy between phenol and extractant means the stronger hydrogen bonds formed by them and made complex formed by them more stable, so the phenol was easier to be extracted by extractant.

Table 6  
Interaction energies between phenol and RNH<sub>2</sub>

R	RNH <sub>2</sub> (kJ/mol)
C <sub>9</sub> H <sub>19</sub>	16.4
C <sub>10</sub> H <sub>21</sub>	16.5
C <sub>11</sub> H <sub>23</sub>	18.9
C <sub>12</sub> H <sub>25</sub>	19.2
C <sub>13</sub> H <sub>27</sub>	20.4
C <sub>14</sub> H <sub>29</sub>	21.3

Table 7  
Interaction energies between phenol and RCOOH

R	RCOOH (kJ/mol)
C <sub>6</sub> H <sub>13</sub>	19.9
C <sub>7</sub> H <sub>15</sub>	20.4
C <sub>8</sub> H <sub>17</sub>	23.4
C <sub>9</sub> H <sub>19</sub>	22.0
C <sub>10</sub> H <sub>21</sub>	23.0



Table 8  
Interaction energies between phenol and ROH

R	ROH (kJ/mol)
CH <sub>3</sub>	40.0
CH <sub>3</sub> CH	38.5
C <sub>3</sub> H <sub>7</sub>	36.9
C <sub>4</sub> H <sub>9</sub>	37.5
C <sub>5</sub> H <sub>11</sub>	38.4
C <sub>6</sub> H <sub>13</sub>	38.0
C <sub>7</sub> H <sub>15</sub>	36.5
C <sub>8</sub> H <sub>17</sub>	37.4
C <sub>9</sub> H <sub>19</sub>	36.2
C <sub>10</sub> H <sub>21</sub>	36.9
C <sub>11</sub> H <sub>23</sub>	35.8
C <sub>12</sub> H <sub>25</sub>	36.2
C <sub>13</sub> H <sub>17</sub>	36.4
C <sub>14</sub> H <sub>29</sub>	36.0

The calculation results of interaction energies between phenol and RNH<sub>2</sub> (Table 6), and RCOOH (Table 7) indicated that as the increasing of carbon chains of amines and acids, the interaction energies were increasing slightly. The phenol was extracted easily by amines and acids with longer hydrocarbon chains than that with shorter ones. The contrary conclusion was obtained about the extraction efficiency of alcohols (Table 8) with different length

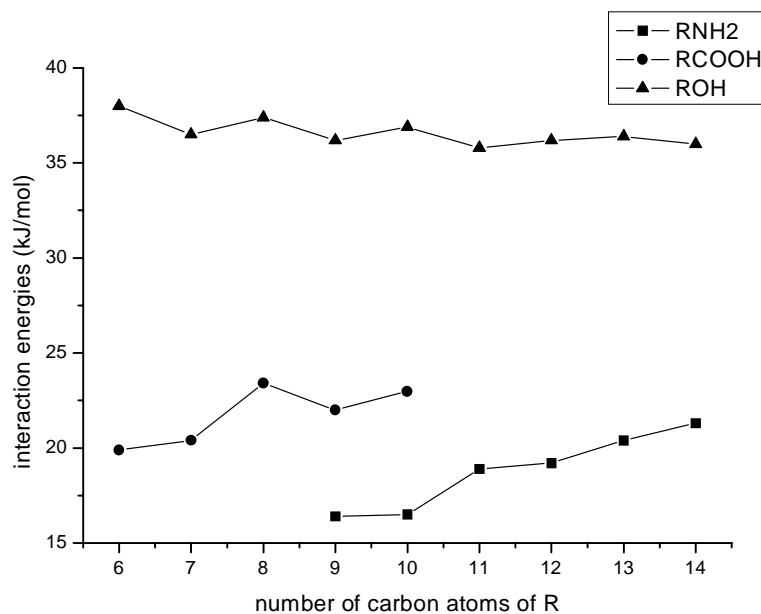


Fig. 6. Interaction energies between phenol and different RNH<sub>2</sub>, RCOOH, and ROH.

of hydrocarbon chains. Alcohols with shorter hydrocarbon chains (e.g. octanol) had better extraction efficiencies than those with longer ones. The interaction energies calculated are in good agreement with extraction efficiencies experimentally shown in Tables 3–5. Alcohols with <8 carbon atoms had greater solubilities in water, so the extraction efficiencies were lower than that of octanol. From Fig. 5, alcohols had better extraction efficiencies than amines and acids. Octanol can be used as extractant for small solubility (0.54 g/l water, 20 °C) and high extraction efficiency.

