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Treatment of high-concentration phenolic wastewater by pyridine–coal tar complexation extraction system

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ABSTRACT

To effectively and economically separate and recycle the useful phenols from industrial effluents, as well as provide a comprehensive method for reutilization of coal tar to improve its economic value, the pyridine–coal tar originating from lignite gasification process was innovatively developed as a promising extractant. The extraction characteristics of the pyridine–coal tar were studied via treatment of 4,000 mg/L phenolic wastewater. Maximum extraction power of phenol on the extractant was obtained with 8% pyridine, 1.4:1 of phase ratio, 160 rpm of rotary speed at weak acid or neutral pH, which the dephenolization efficiency was as high as 90% within 5 min at 50˚C. The extracted phenol in pyridine–coal tar could be recovered, and the regenerated extractant can be reused for at least 5 cycles with no obvious loss in the dephenolization efficiency. The pyridine–coal tar was also used to extract phenol from practical phenolic wastewater, and the dephenolization efficiency was 86.7%. Based on the above experimental results, an optimized dephenolization process is proposed. This study might pave the way toward designing novel complexation extraction system with great potential for environment remediation.

Keywords: Phenolic wastewater; Complexation extraction process; Coal tar; Pyridine; Reverse extraction

1. Introduction

Phenol and its derivatives are major toxic pollutants, frequently found in various kinds of industrial wastewater, such as those from oil refineries, petrochemical plants, ceramic plants, coal conversion processes, phenolic resin industries, and pharmaceuticals [1,2]. Phenolic compounds may quickly penetrate skin, cause severe irritation to eyes and respiratory tract, and even be fatal by ingestion, inhalation, or skin absorption. Phenol is listed among the priority organic pollutants by the US Environmental Protection Agency [3]. It is considered to be potentially carcinogenic to humans and may be lethal to fish at concentrations of 5–25 mg/L [4]. In addition, phenolic compounds are important raw materials for the organic chemical industry and have a wide range of applications in producing bisphenol A, caprolactam, alkyl phenols, adipic acid, and so on [5,6]. Developing promising strategies to effectively remove phenols from wastewater is hence of great significance.

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Different techniques have been developed for phenol removal from polluted water in many industrial processes, including chemical oxidation [7–9], electrochemical reduction [10,11], biodegradation [12–14], membrane separation [15,16], adsorption [17], and solvent extraction [18]. The widely applied solvent extraction method is simple and rapid, and various materials have been used as extractant, such as bis (2-ethylhexyl) sulfoxide (BESO) [19], cumene [20], 1-butylimidazole (BIMZ) [18], and octanol [21]. Moreover, it is well known that the solvent extraction method, characterized by its easiness to operate and convenience to scale up, has been viewed as a recuperative process and received much attention in recent years [22]. However, several drawbacks (such as serious back mixing, the loss of solvent, and low dephenolization efficiency) urgently need to be overcome before solvent extraction method is applied in practice.

Lignite and sub-bituminous coal are abundant, accounting for 53% of all coal resources in the world and 46% in China [23], and coal gasification technology is developed since China is rich in coal and poor in oil and gas [24]. However, the lignite pressurized gasification wastewater contains high concentrations of phenolic compounds and coal tar [25], and nearly 90% low-rank coal tar is consumed by direct combustion for power generation, which is considered as an inefficient use of coal energy in an environmentally unfriendly way. The concentration of phenols in coal tar is up to 30–36%, indicating that coal tar itself is good solvent for phenols. The pyridine bases existing in the coal tar possess the features of Lewis base, and it can react with the Lewis acidic form of phenol, resulting in the formation of the complex that is extracted into the organic phase. If the coal tar can be further prepared into a pyridine–coal tar complexation system, the pyridine–coal tar not only can be used to effectively reduce the phenol concentration from industrial effluent for recycling the useful phenols, but also provide a new feasible way for the comprehensive utilization of coal tar and improving its economic value, which makes a great contribution to the water environment governance and economic development. Furthermore, it is worth noting that low cost and wide availability of coal tar are also the advantages for it as an effective extractant for treating phenolic wastewater.

