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Separation and Recycle of Phenol from Wastewater by Liquid–Liquid Extraction

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ABSTRACT

Laboratory-scale experiments and pilot scale experiments were performed to study the separation and recycle of phenol from wastewater with 200 to 6000 mg/L phenol and 5% salt. Liquid–liquid extraction (LLE) was an efficient means to separate phenol from wastewater. Some commercial extraction reagents, such as N-503, ABK, and QH1, were used to compare the extractive efficiency. The extraction time, mixed intensity, and separated factor were the key factors during the process of extraction and reverse extraction. In this work, the conditions of extraction were studied, and optimum conditions were obtained, except for conditions of pH 3.0, 1 atm, and ambient temperature. Stirred time (t_1) and separated time (t_2) were 3 seconds and 6 seconds, respectively. The optimum mixed Renault's value was in the range of 309,000 to 367,000, and the mass ratio of extraction reagent to wastewater was 1 to 3.

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A pilot-scale extractive system was designed based on the laboratory-scale experiment, which has been working for 5 years in a plant located in China.

Key Words: Phenolic wastewater; Liquid–liquid extraction; Separation and recycle; Extractive machine.

INTRODUCTION

Phenolic wastewaters discharged from some plants, such as chemical industries, oil refining, and resin plants, especially those from phenolic resins, contain high concentrations (10 g/L) of phenolic compounds.[1] Some methods were proposed to treat phenolic wastewater during the past 10 years. Although adsorption,[2–6] biodegradation,[7–12] wet air oxidation (WAO),[13–17] and super critical water oxidation (SCWO)[18] are reported to remove the phenolic compounds effectively from wastewater, some disadvantages exist with these methods.

Adsorption with activated carbon is a widely used means to remove low concentration phenol (<200 mg/L) from wastewater. However, due to the high costs of activated carbon, some cheap adsorbents such as fly ash, bentonite, and paper mill sludge are used to adsorb phenols. They were used to treat wastewater containing low concentrations of phenol because of their low adsorptive capacity.

Biodegradation efficiency depends on the ability of microorganisms to decompose the phenol in aerobic or anaerobic conditions. Generally, microorganisms cannot survive in the conditions of a high concentration of phenol (>1000 mg/L) and salt (5%). It is difficult to remove phenol in high concentrations by biodegradation. Moreover, long biodegradation time (on the order of a few days), a huge establishment, and a mass of activated sludge are disadvantages the method.

WAO and SCWO are efficient means to treat high concentrations of phenolic wastewater, but have limitations. Higher energy demands are needed as they were operated under the conditions of 200 to 300°C, 10 to 30 MPa. High-quality material for equipment and more expensive investment were also necessary for these means. Generally, WAO and SCWO can remove 60 to 70% of phenolic compounds in wastewater, so further treatment is needed to make the wastewater attain a environmentally acceptable standard.

Besides those disadvantages listed, the phenol resource in wastewater cannot be recovered. Liquid–liquid extraction (LLE) can separate the phenol effectively from phenolic wastewater. It can be operated at low cost with large range of concentrations of phenol (>200 mg/L) and high concentrations of salt (5%).

PRINCIPLES AND METHODS

Principles

LLE is used for phase separation widely. For a wastewater (W) and an extraction reagent (R), an equilibrium exists between W and R [eq. (1) and Fig. 1]:

$$ph_W \leftrightarrow ph_R \tag{1}$$

where $\mathrm{ph_W}$ is the phenol concentration in wastewater and $\mathrm{ph_R}$ is the phenol concentration in the extraction reagent.
After being mixed and separated completely, due to the competing equilibrium, the phenol concentration $\mathrm{ph_W}$ and $\mathrm{ph_R}$ will become unchanged. Distribution ratio ($\mathrm{D_r}$) is defined as the phenol concentration in extractive reagent to that in wastewater, as shown in eq. (2).[19]

$$D_r = \frac{ph_R}{ph_W} \tag{2}$$

In the process of extraction, extractive reagents cannot be separated completely as they may be dissolved and emulsified. To a certain extraction reagent, $\mathrm{D_r}$ should be constant. The extraction can be promoted efficiency by shortening the equilibrium time (t), decreasing the emulsification and

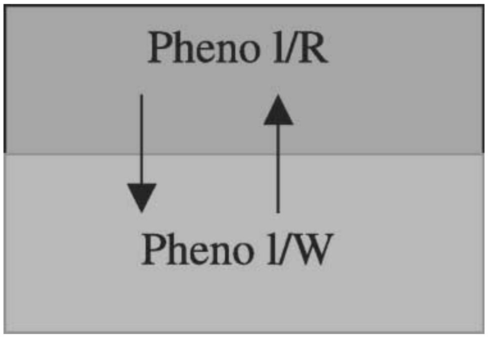

Figure 1. A diagram of the liquid–liquid extraction process.

separating two phases completely. In this study, three kinds of commercial extractive reagents, N-503, ABK, and QH1, were used. Their properties are listed in Table 1.

