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Efficient removal of naphthalene-2-ol from aqueous solutions by solvent extraction

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ABSTRACT

Naphthalene-2-ol is a typical biologically recalcitrant pollutant in dye wastewater. Solvent extraction of naphthalene-2-ol from aqueous solutions using mixed solvents was investigated. Various extractants and diluents were evaluated, and the effects of volume ratio of extractant to diluent, initial pH, initial concentration of naphthalene-2-ol in aqueous solution, extraction time, temperature, volume ratio of organic phase to aqueous phase (O/A), stirring rate and extraction stages, on extraction efficiency were examined separately. Regeneration and reuse of the spent extractant were also investigated. Results showed that tributyl phosphate (TBP) achieved 98% extraction efficiency for naphthalene-2-ol in a single stage extraction, the highest among the 12 extractants evaluated. Extraction efficiency was optimized when cyclohexane and *n*-octane were used as diluents. The solvent combination of 20% TBP, 20% *n*-octanol and 60% cyclohexane (V/V) obtained the maximum extraction efficiency for naphthalene-2-ol, 99.3%, within 20 min using three cross-current extraction stages under the following extraction conditions: O/A ratio of 1:1, initial pH of 3, 25°C and stirring rate of 150 r/min. Recovery of mixed solvents was achieved by using 15% (W/W) NaOH solution at an O:A ratio of 1:1 and a contact time of 15 min. The mixed solvents achieved an extraction capacity for naphthalene-2-ol stably higher than 90% during five cycles after regeneration.

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Introduction

Phenolic compounds as pollutants have received close attention due to their toxicity and possible bioaccumulation in the environment (Ku and Lee, 2000). Phenolic compounds are a group of chemicals containing one or more aromatic rings bearing one or more hydroxyl groups (Dai and Mumper,

2010), and common phenolic compounds include phenol, cresols, naphthol, dihydric phenols, etc. (Dai et al., 2008).

Phenolic compounds are typical organic components in industrial wastewaters from coal gasification plants, coking plants, oil refineries, and printing and dyeing mills (Wang et al., 2012). Wastewaters containing phenolic compounds can be a threat to public health and the environment when

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released without proper recovery or treatment, and can lead to harmful and lethal effects toward aquatic organisms even at relatively low concentrations of 5 to 25 mg/L (Broholm and Arvin, 2000) as well as objectionable taste in drinking water.

Thus, the discharge of phenolic compounds has been strictly regulated by many governments and organizations. The maximum emission concentration of phenolic compounds in water free from chlorine is 0.1 mg/L, while that in water containing chlorine is 0.001–0.002 mg/L (González-Muñoz et al., 2003). The European Union also lists several phenolic compounds as priority pollutants, and the 80/778/EC directive regulates that the total level of phenolic compounds in drinking water should be below 0.0005 mg/L (Jiang et al., 2003).

Naphthalene-2-ol is a dye intermediate, and is generally present in industrial wastewater. Naphthalene-2-ol, whose toxicity is similar to that of phenol, can strongly irritate human skin and mucus membranes. When entering the human body through percutaneous absorption, naphthalene-2-ol is toxic to blood circulation and the liver, and can also induce cancer and abnormalities (Dai et al., 2008). Unfortunately, few publications on the removal of naphthalene-2-ol from aqueous solutions are available. Therefore, investigations on the treatment of aqueous solutions containing naphthalene-2-ol are needed.

However, naphthalene-2-ol is a naphthalene homolog of phenol, and a number of treatment processes for the phenolic compound removal from aqueous solutions have been reported due to the toxicity and poor biodegradability of phenolic compounds (Bokhove et al., 2012). The treatment processes can be classified as destruction methods and recovery methods according to the final destination of the phenolic compounds. Among the destruction methods, there are biological treatments (Broholm and Arvin, 2000; Pinto et al., 2002), incineration, and wet air oxidation. The recovery methods include liquid–liquid extraction (Palma et al., 2010; Yang et al., 2006), adsorption (Li et al., 2003a; Wang et al., 2014; Zhao et al., 2014), solvent-impregnated resins (Burghoff et al., 2008), ionic exchange with resins, and membrane processes, such as extraction with membranes (Kujawski et al., 2004) or supported liquid membranes (Zidi et al., 2010, 2011).

Among these methods, solvent extraction has received close attention. It has been regarded as a promising, feasible and widely used technique for the concentration, separation and purification of various phenolic compounds from aqueous solutions in terms of its ease of use, high selectivity, high yield, high productivity, and wide-ranging applicability (Wang et al., 2012; Stalikas, 2007).

Many solvents such as organophosphorus solvents, hydrocarbon solvents, and aliphatic amines have been used for the extraction of phenolic compounds (Burghoff et al., 2009; Li et al., 2003b). Organic solvents used in the extraction process can be divided into three major types: conventional oxygen-bearing and hydrocarbon extractants, organophosphorous compounds, and high molecular weight aliphatic amines (Yang et al., 1991). Organophosphorous compounds and aliphatic amines are effective extractants, and provide higher distribution coefficients than those of conventional oxygen-bearing and hydrocarbon extractants (Dai et al., 2008). When other factors including costs and physicochemical properties of extractants are taken into consideration, organophosphorous compounds are usually preferred. In

particular, the chemical stability of organophosphorous compounds plays an important role in process selection (Yang et al., 2006).

Therefore, it was reasonable to hypothesize that solvent extraction using organophosphorous compounds could probably be feasible for naphthalene-2-ol removal from aqueous solutions.