In this study, an innovative highly effective extractant was provided for the treatment of phenolic wastewater. The objective of this work is to investigate the extraction potential of a pyridine–coal tar complexation extraction system for phenol removal from effluent. The novel coal tar extractant was obtained from lignite gasification process (170–230℃), and then treated by sodium hydroxide and sulfuric acid with the desired initial concentration, followed by adding the pyridine distilled from the acid residues decomposed by ammonia (Fig. 1). The extraction properties of the pyridine–coal tar complexation extraction system were evaluated using both simulated phenolic wastewater and phenolic effluent from a gasification plant, respectively. The effects of experimental parameters such as the content of pyridine in the treated coal tar, initial pH, phase ratio, and rotary speed were studied.

2. Materials and methods

2.1. Chemicals and solutions

4,000 mg/L simulated phenolic wastewater was used as wastewater samples. The coal tar (170–230℃) with the phenol concentration of 30–36% was derived from lignite gasification process in Jiehua Chem Group Co., Ltd. The chemical and physical characteristics of pyridine and phenol are summarized in Table 1. Phosphoric acid, copper sulfate, sodium hydroxide, sulfuric acid, phenol, and 4-aminoantipyrine were all of commercially available analytical grade and purchased from Aladdin Reagent Co., Ltd (China). Ammonium hydroxide (GR Grade, 25–28%) was obtained from Tianjin Yongda Chemicals Reagent Co. Ltd (China). All reagents were used as received

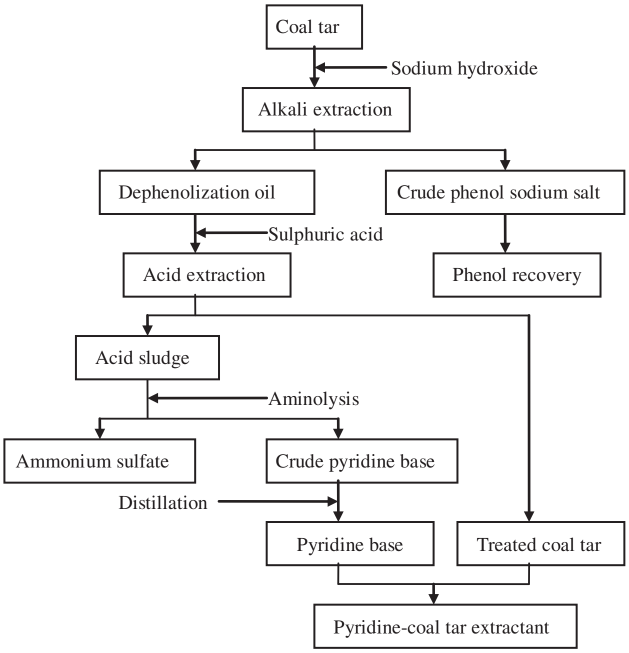
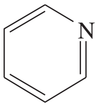
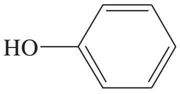


Fig. 1. Preparation of pyridine–coal tar extractant.

Table 1
The chemical and physical properties for the pure compounds

Name	Pyridine	Phenol
Formula	C_5H_5 N	C_6H_6O
Structure		
MW (g/mol)	79.10	94.11
λ max (nm)	256	270.75
pK_a	5.25	9.95 (in water)
Relative density	0.9827	1.07

without further purification. Distilled water was used in all experiments for preparation of various reagent solutions.

2.2. Experiments

2.2.1. Preparation of pyridine–coal tar extractant

The highly unsaturated compounds, as well as nitrogen, oxygen, and sulfur compound are present in the coal tar, resulting a decrease in the extraction power of coal tar. Thus, refining treatment is required for coal tar, mainly including the alkali dephenolization and acid extraction. Briefly, a certain concentration of NaOH was added into 100 ml of coal tar, followed by shaking it back and forth in a thermostat air shaker (50 ± 1℃) for 5 min at 160 rpm. The obtained mixture was then moved from conical flask into a separating funnel for phase separation. Afterwards, the upper oil phase was taken to measure the volume, and reacted with simulated phenolic wastewater (4,000 mg/L) to determine the optimal concentration and volume of NaOH during the course of alkali dephenolization.