Methods

The time (t) to reach the competing equilibrium was divided into stirred time (t_1) and separated time (t_2). During t_1, the extractive reagent was shattered into small drops and mixed with phenolic wastewater. The phenol in wastewater was extracted to reagent based on eq. (1) and (2). On one hand, the more violent the agitation was, the smaller the drops were and the bigger the surface area for phenol to contact with reagent, therefore, the faster the phenol transfer from wastewater. On the other hand, too violent agitation emulsified the reagent and made it difficult to be separated from wastewater. In period t_2, the small reagent drops containing a high concentration of phenol were separated by a machine, a high-speed centrifuge. The separation factor (S_f) of the centrifuge is defined as the ratio of centrifugal force (F) to gravitation (G), as shown in eq. (3).

$$S_f = \frac{F}{G} \tag{3}$$

The ratio of extractive reagent to phenolic wastewater was another important parameter influencing the extractive efficiency and the efficiency was also influenced by pH. A laboratory-scale LLE was set up to consider these

Table 1. Properties of extractive reagents.

	N-503	ABK	QH1
Manufacturer	ShangHai Institute of Organic Chemistry	Tsinghua University	University of Science and Technology of China
Chemical formula	$CH_3CON(CH_3CHC_6H_{13})_2$	Unpublished	Unpublished
Solubility (mg/L)	100	300	250
Density (kg/m^3)	820	840	827
Dynamic viscosity (mPa · s)	4	5	9
Boiling point (°C)	202	185	191
Price (2002) ($)	4,800	4,200	3,200

concerns, and an adjustable high-speed QY-165 extractive machine was used to complete this experiment.

Materials

Gas Chromatogram

Prior to and after extraction, the wastewater was analyzed by gas chromatogram (GC/FID) (GC122, Shanghai Analytical Instruments Co. Ltd.). The phenol compound studied was 3-nitrophenol. The calibration graph was made by different concentrations of phenol (10 mg/L, 20 mg/L, 40 mg/L, 60 mg/L, and 100 mg/L). Each of concentrations was repeated 20 times. In all cases, chromatographic conditions were the following: 5:1 split injector; 2 μL were injected directly in the gas chromatograph, injector at 250°C, 85°C/min, 20 to 105°C at 10°C/min, 105 to 290 at 20°C/min; temperature of column is 220°C; and diameter of 3 mm.

QY-165 Extractive Machine

The maximal rotational speed of QY-165 extractive machine (University of Science and Technology of China) is 6500 rotations per minute (rpm). The phases of reagent and wastewater were separated by QY-165 in different separation factors. The separation factor was defined as the ratio of centrifugal force to gravitation, it can be calculated using eq. (4).[20]

$$S_f = \frac{mr\omega^2}{mg} = \frac{r\omega^2}{g} \tag{4}$$

where m denotes the mass of liquid, ω denotes cornual speed of the rotary drum of the extractive machine, g denotes acceleration of gravity, and r denotes the radius of the rotating drum.

The QY-165 extractive machine was designed according to the demands of extractive experiments. Agitation and separation were performed in different parts of the machine. The rotation speed, the stirred intensity, and ratio of reagent to wastewater were adjustable to meet the experiment's needs. The principle of extraction and structure are shown in Fig. 2. The wastewater and extractant met in a mixed chamber, the stirrer made two kinds of liquid mix along with accelerating the mixture into a drum. In the process, the phenol in wastewater was extracted into extractant. The mixture was layered by

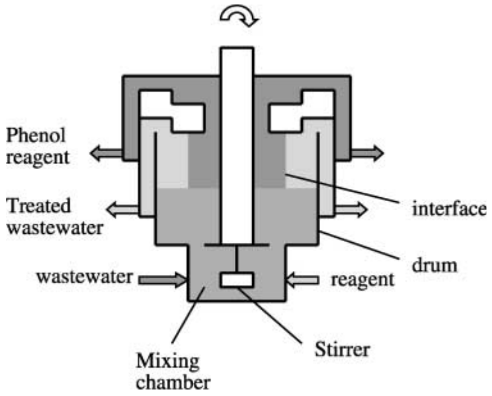

Figure 2. Diagram of extractive principle in extractor.