In this study, the extraction of naphthalene-2-ol by organophosphorous solvents was investigated. The main objectives of this work were to examine the feasibility of the removal of naphthalene-2-ol from aqueous solutions by solvent extraction and to evaluate the effects of extractant and diluent type, volume ratio of extractant to diluent, extraction time, initial concentration, temperature, pH, stirring rate, volume ratio of organic phase to aqueous phase (O/A), and extraction stages on the extraction efficiency and distribution coefficient. In addition, the feasibility of back extraction with alkali to regenerate the spent extractant was also assessed. These results could serve as a reference for further investigations and process designs.

1. Materials and methods

1.1. Chemicals and wastewater samples

All the chemicals were of analytical-reagent grade. Tributyl phosphate (TBP), a phosphorus-bonded oxygen donor, is a colorless liquid with the molar mass of 266.32 g/mol and density of 976.6 kg/m³, and was produced by Shanghai Chemical Reagents Co. Ltd. (China) with purity of 98%. Naphthalene-2-ol was from Tianjin Kemiou Chemical Reagent Co. Ltd. (China) with purity of 98%. The main properties of naphthalene-2-ol, including some toxicity data, are shown in Table 1. Dimethyl carbonate (DMC) was purchased from Aladdin Industrial Corporation (China) with purity of 99%. Cyclohexane, *n*-hexane, kerosene, xylene, MIBK, toluene, *n*-butylacetate, benzene, 1,2-dichloroethane, and *n*-octanol were from Shanghai Chemical Reagents Co. Ltd. (China). All of the solvents were washed with distilled water to remove water-soluble impurities. The main properties of the solvents used in this study are shown in Table 2.

In a typical experimental procedure, naphthalene-2-ol was dissolved in ultra-pure water to prepare aqueous solution samples. The initial concentrations of naphthalene-2-ol solutions were all 100 mg/L except as noted. All the aqueous solution samples were prepared before the experiments.

Table 1 – The main properties of naphthalene-2-ol.

Property	Description
Stability	Stable (Combustible. Dust may form explosive mixture with air. Incompatible with strong oxidizing agents, phenol.)
Appearance	White or off-white powder with a slight
Toxicity	ORL-RAT LD ₅₀ 1960 mg/kg, IPR-MUS LD ₅₀ 98 mg/kg
Safety	Warning. Safety glasses, adequate ventilation.
Melting point	120–124°C
Boiling point	285.5 ± 0.0°C at 760 mmHg
Flash point	144.0 ± 10.6°C
Density	1.2 ± 0.1 g/cm ³
Water solubility	1512 mg/L

Table 2 – The main properties of the solvents.

Solvent	Toxicity ORL-RAT LD ₅₀ (mg/kg)	Density (g/cm ³)	Boiling point (°C)	Melting point (°C)	Water solubility at 20°C
Hexane	28700	0.7 ± 0.1	65–70	–95	0.002%
Kerosene	15000	0.9 ± 0.1	150–250	–40	Insoluble
Cyclohexane	12705	0.8 ± 0.1	80–81	4–7	Insoluble
Xylene	4300	0.9 ± 0.1	143–145	–25	0.02%
Benzene	930	0.9 ± 0.1	80	5	0.07%
Butyl acetate	10768	0.9 ± 0.1	126	–78	1%
Toluene	636	0.9 ± 0.1	110.6	–93	Very slightly soluble
1-Octanol	3200	0.8 ± 0.1	193–195	–16	Insoluble
1,2-Dichloroethane	680	1.2 ± 0.1	83	–35	0.9%
MIBK	2080	0.8 ± 0.1	116	–80	2%
DMC	13000	1.0 ± 0.1	90	1	Insoluble
TBP	3000	1.0 ± 0.1	289	–80	0.04%

1.2. Experimental methods

1.2.1. Solvent extraction procedures

All the extraction experiments were conducted with 250 mL conical flasks with covers in a stirred thermostated batch system at desired temperatures. Unless otherwise noted, 50 mL naphthalene-2-ol solution was added to each conical flask, and the pH value was adjusted to the required value. Then the mixed solvents were added to the reaction system according to the volume ratio of 1:1. The value of pH was adjusted by adding NaOH or H₂SO₄ solution, and monitored with a pH meter.

Conical flasks containing the mixture were shaken in a stirred thermostated batch system at a variable stirring rate, and then were left to reach liquid–liquid equilibrium (LLE) in separatory funnels for some time before the two phases were separated. Shaking and settling times were optimized to guarantee that LLE was reached and that the separation of the two phases was achieved.

Then the upper layer (organic phase) was removed, and an aqueous phase sample was taken from the bottom layer for solute concentration analysis. Duplicate experiments were carried out and samples from the aqueous phase were also analyzed in duplicate. The average values are reported in this paper.

1.2.2. Analytical methods

The initial and final solute concentrations in aqueous solution samples were measured by a UV/Visible spectrophotometer (Shimadzu UV2550, Japan) at the maximum absorption wavelength of 295 and 275 nm for naphthalene-1-ol and naphthalene-2-ol, respectively. Solute concentrations in the organic phase were calculated on the basis of material balance. Duplicate experiments were performed to make sure the experimental data were reproducible.

The extraction efficiency and distribution coefficient were used to assess the removal efficiency of naphthalene-2-ol by extraction.