To further improve the coal tar quality as the phenol extractant, 100 ml of the above dephenolization oil was slowly poured into the H_2SO_4 with different initial concentrations, which was then kept shaking at 140 rpm for 8 min under room temperature. After reaction, resulting mixture was transferred to a separatory funnel, standing and sedimenting for 30 min. Thus, treated coal tar and acid sludge were clearly distinguished.

Considering that pyridine compounds in coal tar were also neutralized by the H_2SO_4 to form the acid-soluble pyridine sulfate (Eqs. (1) and (2)), the acid sludge was collected and subsequently decomposed by 18–20% industrial ammonia solution (Eq. (3)) until a pH value of 7 and 8 was reached, generating oil-like dark liquid (heavy pyridine salt) with relative density d4 20 > 1.0, content of pyridine base >70%, moisture >15%. Besides heavy pyridine, ammonium sulfate was simultaneously obtained via the method provided in this study, which could avoid the discharging of waste liquor.

$$C_5H_5N + H_2SO_4 \rightarrow C_5H_5NH \cdot HSO_4 \tag{1}$$

$$2C_5H_5N + H_2SO_4 \rightarrow (C_5H_5NH)_2SO_4 \tag{2}$$

$$\begin{aligned}&(C_5H_5NH)_2SO_4 + 2NH_3H_2O\\&\quad \rightarrow 2C_5H_5N + (NH_4)_2SO_4 + H_2O\end{aligned} \tag{3}$$

Sequentially, the obtained heavy pyridine salt was placed into a round-bottom flask equipped with digital display electric jacket. According to different boiling points of pyridine and its homologs, distilled temperature was divided into 100–110℃, 110–130℃, 130–180℃, and 180–230℃ to collect the distillates for subsequent characterization. Finally, distilled pyridine with various contents was added into the refining coal tar and then kept shaking for 20 min at 120 rpm to ensure sufficient mixing. The preparation flowchart of the pyridine–coal tar extractant is shown in Fig. 1.

2.2.2. Extraction and reverse extraction experiment

A certain amount of 4,000 mg/L simulated phenolic wastewater and extractant were mixed in proportion in a conical flask before being placed in a thermostatic shaker with a desired rotary speed under given temperature for removal of phenol. Then, the reactants in the conical flask were transferred into a separatory funnel in every certain time interval for phase separation. The clear solution in bottom layer is separated for phenol concentration analyses. The distribution coefficient (*D*) and dephenolization efficiency (*E*) were estimated by the following equations:

$$D = \frac{C_{\text{ex,eq}}}{C_{\text{ph,eq}}} \tag{4}$$

$$E(\%) = \frac{C_{\text{ph,ini}} - C_{\text{ex,eq}}}{C_{\text{ph,ini}}} \times 100\% \tag{5}$$

where $C_{\text{ph,ini}}$ denotes the initial phenol concentration (mg/L) in phenol solution; $C_{\text{ex,eq}}$ and $C_{\text{ph,eq}}$ are the concentration (mg/L) of phenol in the extraction phase and phenol solution at equilibrium state, respectively.

The reverse extraction experiment was also conducted using NaOH solution for stripping the loaded organic phase in a thermostatic shaker with fixed rotary speed at the selected temperature for an appropriate time period, and then the regenerated extraction agent was used for the following recycling test of extractant. The stripping efficiency (*S*) is defined as the mass ratio of phenol in the stripping reagent at equilibrium and in the loaded organic phase at initial state, and the equations could be represented as follows:

$$S(\%) = \frac{C_{\mathrm{s,eq}} \times V_{\mathrm{s}}}{C_{\mathrm{ex,ini}} \times V_{\mathrm{ex}}} \times 100\% \tag{6}$$

where $C_{\mathrm{s,eq}}$ and $C_{\mathrm{ex,ini}}$ are the equilibrium concentration (mg/L) and the initial concentration (mg/L) of phenol in the stripping reagent and loaded organic phase, respectively; V_{s} and V_{ex} represent the volume (ml) of stripping reagent and extractant, respectively.

The phenol concentration in the aqueous solution and the stripping reagent were measured by means of 4-aminoantipyrene spectrophotometric method using a 752 N UV–vis spectrophotometer (Shanghai Precision Scientific Instruments Co., Ltd, China) at 510 nm [20]. The phenol concentration in the extractant can be calculated via mass balance. The pH of reaction samples is determined with a PHS-2F precision pH meter (Shanghai Precision Scientific Instruments Co., Ltd China), and adjusted by solutions of 0.1 M HCl and 0.05 M NaOH.