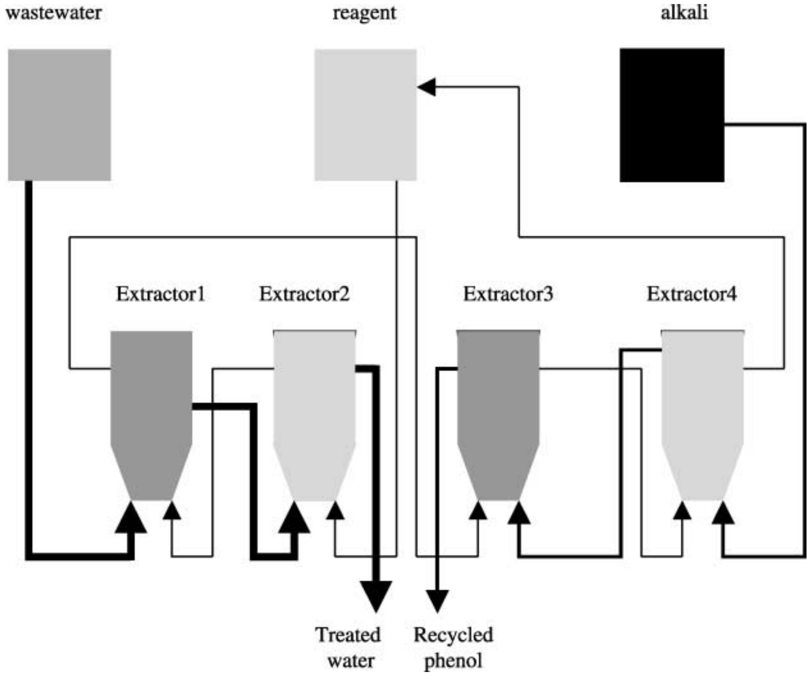

Figure 3. Flowchart of the pilot scale LLE system.

the centrifugal effect; the heavier wastewater and lighter extractant were discharged in different pipes. After the laboratory-scale experiment, a pilot-scale LLE system was set up as shown in Fig. 3. The phenol concentration of 6500 mg/L and 5% salts wastewater was also used in this experiment.

RESULTS

Laboratory-Scale Experiment

The experiments showed that the physical characteristics of wastewater after extraction, such as volume, density viscosity, were almost same as that of before the extraction. The concentration of the remnant phenol in wastewater was in direct ratio with that of reagent in wastewater, so the separation efficiency of the extractive reagent was almost equal to the efficiency of phenol in wastewater. The concentration of extractive reagent in wastewater after extraction was defined as remnant reagent. The results of extraction in different conditions are listed in Table 2 through Table 5.

It is shown in Fig. 4 through Fig. 7 that the remnant reagent in wastewater was decreased with increasing separation time. When t_2 was sufficient for reagent separating, the remnant reagent was no longer decreased, e.g., 8 seconds in Fig. 4, 7 seconds in Fig. 5, and 6 seconds in Fig. 6. In Fig. 7, some reagents were emulsified and dissolved in wastewater and, thus, cannot be separated. The equilibrious concentration of reagent in wastewater was different under different separation factors.

Table 2. Remnant reagent in wastewater with a separation factor 500.

Separated time (secs)	N-503	QY1	ABK
1	8432	8640	8724
2	6230	6745	6562
3	3937	4213	4587
4	2508	2820	3013
6	1519	1377	2522
8	1178	1224	1724
12	1256	1276	1734
16	1233	1367	1732
20	1180	1298	1789

Table 3. Remnant reagent in wastewater under a separation factor 1000.