The extraction efficiency (EE, %) for naphthalene-2-ol, which is defined as the ratio of naphthalene-2-ol concentration in the organic phase to the initial concentration in the aqueous phase by assuming ideal mixing, is calculated by Eq. (1),

$$EE = ((C_0 - C_t)/C_0) \times 100\% \quad (1)$$

where, C_0 (mg/L) is initial naphthalene-2-ol concentration, and C_t (mg/L) is final naphthalene-2-ol concentration.

The distribution coefficient (D), which is defined as the ratio of naphthalene-2-ol concentration in the organic phase to the residual concentration in the aqueous phase, is calculated by Eq. (2),

$$D = (C_0 - C_t)/C_t \quad (2)$$

2. Results and discussion

2.1. Screening of extractants and diluents

The performance of an extractant is largely dependent on its distribution coefficient between the organic phase and aqueous phase, and a high distribution efficient is crucial to achieve a high extraction efficiency. Therefore, a very important consideration for selection of an extractant is the distribution coefficient. Moreover, as an industrial extractant, the density and other physical properties are very important, together with its cost. To select proper extractants for naphthalene-2-ol recovery, a set of experiments were carried out under identical conditions with different extractants, including *n*-hexane, kerosene, cyclohexane, xylene, MIBK, toluene, *n*-butyl acetate, benzene, 1,2-dichloroethane, *n*-octanol, DMC and TBP. The experimental results are presented in Fig. 1.

From Fig. 1 it can be seen that TBP achieved the best results in terms of distribution coefficient (59.5) and extraction efficiency (98.35%), and followed by DMC and MIBK. In addition, Table 3 shows that the time to reach equilibrium for TBP was shortest among the selected solvents that had relatively high EE.

TBP is an organic phosphorus compound, consisting of a phosphoryl group which serves as a strong Lewis base due to its high polarity and extraction efficiency (Dai et al., 2008). Beyond that, TBP was selected because of its relatively low water co-extraction (4.67% by weight at 20°C), very low solubility in the aqueous phase (0.04% by weight at 20°C) and low toxicity among the effective extractants in this study. From an economic standpoint, the cost of extraction using TBP was relatively low compared with DMC etc. and the operating conditions of the extraction process using TBP were easy to implement. Taking into account these physico-chemical

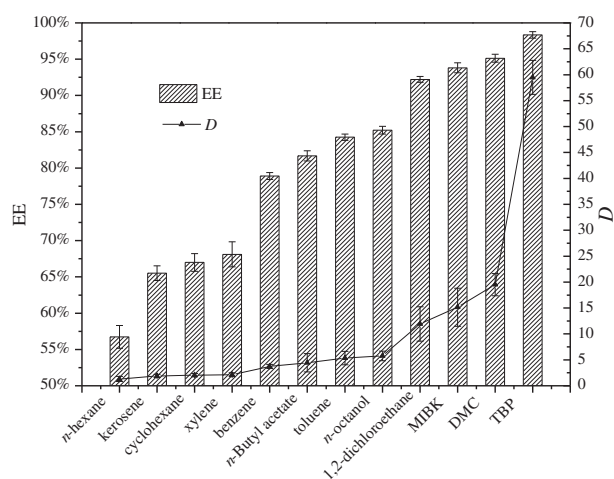


Fig. 1 – The effect of extractant type on the extraction efficiency (EE) and distribution coefficient (D).

properties and cost, TBP was chosen as the extractant in this study. TBP was also chosen as the preferred extractant in other cases (Morales et al., 2003; Zidi et al., 2010; Messikh et al., 2007; Keshav et al., 2009a).

Extractants are generally dissolved in diluents that improve their physical properties such as viscosity, surface tension, etc. (Uslu and Kırbaşlar, 2010a, 2010b). These properties affect the extraction efficiency and phase separation, and do not affect the amount of phenolic compounds extracted at equilibrium when the extractant concentration is relatively high (Uslu and Kırbaşlar, 2010a). Therefore, common organic solvents including *n*-hexane, kerosene, *n*-octanol and cyclohexane were tested as diluents for the extraction of naphthalene-2-ol with TBP. These diluents have also been applied in the extraction of other recalcitrant pollutants (Keshav et al., 2009a; Li et al., 2006; Hong and Hong, 2000; Uslu and Kırbaşlar, 2010b). Table 4 shows the experimental results for the extraction process of 100 mg/L naphthalene-2-ol using 20% TBP (V/V) in different diluents. It can be seen that higher extraction efficiencies could be obtained when cyclohexane or *n*-octanol was used as diluent for TBP; however, the best efficiency was achieved by using a mixture of cyclohexane and *n*-octanol. Mixtures of polar and non-polar diluents have been found to increase extraction efficiency (King et al., 1990). In the study of monocarboxylic acid extraction,

Table 4 – The effect of diluent type on the extraction efficiency and distribution coefficient.

Solvent	EE	D
TBP	98.35%	59.49
<i>n</i> -Hexane	56.73%	1.31
Kerosene	65.51%	1.90
Cyclohexane	66.99%	2.03
<i>n</i> -Octanol	85.20%	5.76
20% TBP + 80% kerosene	98.51%	65.97
20% TBP + 80% <i>n</i> -hexane	98.79%	81.40
20% TBP + 80% cyclohexane	98.91%	90.48
20% TBP + 80% <i>n</i> -octanol	99.13%	114.54
20% TBP + 20% <i>n</i> -octanol + 60% cyclohexane	99.33%	149.11

when an amine was used as extractant in a mixture with a non-polar diluent and an active polar diluent, the extraction efficiency for monocarboxylic acids was increased to some extent. In addition, the application of mixtures of polar and non-polar diluents could reduce the separation time and emulsion formation between the organic phase and the aqueous phase (Morales et al., 2003). A similar result was obtained in this study. Table 4 shows that the combination of TBP in 2 diluents (cyclohexane and *n*-octanol) obtained the best extraction efficiency (99.33%) and distribution coefficient (149.11). Moreover, the extraction and separation times of this combination were the shortest of all diluents and both of the diluents had relatively low solubility in water (see Tables 2 and 3). According to the toxicity data of Table 2, this mixture of diluents had relatively low toxicity compared to the other diluents in the experiment. Therefore, mixtures of *n*-octanol and cyclohexane were selected as diluents.