3. Results and discussions

3.1. Optimization for alkali dephenolization and acid extraction process

As can be seen from Table 2, the stratification rates were relatively fast under different NaOH concentrations, and the residual oil volume decreased with the increase in NaOH concentration. This is due to the fact that only phenolic compound can be removed under low NaOH concentration (8–10%). However, the remaining acidic compounds in the oil could be also removed when NaOH concentration was higher than 10%, resulting in less residual oil volume, slightly longer stratification time, and better oil phase quality. It also can be seen that the dephenolization efficiency increases greatly over a range of NaOH concentration from 8 to 20%. After that, no significant changes in dephenolization efficiency were detected. Thus, 20% NaOH solution was used for alkali washing of coal tar.

From Fig. 2, it is evident that the dephenolization efficiency increased with increasing the volume of 20% NaOH solution, namely the ratio of alkali–oil phase volumes (the volume of oil was fixed at 100 ml). The inflection point of dephenolization efficiency was achieved with alkali–oil phase ratio of 0.8:1, indicating that a majority of phenolic compounds in the coal tar were removed through the alkaline washing. Then the dephenolization efficiency had no obvious change as the volume of alkali solution kept increasing. Therefore, the alkali–oil phase ratio might be kept at 0.8:1 in the process of alkali washing.

Then proceed to the next step in Fig. 1, acid extraction was carried out for purification of dephenolization oil. As shown in Table 3, it can be found that more compounds were removed with the increase in H_2SO_4 concentration, resulting in the decrease in residual coal tar volume and stratification time. The maximum residual volume of coal tar was obtained (84 ml) with less impurity, better transparency, and neutrality under 92% H_2SO_4 dosage of 20 ml. However, there was no significant change in the quality of washed oil when H_2SO_4 dosage was higher than 20 ml. Thus, 92% H_2SO_4 with volume ratio of 1:5 was expected to extract the alkali-washed coal tar.

3.2. Analysis of distilled pyridine base

Subsequently, pyridine was recovered from acid residues via aminolysis and distillation (see Fig. 1). As shown in Table 4, it was found that the fraction ranging from 110–130℃ to 130–180℃ was yellow transparent with obvious pyridine smell, consistent with the characteristics of pyridine and its homologs. Moreover, it can be inferred that the above liquid is the pyridine substances compared to the literatures [26,27]. However, the distillates of 100–110℃ and 180–230℃ are attributed to heavy pyridinium entrained water and quinoline substances, respectively. Thus, the pyridine fractions (110–130℃ to 130–180℃) were taken for reuniting with the treated coal tar, which successfully changes the composition of extractant, resulting in the enhancement of dephenolization efficiency. Furthermore, the comprehensive utilization of acid slag can be realized through innocent treatment to recovery of the valuable pyridine.

3.3. The composition and nature of the final extractant

The comparison of the main composition and nature between original coal tar and final extractant

Table 2
The influence of NaOH concentration on treated coal tar[a]

Concentration of alkali (%)	Volume of alkali (ml)	Remaining volume of oil (ml)	Separation time (min)	Dephenolization efficiency (%)	The conditions of washed coal tar		
					Transparency	Impurity	Color
8	200	72	0.6	68.32	Opaque	More	Dark red
10	160	68	1.0	69.90	Opaque	Less	Kelly
15	108	64	1.0	72.97	Less transparent	Less	Light red
20	80	64	1.0	79.12	Less transparent	Less	Pink
25	64	62	1.5	79.05	Transparent	Few	Pink
30	56	61	2.0	77.29	Transparent	Few	Pink

[a] All rows are based on 100 ml of coal tar.