Time t_2 (secs)	N-503	QY1	ABK
1	5024	5729	5530
2	2927	3747	3230
3	1611	2154	1816
4	972	1682	912
6	455	970	521
8	270	422	257
12	254	439	256
16	257	426	248
20	246	418	282

In this experiment, when $t_2 = 6$ seconds, the liquid drops of extractive reagent were separated completely. According to Newton's law, centrifugal force is equal to the product of the mass of the liquid drops and acceleration, as shown in eq. (5).

$$F = mr\omega^2 - F_r = ma \tag{5}$$

Where a denotes acceleration of a liquid drop, r denotes the radius of the extractive machine, ω denotes the cornual rate of the extractive machine,

Table 4. Remnant reagent in wastewater under a separation factor 1500.

	N-503	QY1	ABK
1	4533	5476	5289
2	2429	2632	2972
3	1120	1257	1422
4	623	845	762
6	247	467	385
8	252	482	370
12	257	477	379
16	243	454	365
20	232	485	392

Table 5. Remnant reagent in wastewater under a separation factor 2000.

	N-503	QY1	ABK
1	4754	5322	5150
2	2327	2810	2849
3	1080	1170	1327
4	594	650	692
6	241	471	360
8	234	469	376
12	247	497	382
16	249	502	401
20	247	463	365

and F_r denotes the resistance of the liquid drop in mixed liquid.

$$\frac{ds}{dt} = v_0 + at \tag{6}$$

$$\omega = n \times 2\pi \tag{7}$$

$$a = r\omega^2 = s\omega^2 = s4\pi^2 n^2 \tag{8}$$

$$F_r = \zeta A \cdot \rho u^2 / 2 \tag{9}$$

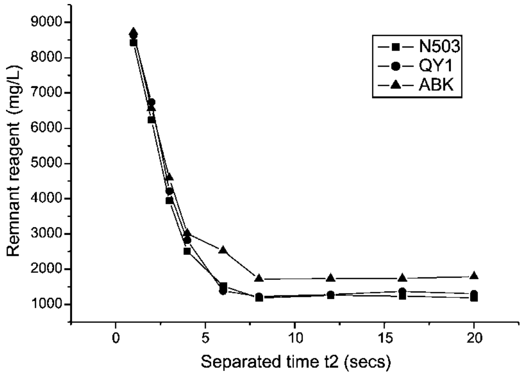

Figure 4. The remnant reagent (mg/L) with separated time t_2 under separation factor 500.

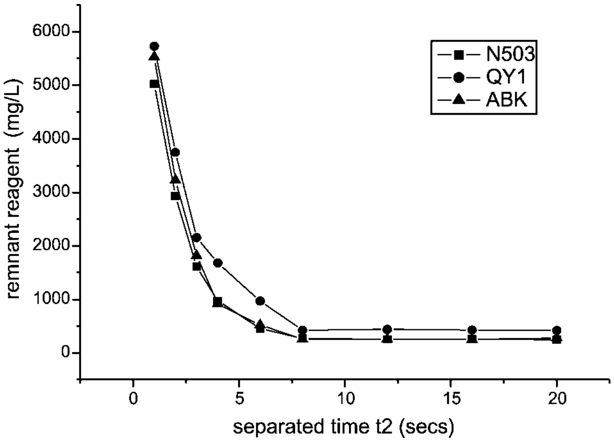

Figure 5. The remnant reagent with separated time t_2 under separation factor 1000.

where ζ denotes coefficient of resistance, A denotes cross-sectional area square of the liquid drop.

F_r was difficult to determine by normal instruments, but it was a positive value, so the minimal t_2 was calculated based on equilibria (6), (7), and (8).

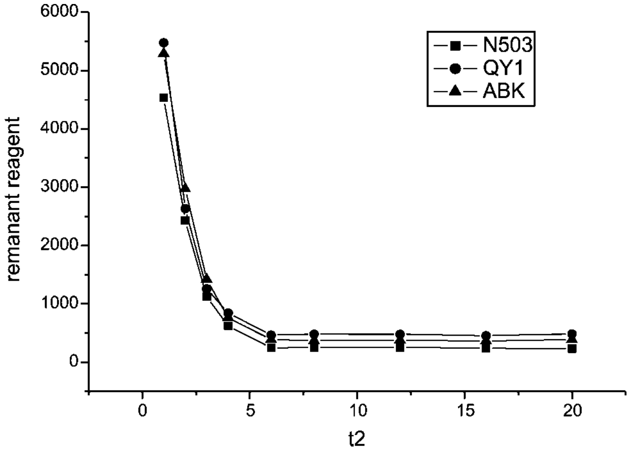

Figure 6. The remnant reagent with separated time t_2 under separation factor 1500.