### 3.3. Pilot-scale LLES

After lab-scale experiment, a pilot-scale extractor was designed based on the lab-scale experimental results. The mixture and separation of phenolic wastewater and extractant were performed in one machine.

Extraction of phenol from wastewater is a rapid, reagent-saving treatment technique for phenolic wastewater. To find a suitable extractant for phenol and to design a high efficient extraction system are both important. To demonstrate the feasibility of this technique, a pilot-scale system was set-up to extract phenol from phenolic wastewater. Continuous countercurrent flow of wastewater with reagent during the extraction process had high extraction efficiency, short extraction times and low reagent consumption.

The pilot-scale extraction system was set-up based on the lab-scale experiments. With the same conditions as the lab-scale experiment, the results as shown in Table 9 were obtained. Fig. 7 illustrates the schematic diagram of the pilot-scale system. The system was used in several chemical plants successfully in China.

In this system, the phenolic wastewater was extracted by two extractors and the extractant containing high concentrations of phenol was reversibly extracted by alkali in other two extractors, thus the extractive efficiency was higher than that obtained in lab-scale experiment.

Table 9  
Extraction efficiency in the pilot-scale extraction system

	C <sub>8</sub> H <sub>17</sub> OH	C <sub>10</sub> H <sub>21</sub> OH	C <sub>12</sub> H <sub>25</sub> OH	C <sub>6</sub> H <sub>13</sub> NH <sub>2</sub>	C <sub>7</sub> H <sub>15</sub> NH <sub>2</sub>	C <sub>12</sub> H <sub>25</sub> COOH	C <sub>14</sub> H <sub>29</sub> COOH
Original phenol (mg/l)	6000						
Residual phenol (mg/l)	24	46	5	2450	1970	2820	2675
Efficiency	99.6	99.2	99.9	59.9	67.1	53.0	55.6
Original COD (mg/l)	18200						
Residual COD (mg/l)	782	1450	880	8400	7240	8820	8670
Efficiency	95.7	92.0	95.2	53.8	60.2	51.5	52.4

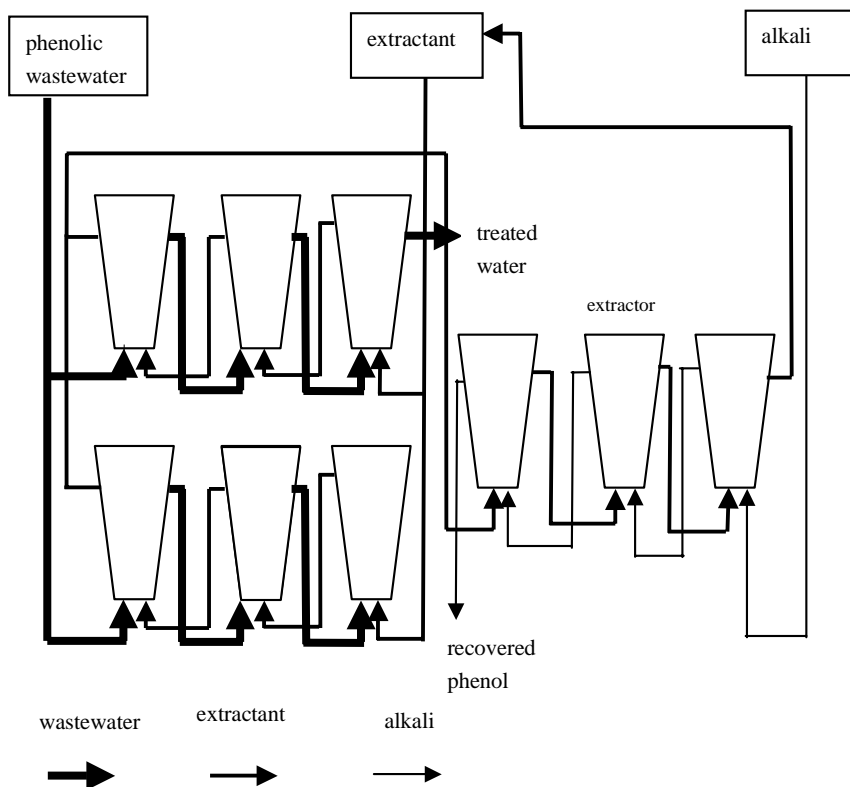


Fig. 7. Flow chart of the pilot-scale LLES.