As shown in Table 2, some solvents were slightly soluble in water and the toxicity of these solvents would degrade the water quality to some degree, so processes for the treatment of the raffinate should be developed. Generally speaking, the residual solvents in the raffinate could be disposed of by absorption with some common absorbents, such as activated carbon, or extracted with other organic solvents that are insoluble in water.

2.2. Effect of volume ratio of extractant to diluent

TBP can dissolve in common organic solvents such as aliphatic and aromatic hydrocarbons, alcohols, and esters. Because of the presence of both electron donor and electron acceptor groups in =P(O)OH , there exist some specific interactions (Dai et al., 2008; Kumar et al., 2011), such as self-association and molecular complex formation, between TBP and diluents or other solutes. All these properties affect the extraction process. In the study of monocarboxylic acid extraction, six concentrations of TBP dissolved in dodecane (10%:90%–80%:20%), and six concentrations of a mixture TOA + decane-1-ol (1:1, V/V) were added to dodecane ($V_{\text{dodecane}}:V_{\text{mixture}}$ varied from 80%:20% to 0%:100%) (Morales et al., 2003). To estimate the effect of the volume ratio of extractant to diluent on the extraction of propionic acid, TOA (20%–40%) or TBP (20%–40%) in kerosene was used in the study, respectively (Keshav et al., 2009a). It was found from the investigation that the proper volume ratio of extractant to diluent can improve the EE to some extent. In order to improve the extraction

Table 3 – The time for main extractants to reach equilibrium.

Extractants	EE _{max}	D _{max}	Extraction time (min)
TBP	98.38%	60.73	25
DMC	95.40%	20.74	28
MIBK	94.02%	15.72	30
1,2-Dichloroethane	92.31%	12.00	30
TBP + kerosene	98.51%	65.97	24
TBP + <i>n</i> -hexane	98.79%	81.40	24
TBP + cyclohexane	98.91%	90.48	22
TBP + <i>n</i> -octanol	99.13%	114.54	23
TBP + <i>n</i> -octanol + cyclohexane	99.33%	149.11	20

EE: extraction efficiency; D: distribution coefficient.

ability of TBP, the effect of the volume ratio of diluents to TBP was examined (see Table 5).

From Table 5, it can be seen that both *D* and *EE* for naphthalene-2-ol increased with increasing TBP concentration during the extraction process. In addition, diluents could improve the *EE* and *D* to some extent at the same volume ratio of TBP. By comparing the *EE* and *D* of naphthalene-2-ol in this study to that of naphthalene-2-ol given in the Table 4 using some common organic solvents without TBP addition, it was found that TBP addition improved the extraction efficiency greatly. A third phase (emulsion phase) was observed at the interface between the aqueous phase and the organic phase when the volume ratio of TBP was larger than 30%, and phase separation was difficult to achieve. Table 5 shows that the combination of 20% TBP, 20% *n*-octanol and 60% cyclohexane (V/V/V) achieved the highest extraction efficiency (99.33%) and distribution coefficient (149.11), so this volume ratio was chosen in the following experiments.

2.3. Effect of pH

The effect of initial pH value on the extraction efficiency of naphthalene-2-ol from aqueous solutions was studied using the mixture of 20% TBP, 20% *n*-octanol and 60% cyclohexane (V/V/V) as the extractant, with the initial pH ranging from 0.5 to 10. Sulfuric acid and sodium hydroxide at 5% concentration (W/W) were used for the adjustment of the initial pH, depending on the desired pH value. The pH values were recorded throughout the duration of each experiment, and any pH change was noted.

The effect of pH on the extraction efficiency is illustrated in Fig. 2. In the pH range of 0.5 to 3, *D* and *EE* increased slightly with an increase in the initial pH of the aqueous phase. In the pH range of 3 to 7, *EE* remained stable, while *D* declined when pH was increased. When the initial pH was higher than 8, both *D* and *EE* declined sharply with increasing initial pH value. Similar results could be seen in the study of the reactive extraction of *o*-aminophenol using trialkylphosphine oxide (Li et al., 2006). These data could be explained by the variation of the molar fraction of undissociated naphthalene-2-ol, because TBP reacted only with undissociated phenolic compounds by

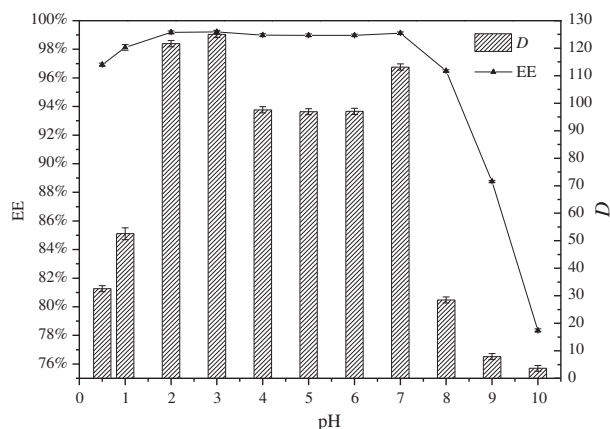


Fig. 2 – The effect of pH value on the extraction efficiency (*EE*) and distribution coefficient (*D*).