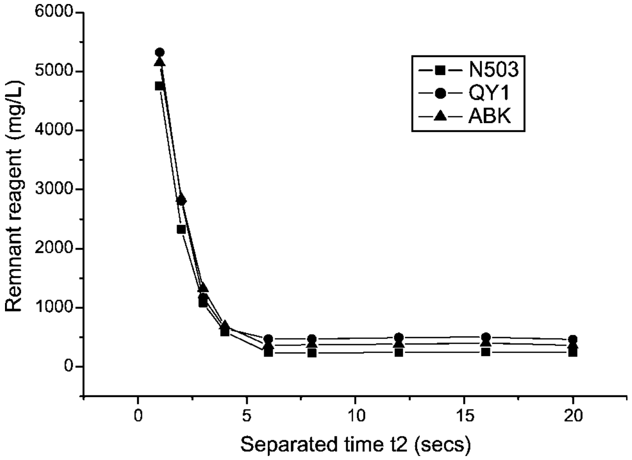

Figure 7. The remnant reagent with separated time t_2 under separation factor 2000.

Experimental time (t_2) must be longer than the $t_{2\min}$, as shown in eq. (10).

$$T_{2\min} = \sqrt{\frac{\ln s - \ln s_0}{4n^2\pi^2}} \tag{10}$$

here in, $s = 82.5\,\text{mm}$, $s_0 = 15\,\text{mm}$, and $T_{2\min} = 0.02$ seconds.

One of most important factors affecting the separation of phenol was the intensity of agitation. The more intensive the agitation, the bigger the interface between reagent and wastewater, the easier the phenol goes into the reagent. However, the emulsification of the reagent decreased the difference of specific gravity between reagent and wastewater. The phenol cannot be separated efficiently. It is shown in Tables 6 through 8 and Figs. 8 to 10.

The Renault's value was defined as following:

$$R_e = \frac{d^2 n\rho}{\mu} \tag{11}$$

where μ denotes viscosity of mixed liquid [calculated by eq. (13)], ρ denotes the density of the mixed liquid [calculated by eq. (14)], d denotes the diameter of the beater, and n denotes rotation speed, as rotations per second (rps).

Table 6. Physical properties of mixed liquid of three kinds of extractive reagent with wastewater.

	N-503	QY1	ABK
ρkg/m^3	955	957	960
μ (mPa·s)	1.75	3	2

Under the separation factor 1500:

$$n = \sqrt{\frac{S_f g}{2\pi^2 d_0}} = 67.2 \ \ \text{(rps)} \tag{12}$$

$$\mu = m_R\% \times \mu_R + m_W\% \times \mu_W \tag{13}$$

$$\rho = m_R\% \times \rho_R + m_W\% \times \rho_W \tag{14}$$

where d_0 denotes the diameter of the rotating drum of QY-165, $d_0 = 165\,\text{mm}$; m_R, m_W denotes the mass of reagent and wastewater, respectively; μ_R, μ_W denotes the dynamical viscosity of reagent and wastewater, respectively; $\mu_W = 1\,\text{mPa s}$; ρ_R, ρ_W denotes the density of reagent and wastewater, respectively; and $\rho_W = 1000\,\text{kg/m}^3$. The experimental results of three kinds

Table 7. Extractive efficiencies of N-503 of five different diameters of stirrer in different stirred time at $t_2 = 6$ seconds.

	Extractive efficiency				
d = m	0.06	0.08	0.10	0.12	0.14
Re × 10^5	1.32	2.35	3.67	5.28	7.19
1	75.2	78.3	82.6	80.4	81.7
1.5	88.0	89.4	91.5	85.9	86.4
2	92.3	93.3	95.3	92.2	86.7
2.5	95.5	95.6	97.2	92.3	84.8
3	96.8	98.2	99.9	95.4	82.3
3.5	96.4	98.7	98.1	92.6	72.3
4	96.6	92.1	95.5	75.0	60.5
4.5	82.1	87.6	90.0	62.1	45.2
5	73.0	81.2	88.6	40.6	35.7
6	51.5	72.4	82.2	38.3	28.5

Table 8. Extractive efficiencies of QY1 of five different diameters of stirrer in different stirred time at $t_2 = 6$ seconds.