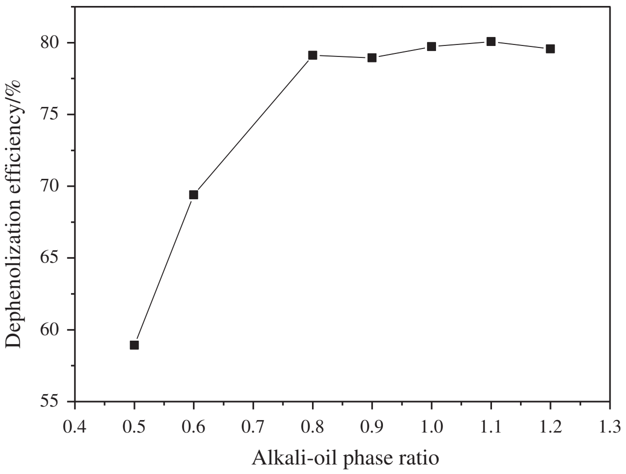


Fig. 2. Effect of alkali–oil phase ratio on dephenolization efficiency (Volume of oil = 100 ml, concentration of NaOH = 20%, rotary speed = 160 r/min, temperature = 50 ± 1℃, time = 5 min).

are listed in Table 5. It can be seen that the final extractant, pyridine–coal tar, was stabilized and purified with less impurities, lower density, viscosity, and phenol concentration (<5%), as well as higher diaphaneity, which can meet the requirements of subsequent dephenolization. It is worth noting that the pyridine dissolved in the refined coal tar is negligible (<0.4%) compared with that in the final extractant (8–20%), the optimum contents of pyridine added into the treated coal tar are discussed in more detail below.

3.4. Reaction mechanism of complex extraction

Since the majority of pyridine bases are removed during the coal tar refining process, the extraction of phenol using treated coal tar is a typical liquid–liquid extraction process based on physical distribution. However, the reversible complexation reaction of pyridine (Lewis base) and phenol (Lewis acid) can take place when the pyridine is added into the treated oil, resulting in the phenol form in feed solution phase differing from that in extraction phase. Therefore, it is essential to take into account extraction equilibrium equations for calculation of the distribution coefficient. It was assumed that the extracted complex ratio of phenol to pyridine is 1:*n*, and the extraction equilibrium equation is as follows:

$$\mathrm{ArOH} + n \cdot \mathrm{C_7H_9N} \overset{K}{\rightleftarrows} \overline{\mathrm{ArOH} \cdot n\mathrm{C_7H_9N}} \qquad (7)$$

where ArOH represents the volatile phenol in the feed solution phase, and the extracted complex in the organic phase is denoted as $\overline{\mathrm{ArOH} \cdot n\mathrm{C_7H_9N}}$. In the pyridine–coal tar system for extracting phenol, the apparent extraction equilibrium constant can be represented as:

$$K = \frac{\overline{[\mathrm{ArOH} \cdot n\mathrm{C_7H_9N}]}}{[\mathrm{ArOH}][\mathrm{C_7H_9N}]^{\mathrm{n}}} \qquad (8)$$

The dissociation equilibrium for phenol in the aqueous phase is as follows:

$$\mathrm{ArOH} \overset{K_{\mathrm{H}}}{\rightleftarrows} \mathrm{H^+} + \mathrm{ArO^-} \qquad (9)$$

The corresponding dissociation constant (K_{H}) of phenol is shown as:

$$K_{\mathrm{H}} = \frac{[\mathrm{H^+}][\mathrm{ArO^-}]}{[\mathrm{ArOH}]} \qquad (10)$$

Table 3
The influence of different concentrations of H_2SO_4 on coal tar treated[a]

Concentration of sulfuric acid (%)	Sulfuric acid volume (ml)	Remaining volume of oil (ml)	Separation time (min)	Condition of acid sludge	Condition of oil
98	20	76	0.8	Multi acid residue, thickens, black, and difficult to clean with large sour smell	Lighter color, relative transparent, and pink
92	10	80	1	Sour slag thicker, dark red with obvious odor, no significant change after volume reached 20 ml	As the volume of sulfuric acid reached 20 ml, more remaining volume of oil, better transparency, fewer impurities with light red
	15	82	1		
	20	84	1		
	25	84	1.2		
	30	82	1.5		
75	30	80	2	Sour slag thicker, deep red, large amount of slag	Dark red, poor transparency
60	40	81	3	Relatively dilute acid slag, deep red	Red brown, poor transparency with tar odor
20	100	92	3	Produce pyridine sulfate, sour slag dilute and less	No obvious color change, less transparency with more impurities, and larger odor

[a]All rows are based on 100 ml of dephenolization oil.