forming hydrogen bonds with hydroxyl groups. However, most phenolic compounds act like weak acids in aqueous solution (Ku and Lee, 2000; Yang et al., 2006), and the form of naphthalene-2-ol (dissociated or undissociated) was strongly dependent on the pH value of the aqueous phase. According to Fig. 2, *EE* and *D* yielded the best results (99.21% and 125.02) at pH 3. Therefore, the initial pH value of aqueous solutions was set at 3 in the following experiments. However, the initial pH values of the aqueous solution samples were about 5 without any adjustment, and the *EE* for naphthalene-2-ol remained nearly 99% at pH of 5 (see Fig. 2). So, it is recommended that the pH value should be set at about 5 in industrial applications.

2.4. Effect of temperature

Some investigations on the impacts of extraction time on the extraction efficiency have been performed. The effect of temperature on the extraction of propionic acid using 30% and 40% TOA in 1-decanol was studied in the temperature range of 30–50°C (Keshav et al., 2009b). In the extraction experiment of phenol, the effect of temperature was investigated in the range 20–30°C (Messikh et al., 2007). Both of the studies showed that a relatively low temperature was a preferable choice in the experiment. To study the effect of extraction temperature, extraction was performed at temperatures ranging from 25 to 60°C, and the data is presented in Fig. 3. Since the distribution coefficient is directly proportional to the equilibrium constant *K*, the Clausius–Clapeyron equation (Li et al., 2004).

$$\frac{\partial \log K}{\partial (1/T)} = -\frac{\Delta H^0}{2.303R}$$

could be rearranged as

$$\frac{\partial \log D}{\partial (1/T)} = -\frac{\Delta H^0}{2.303R}$$

In Fig. 3, $\log D$ increased linearly with $1/T$, and ΔH^0 was calculated to be -36.95 kJ/mol, which indicated that the extraction of naphthalene-2-ol was an exothermic process. Thus a relatively low extraction temperature was beneficial to the extraction. In addition, low extraction temperature was conducive to reducing energy consumption. Based on the

Table 5 – The effect of volume ratio of the extractant and diluent on the extraction efficiency and distribution coefficient.

TBP: <i>n</i> -octanol:cyclohexane (volume ratio)	EE	D
5%:10%:85%	98.23%	55.95
5%:15%:80%	98.49%	70.49
5%:20%:75%	98.94%	94.67
10%:10%:80%	98.33%	59.09
10%:15%:75%	98.69%	75.60
10%:20%:70%	98.96%	96.21
15%:15%:70%	98.84%	84.98
15%:20%:65%	99.16%	118.07
15%:30%:55%	99.18%	120.77
20%:20%:60%	99.33%	149.11
20%:30%:50%	99.07%	106.51
25%:20%:55%	98.97%	96.63
25%:30%:45%	97.69%	42.23
30%:30%:40%	98.41%	62.30
30%:40%:30%	97.75%	44.13

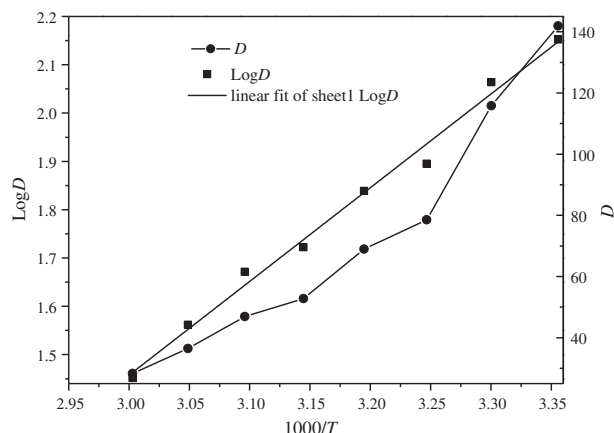


Fig. 3 – The effect of temperature on the extraction process and distribution coefficient (D).

above analysis, the remaining experiments were carried out at 25°C.

2.5. Effect of stirring rate

The stirring rate plays an important role in determining the mass transfer rate. A lower stirring rate often leads to a lower rate of mass transfer between the organic phase and the aqueous phase and a consequent higher cost for wastewater treatment, while a higher stirring rate usually results in emulsification between the two phases and a possible problem in subsequent phase separation. So an optimal stirring rate probably exists.

In a study of liquid–liquid extraction of phenol using TBP, the effect of stirring rate was investigated in the range of 200–500 r/min, and it was found that lowest value of the stirring rate (200 r/min) led to a high extraction efficiency exceeding 95% (Messikh et al., 2007). In this segment, the effect of stirring rate on the extraction of naphthalene-2-ol was studied in the range of 0–300 r/min, and results are shown in Fig. 4. The extraction efficiency increased steadily with increased stirring