	Extractive efficiency				
d = m	0.06	0.08	0.10	0.12	0.14
Re × 10^5	0.772	1.37	2.14	3.09	4.20
1	62.5	76.3	82.5	85.7	79.7
1.5	84.4	78.4	86.9	92.6	80.2
2	88.2	85.5	94.4	97.7	84.4
2.5	92.1	90.3	98.6	99.9	80.3
3	94.5	95.7	97.2	96.3	72.9
3.5	95.7	95.4	93.5	91.1	65.5
4	96.2	92.1	90	83.6	54.4
4.5	88.7	85.6	86	75	52.2
5	82.5	83.3	78.5	70.2	48.4
6	76.6	72.3	70.4	65.1	32.5

of reagents under different conditions are shown in Tables 6 to 9 and Figs. 8 to 10.

From the results shown in Tables 7 and 9, there were good effects for a diameter of 0.10 m. In Table 8, the optimal diameter of beater is 0.12 m.

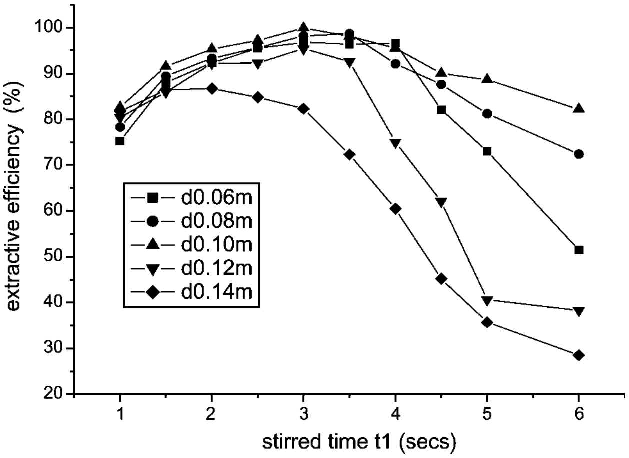

Figure 8. The extractive efficiency of N-503 at different stirred times.

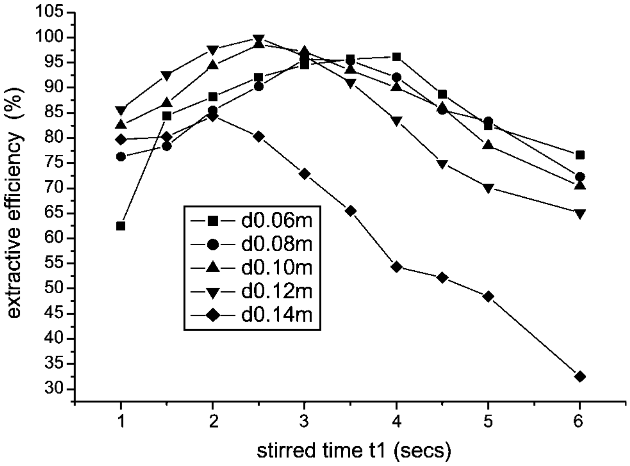

Figure 9. The extractive efficiency of QY1 at different stirred times.

The optimal Renault's value is in the range of 309,000 to 367,000. As the diameter of beater increases, as the Renault's value increased, the efficiency of separation is adversely effected by emulsification.

A pilot-scale countercurrent LLE system, shown in Fig. 3, was used in a plant located in Shanghai, China. From Fig. 3, the original wastewater with

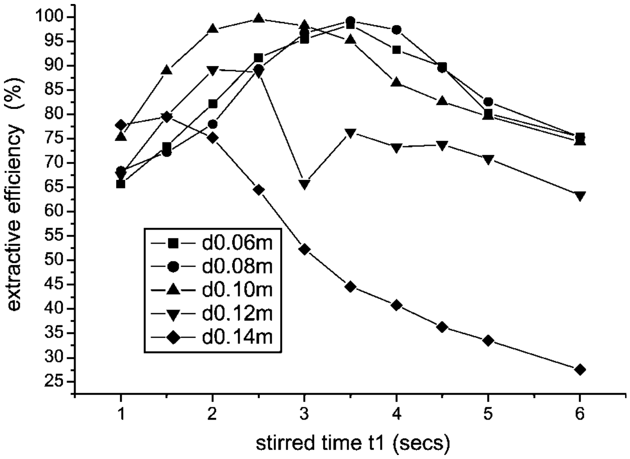

Figure 10. The extractive efficiency of ABK at different stirred times.

Table 9. Extractive efficiencies of ABK of five different diameters of stirrer in different stirred time at $t_2 = 6$ seconds.