Table 4
Pyridine distillation fractions

Acid slag volume (ml)	Heavy pyridine volume (ml)	Distillate temperature (℃)	Fraction volume (ml)	Comments on a form
1,000	150	100–110	~40	Upper floating yellowish liquid, lower colorless liquid
		110–130	<20	Yellowish transparent liquid with obvious odor, pyridine alkali smell
		130–180	<25	Yellow transparent liquid with obvious odor, pyridine alkali smell
		180–230	~65	Brown red liquid with rancid taste

Table 5
Comparison of the composition and nature between original coal tar and final extractant

	Specific gravity d4 20/kg L^{-1}	Degree Engler (E50)	Solution pH	Phenol content (%)	Pyridines (%)	Sulfide (%)	The oil composition (%)			
							Non hydrocarbon	Alkane	Olefin	Aromatic hydrocarbon
Original coal tar	0.95	1.17	7	30–36	5–7	3–5	32.4	16.0	16.4	35.2
Final extractant	0.884	1.03	7–8	<5	8–20	0.23	2.4	72.3	5.6	19.7

The distribution coefficient of extraction equilibrium D can be expressed in terms of apparent extraction equilibrium constant K and dissociation equilibrium constants K_H from Eqs. (8) and (10).

$$D = \frac{\overline{[\mathrm{ArOH} \cdot n\mathrm{C_7H_9N}]}}{[\mathrm{ArOH}] + [\mathrm{ArO^-}]} = \frac{\overline{[\mathrm{ArOH} \cdot n\mathrm{C_7H_9N}]}}{[\mathrm{ArOH}](1 + 10^{\mathrm{pH} - \mathrm{p}K_\mathrm{H}})} = \frac{K\overline{[\mathrm{C_7H_9N}]}^{n}}{(1 + 10^{\mathrm{pH} - \mathrm{p}K_\mathrm{H}})} \tag{11}$$

Table 6
The distribution coefficient, log D and log [C_7H_9 N] data at different initial phenol concentrations

Phenol concentration (mg/L)					
Organic phase	Aqueous phase	Distribution coefficient	log D	log [C_7H_9 N]	R^2
235.2	1648.0	1.427184	0.15448	0.1056	0.997
3125.2	874.8	3.572474	0.552969	0.44224	
3399.6	600.4	5.662225	0.752987	0.56497	
3628.8	371.2	9.775862	0.990155	0.75518	
3652.4	347.6	10.50748	1.021499	0.77395	

Extraction equilibrium distribution coefficient D and pyridine concentration can be determined by testing under different concentrations of pyridine. The term of $1 + 10^{\mathrm{pH}-\mathrm{p}K_{\mathrm{H}}}$ is constant because of the unchanged [H^+] in the extraction process, and then take logarithm for both sides of Eq. (8):

$$\log D = n\log[C_7H_9N] + B \tag{12}$$

Obviously, the relationship between log D and log [C_7H_9 N] can be well described by linear regression with high correlation coefficients R^2 (see Table 6 and Fig. 3). Considering the dissolving capacity of treated coal tar for phenol, the slope value of $n = 1.303$ indicates 1:1 stoichiometric association of the phenol–pyridine complex in the organic phase. Therefore, the extraction reaction at equilibrium state can be expressed as follows:

$$\mathrm{ArOH} + C_7H_9N \rightleftarrows \overline{\mathrm{ArOH} \cdot C_7H_9N} \tag{13}$$

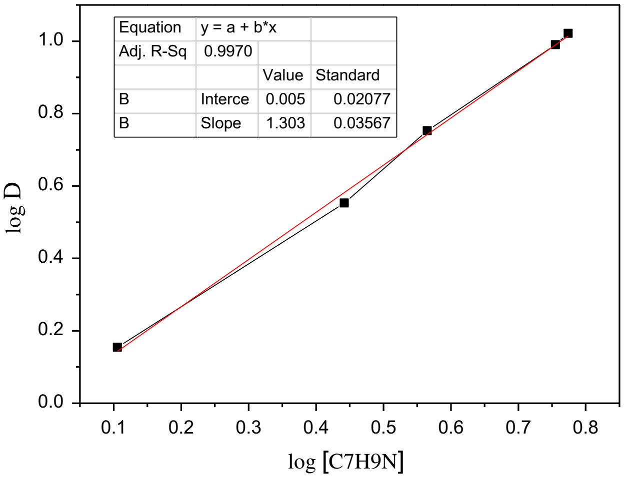


Fig. 3. The relationship between log D and n log [C_7H_9 N] (pyridine/coal tar = 8%, rotary speed = 160 rpm, pH 7, R = 1.4:1 (organic/aqueous), extraction temperature = 50℃, and extraction time = 5 min).