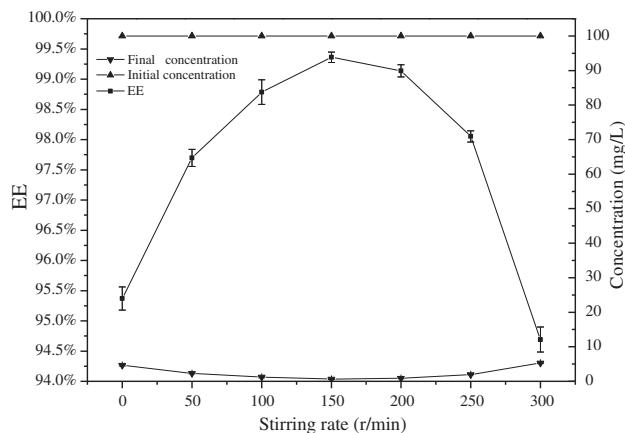


Fig. 4 – The effect of stirring rate on the extraction efficiency (EE) and final concentration of naphthalene-2-ol of the synthetic wastewater.

rate in the range of 0–150 r/min, while the extraction efficiency decreased when the stirring rate was further increased from 150 to 300 r/min. The optimal stirring rate was 150 r/min, with an extraction efficiency of 99.36%, and all the other experiments were performed at a stirring rate of 150 r/min.

2.6. Effect of extraction time

Extraction time is another vital factor influencing the extraction efficiency. In order to evaluate the role of the time in extraction efficiency, some similar studies have been carried out. The effect of extraction time (0.50–30 min) on the extraction of yttrium(III) was studied using 0.4 mol/L primene-JMT in kerosene while other factors were kept constant (Desouky et al., 2009). To determine the optimal extraction time maximizing the extraction efficiency, extraction time was varied from 5 min to 20 min in the phenol extraction process, and the optimum extraction time was about 15 min (Messikh et al., 2007). The extraction time for liquid–liquid extraction of monocarboxylic acids from aqueous solutions with organic extractants (TBP and TOA) was investigated, and the results showed that the time to reach extraction equilibrium was in the range 3 to 14 min (Morales et al., 2003). For this purpose, the effect of extraction time (0.50–30 min) on the extraction process was studied by using the mixture of TBP, cyclohexane and *n*-octanol while other factors were kept constant (Fig. 5).

As presented in Fig. 5, the extraction efficiencies for both naphthalene-1-ol and naphthalene-2-ol in aqueous phase increased gradually with the increase of extraction time before the maximum values were reached, which indicated that the amount of solute extracted into the organic phase increased as extraction time increased within a certain range. In addition, the data also illustrated that the mixed solvents could also remove naphthalene-1-ol efficiently (higher than 99%).

When the extraction time was longer than 20 min, the extraction efficiency remained constant, indicating that equilibrium had been established. Thus, 20 min was chosen as the extraction time. In addition, 60 min was sufficient for complete separation of the organic and aqueous phases, and

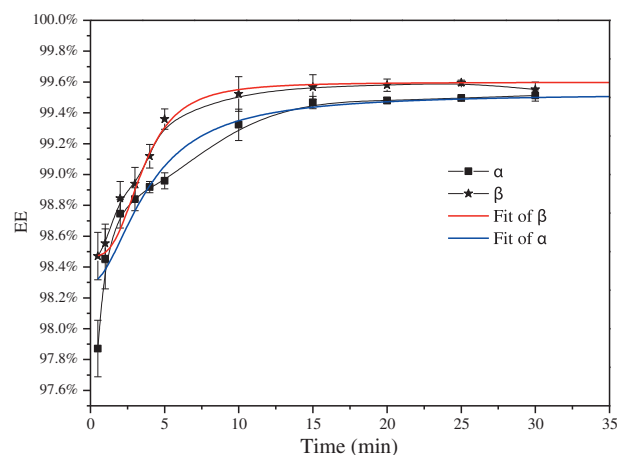


Fig. 5 – The effect of extraction time on the extraction efficiency (EE) of 1-naphthol and naphthalene-2-ol.

was chosen as the phase-separation time in the other experiments.

2.7. Effect of volume ratio of organic phase to aqueous phase

For the industrial application of an extractant, it is preferable if a high extraction efficiency is reached at a low volume ratio of organic phase to aqueous phase (O/A). O/A was found to greatly affect the number of extraction stages, distribution coefficient, and the concentration of naphthalene-2-ol in the raffinate and entrainment (Yang et al., 2006; Desouky et al., 2009). There has been some debate about the impact of O/A ratio on the extraction process. In a study on the extraction process of phenols, the O/A was varied from 1:10 to 1:1 to determine the proper value able to meet the demand of industrial production, and the result showed that the concentration of phenols in the raffinate decreased as the solvent ratio increased (Yang et al., 2006). To determine the proper ratio in the extraction process of organic acids, different values of O/A (1:1; 3:1; and 5:1, V/V) were chosen to estimate the effect of volume ratio on extraction efficiency and distribution coefficient. It was found that EE and D for TBP and TOA in kerosene or dodecane increased respectively on increasing the O/A from 1:1 to 3:1 to 5:1 (Morales et al., 2003; Keshav et al., 2009a). Fig. 6 shows that the extraction efficiency was maximized at 99.44% when O/A reached 1:1, and the concentration of naphthalene-2-ol in the raffinate phase reached the minimum value (0.5 mg/L). Besides, it was also indicated that when the O/A ratio was in the range of 1:1–1:1.5, the extraction efficiency was relatively high (>98.70%). In this study, 1:1 was chosen as the O/A in the other experiments.