	Extractive efficiency				
$Re \times 10^5$	1.16	2.06	3.23	4.65	6.32
d = m	0.06	0.08	0.10	0.12	0.14
1	65.7	68.4	75.3	67.5	77.8
1.5	73.5	72.2	88.9	79.6	79.5
2	82.2	78	97.4	89.2	75.2
2.5	91.7	89.4	99.6	88.7	64.5
3	95.5	96.7	98.2	65.8	52.3
3.5	98.4	99.2	95.2	76.4	44.6
4	93.3	97.4	86.4	73.3	40.8
4.5	89.8	89.5	82.6	73.8	36.3
5	80.2	82.6	79.6	70.9	33.5
6	75.4	75.3	74.4	63.4	27.6

the highest concentration of phenol was poured in extractor 1 and mixed with extractant discharged from extractor 2. The wastewater was mixed with the recycled extractant in extractor 2 to make the treated water discharged from extractor 2, containing a lower concentration of phenol. The extractant discharged from extractor 1, with a higher concentration of phenol, should be heated to 60°C in void of the crystallization of the high concentration of phenol, and then mixed with NaOH in extractor 3 and extractor 4. This was a converse extraction process and a countercurrent technique was also used. The average extracted results are listed in Table 10. More than 99% of the phenol in wastewater was recovered by two stages of extraction with QY1 and two stages of converse extraction with a concentration of 5% NaOH.

Table 10. Average extracted results in pilot-scale LLE system with extractant QY1.

	COD_{Cr} (mg/L)	Phenol (mg/L)	Salt (%)	Chroma (times)	Extractant (mg/L)
Wastewater	17,000	6000	5	80	0
Treated water	500	5–10	5	no	100

DISCUSSION

We found some new results about the pH, ratio, and temperature in our experiments. These are relevant to cost-effective processing of wastewater. In our work, it was found that pH had some effects on separation of phenol from wastewater; pH 2.0 to 3.0 was suitable for the liquid phase extractive system. In this range of pH values, the lower pH value would bring better extractive effect to phenol, but too low a pH value would place strict demands on the extractive equipment, the stainless steel SUS316L used for this LLE system. The ratios of extractive reagent to wastewater were in the range of 1 to 4 for concentration of less than 4000 mg/L phenol, 1 to 3 for 4000 mg/L to 6000 mg/L phenol, and 1 to 2 for more than 6000 mg/L phenol. Concentrations of more than 8000 mg/L phenolic wastewater should be pretreated by acidification and filtration. The change of temperature from 10°C to 50°C had less influence on the effect of separation. The salt concentration was a disadvantage for the material of the equipment. Higher salt concentration of wastewater could rot some kinds of stainless steel, such as SUS304, and made the investment higher.

The main conclusion of this work is that the LLE system had a low operational cost. Some LLE systems have run for 5 years in China. According to the prices of stainless steel and extractive reagent in 2002, the total investment for a chemical factory that discharged 30 tons phenolic wastewater per day was about $70,000. The concentrations of phenol and salt in the wastewater were same as that in our experiment. The operational cost for 1 m^3 wastewater was $2.2, but the recycled phenol was 6 kg (about $4) to the wastewater. The other costs were about $2 for 1 m^3 wastewater. So considering all of the costs, the operational cost could balance with the value of the recycled phenol.

To get a better extractive efficiency, it was important to keep the ratio of extractant to wastewater unchanged, because every extractor machine was designed for a determined range of this ratio. A cheap and effective method was that NaOH, extractant, and wastewater were pumped into a high-sited tank and kept at the static pressure of liquid. No valves were used in the pipes that linked all the extractors.

CONCLUSION

Liquid–liquid extraction was an efficient means to separate phenol from wastewater. Some commercial extraction reagents, such as N-503, ABK, and QH1, were used to compare the extractive efficiency. The extraction time and stirred intensity were the key factors during the process of extraction and reverse extraction. In this work, the conditions of extraction were studied and an optimum condition was obtained, except for a condition of pH 3.0, 1 atm, and ambient temperature. Mixed time (t_1) and separation time (t_2) were 3 seconds and 6 seconds, respectively. The optimum mixed Renault's value was in the range of 309,000 to 367,000, the mass ratio of extraction reagent to wastewater was 1 to 3. Considering all cost and efficiency factors, the QY1 was a better choice for phenolic wastewater extraction.

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