In such a system, the extractant was used repeatedly, and the phenol was effectively recovered. If the concentration of phenol in wastewater is higher than 3000 mg/l, the extraction system would almost be cost-free. From Table 9, the cost estimation was able to be obtained using  $C_8H_{17}OH$  as extractant.

Phenol recovery per  $m^3$  wastewater =  $(6000-24) \text{ mg/l} = 5.98 \text{ kg} = \$ 3.6$ .

Consumption of extractant per  $m^3$  wastewater =  $0.5 \text{ kg} = \$ 0.25$ .

Operational cost including electricity and labor cost =  $\$ 1.25$ .

Depreciation of equipments =  $\$ 1.5$ .

All above prices were obtained from Chinese market. So, the LLES is cost-effective in phenolic wastewater treatment.

#### 4. Conclusions

Extraction is a means available to reuse the phenol and water by separating phenol and salt from wastewater. In this study, a liquid–liquid extraction system was set-up and the

phenolic wastewater containing approximately 6000 mg/l phenol and 5% salts was treated. By using octanol as extractant, more than 99% phenol was recovered in the system under the optimum experimental conditions. The interaction of phenol with amines, alcohols and acids in water was theoretically calculated with GAUSSIAN 98 software. The theoretical calculated results supplied an interpretation for the experimental results. The extraction efficiency is strongly dependent on the interaction energies between phenol and extractants. A pilot-scale LLES based on the experimental results was set-up to treat the phenolic wastewater for more than 5 years, and phenol was recovered efficiently.

### **Acknowledgements**

This research was supported by the CAS, MOST, NSFC and the University of Science and Technology of China.

### **References**

- [1] G. Hill, C.W. Robinson, *Biotechnol. Bioeng.* 17 (1975) 1599–1615.
- [2] M.M. Broholm, A. Erik, J. Contamin. Hydro. 44 (2000) 239–273.
- [3] T. Godjevargova, Z. Aleksieva, D. Ivanova, N. Shivarova, *Process Biochem.* 33 (1998) 831–835.
- [4] M. Kibret, W. Somitsch, *Water Res.* 34 (2000) 1127–1134.
- [5] A. Fortuny, J. Font, A. Fabregat, *Appl. Catal. Part B: Environ.* 19 (1998) 165–173.
- [6] J.F. Akyurtlu, A. Ahyurtlu, S. Kovenklioglu, *Catal. Today* 40 (1998) 343–352.
- [7] J.L. Yu, E.S. Phillip, *Appl. Catal. Part B: Environ.* 28 (2000) 275–288.
- [8] J.R. Portela, E. Nebot, E.M. Ossa, *Chem. Eng. J.* 81 (2001) 287–299.
- [9] A. Mollah, C.W. Robinson, *Water Res.* 30 (1996) 2901–2907.
- [10] K.A. Halhouli, N.A. Darwish, Y. Al-Jahmany, *Sep. Sci. Technol.* 32 (1997) 3027–3036.
- [11] F.A. Banat, B. Al-Bailey, S. Al-Asheh, O. Hayajneh, *Environ. Pollut.* 107 (2000) 391–398.
- [12] V.M. Hebatpuria, A. Hassan, et al., *J. Hazard. Mater.* 70 (1999) 117–138.
- [13] S. Rengaraj, S.H. Moon, R. Sivabalan, B. Arabindoo, V. Murugesan, *J. Hazard. Mater.* 89 (2002) 185–196.
- [14] Available: <http://ull.chemistry.uakran.edu/chemsep/extraction>.
- [15] M.W. Wong, M.J. Frisch, K.B. Wiberg, *J. Am. Chem. Soc.* 113 (1991) 4776.