2.8. Effect of initial naphthalene-2-ol concentration

In the above experiments, the initial concentrations of the aqueous solution samples were all 100 mg/L. However, the initial concentration varies for various industrial wastewater, so the effect of initial concentration on extraction efficiency was investigated in the range of 50–400 mg/L. Fig. 7 shows

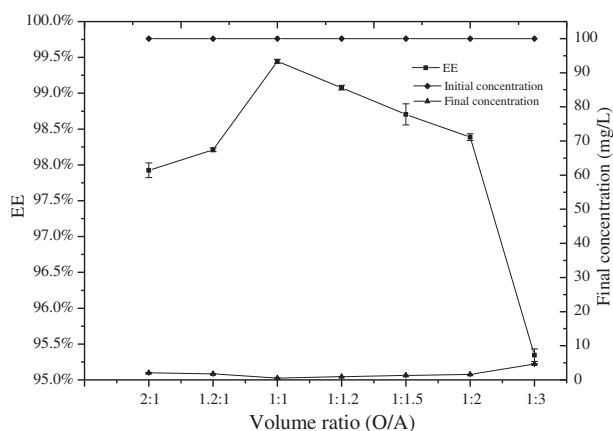


Fig. 6 – The effect of volume ratio (O/A) on the extraction efficiency (EE) and final concentration of naphthalene-2-ol of the synthetic wastewater.

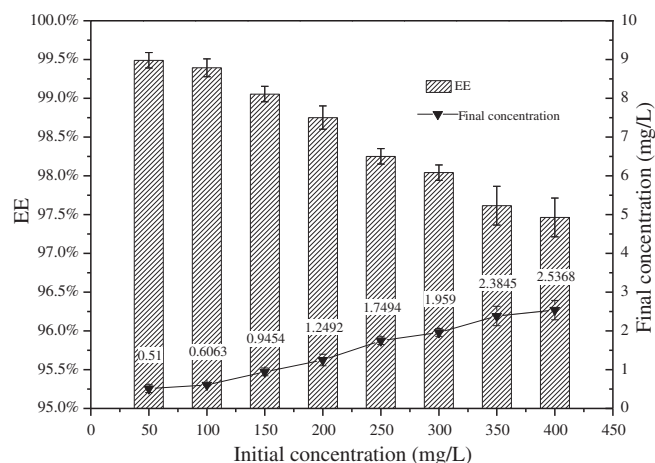


Fig. 7 – The effect of initial concentration of naphthalene-2-ol on the extraction efficiency (EE) and final concentration of naphthalene-2-ol of the aqueous solution samples.

that the extraction efficiency decreased gradually with the increase of the initial concentration, while the final concentration of naphthalene-2-ol in the raffinate increased progressively. However, all the extraction efficiencies were higher than 97%, which proved that the extraction of naphthalene-2-ol by the mixed solvents was feasible over a wide concentration range.

2.9. Extraction efficiency at various extraction stages

Extraction is usually carried out in multiple stages. To determine the number of extraction stages required, the extraction was carried out in two kinds of operation modes: counter-current and cross-current extraction. It can be seen from Fig. 8 that cross-current multistage extraction removed naphthalene-2-ol more efficiently than counter-current extraction. The extraction efficiencies of both the operation modes were higher than that of single-stage extraction (Dai et al., 2008). The naphthalene-2-ol concentration in the

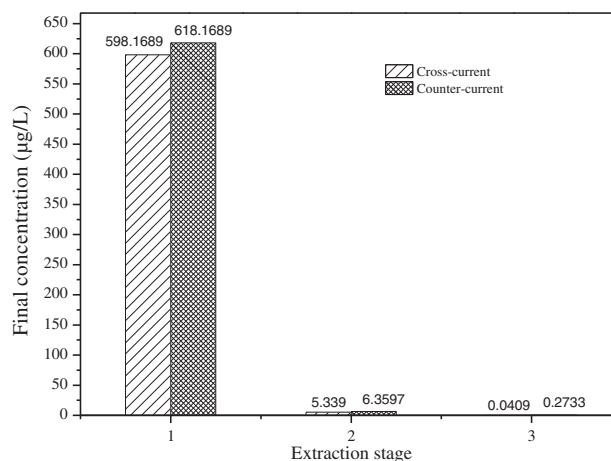


Fig. 8 – The effect of extraction model on the final concentration of naphthalene-2-ol of the aqueous solution samples after 3 extraction stages (initial concentration of 100 mg/L).

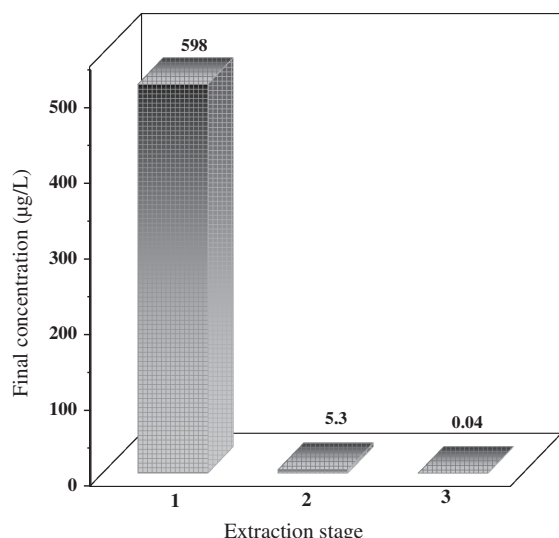


Fig. 9 – The effect of extraction stage on the final concentration of naphthalene-2-ol of the aqueous solution samples (initial concentration of 100 mg/L).

raffinate was less than 0.0005 mg/L when the extraction process was carried out with both of the extraction modes after 3 extraction stages, however, the cross-current extraction achieved higher removal of naphthalene-2-ol (Fig. 9). From the perspective of industrial applications, the counter-current mode is often a preferred choice.

2.10. Regeneration and reuse of solvents

Efficient regeneration and reuse of spent solvents are of pivotal importance for an economically sustainable extraction. Therefore, solvent regeneration was investigated in this study. Usually solvents with a low boiling point can be recovered by distillation, while those with a high boiling point can be regenerated by back extraction, in which alkali can be used for the extraction of phenolic compounds (Yang et al., 2006). According to the boiling points of the solvents used in this study (Table 6), back extraction with alkali seemed more feasible for the recovery than distillation. Back extraction with alkali has also been carried out in other cases

Table 6 – Boiling points and recovery methods of alternative solvents.

Solvent	Boiling point (°C)	Recovery method
1,2-Dichloroethane	83	Distillation
Butyl acetate	126	Distillation
MIBK	116	Distillation
TBP	289	Back extraction with alkali
Kerosene	150–250	Back extraction with alkali
DMC	90	Distillation
Toluene	110.6	Distillation
1-Octanol	193–195	Distillation
Hexane	65–70	Distillation
Cyclohexane	80–81	Distillation
Benzene	80	Distillation
Xylene	143–145	Distillation

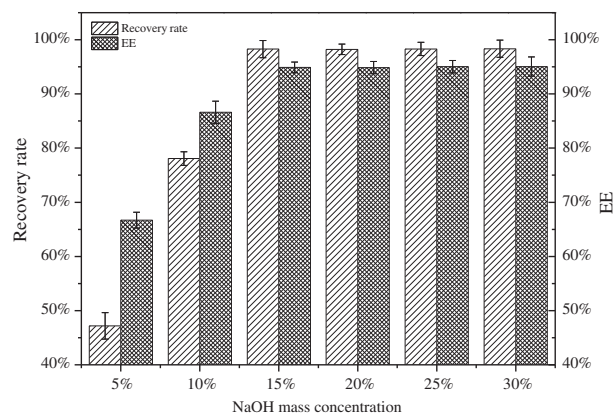


Fig. 10 – The effect of mass concentration of NaOH solution on the recovery rate of naphthalene-2-ol from organic phase and the extraction efficiency (EE) of the spent extractant.

(Yang et al., 2006; Li et al., 2004). Phenolic compounds are Lewis acids, and naphthalene-2-ol, which can react with alkali to form a phenolic salt, can be extracted back into the aqueous phase to regenerate the solvents.

In this study, NaOH solution was used for back extraction, and the effect of the mass concentration of NaOH on the recovery of the solvents was investigated (Fig. 10). As shown in Fig. 10, the extraction efficiency of the spent solvents and the recovery rate of naphthalene-2-ol increased gradually with the increase of the mass concentration of the NaOH solution up to 15% NaOH concentration (W/W), at which point the maximum values were reached. Both the recovery rate of naphthalene-2-ol from the organic phase and the extraction efficiency of recovered solvents were higher than 90%. Therefore, 15% NaOH solution was chosen to recover the solvents.

In addition, the mixed solvents of TBP, *n*-octanol and cyclohexane maintained 90% removal efficiency for naphthalene-2-ol after five regeneration cycles (Fig. 11). Thus, recovery of the mixed solvents by 15% NaOH (W/W) solution at an O/A ratio of 1:1 and contact time of 15 min was considered feasible.

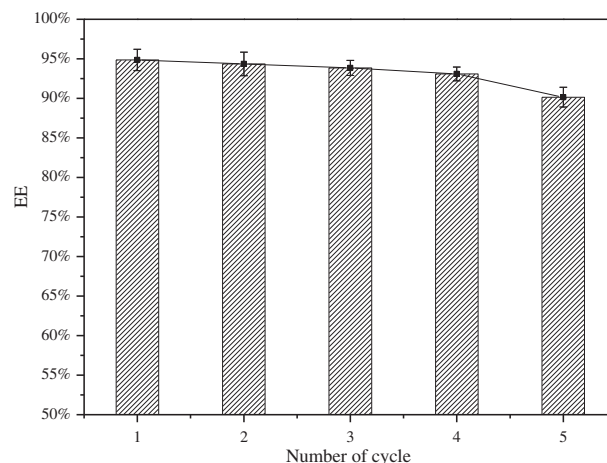


Fig. 11 – The effect of number of regeneration cycles on the extraction efficiency (EE) of the spent extractant.

3. Conclusions

The combination of 20% TBP, 20% *n*-octanol and 60% cyclohexane (V/V/V) achieved the maximum extraction efficiency of 99.33% in a single stage. The concentration of naphthalene-2-ol in the raffinate was less than 0.0005 mg/L when the extraction was carried out in three cross-current extraction stages at an O/A ratio of 1:1, initial pH of 3, stirring rate of 150 r/min and temperature of 25°C within 20 min. The extraction reached LLE in 20 min. Temperature negatively affected the naphthalene-2-ol extraction, which was an exothermic process. High temperature and rapid stirring rate was helpful, or led to more vigorous mixing of the phases and more difficulty for phase separation. An emulsion phase was also observed at the interface between the aqueous and organic phases when the volume ratio of TBP was higher than 30%. Recovery of mixed solvents was achieved satisfactorily by using 15% NaOH (W/W) solution at an O/A ratio of 1:1 and contact time of 15 min. The solvent mixture of TBP, *n*-octanol and cyclohexane maintained its extraction capacity for naphthalene-2-ol reasonably stably during five cycles of regeneration.

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