3.5. *Effect of various parameters on phenol extraction efficiency*

3.5.1. *Extraction time*

As shown in Fig. 4, dephenolization efficiency of the pyridine–coal tar for simulated phenolic wastewater reached equilibrium quickly within 5 min, and no obvious change was found after that. Such a quick equilibrium illustrates a strong complexation between phenol and extractant rather than a sole physical interaction [28]. In consideration of the dephenolization efficiency and industrial energy consumption, 5 min was used as the proper extraction time in all the experiments.

3.5.2. *Initial pH*

Experiments were conducted by changing pH from 2 to 12 to estimate the effect of initial pH on dephenolization efficiency, and the results are shown in Fig. 5. When pH value was in the range of 2–6, more than 90% phenol could be extracted from the aqueous phase and the dephenolization efficiency had little change. However, with further increase in the pH value, the dephenolization efficiency decreased drastically until it was close to zero when the pH value in aqueous solution exceeded the phenol pK_a (9.95). The reasonable explanation is that the phenol ionized to form more water-soluble phenolate salt at a high pH value, which made the extraction harder by pyridine–coal tar from aqueous solution. Considering the operating cost and extraction performance, the optimum pH value should be maintained in weak acid or neutral.

3.5.3. *Phase ratio R*

As shown in Fig. 6, with phase ratio of organic phase and aqueous phase changing from 0.6 to 1.4:1, dephenolization efficiency increased sharply. When

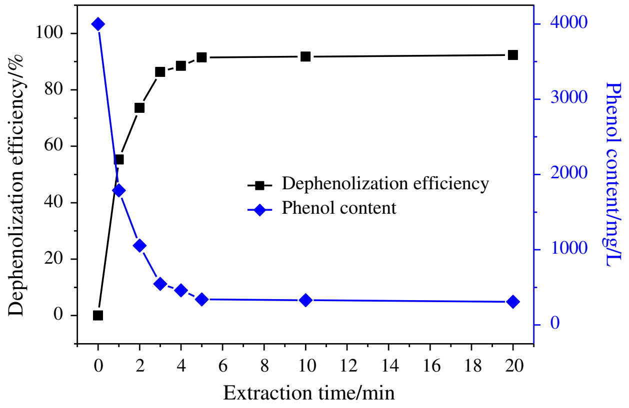


Fig. 4. Effect of extraction time on dephenolization efficiency (pyridine/coal tar = 8%, R = 1.4:1 (organic/aqueous), pH 7, extraction temperature = 50˚C, and rotary speed = 160 rpm).

phase ratio was increased higher than 1.4:1, no significant change on the dephenolization efficiency was observed. This is due to the fact that the better dispersion performance of phenol in organic phase is beneficial for stratification during a short time within a phase ratio R of 1.4:1. However, with the ratio higher than 1.4:1, complexation reaction tended to equilibrium because the equilibrium state of reversible reaction (Eq. (10)) is directly related with proportion of phenol and basic content.

By increasing phase ratio R, more extractant was need to be added into the phenolic wastewater, which not only increased energy consumption in industrial operation, but also decreased the regeneration efficiency of extractant due to the low phenol concentration in extractant, and it made it more difficult for phenol sodium salt to be saturated in stripping process. Therefore, the phase ratio R should be maintained at around 1.4:1 to ensure the dephenolization efficiency in practical application.

3.5.4. Pyridine content

Fig. 7 presents the effect of pyridine content in extractant on dephenolization efficiency. When the pyridine content was 8%, the phenol content decreased to 339.2 mg/L, and the corresponding dephenolization efficiency achieved the maximum of 91.31%. However, dephenolization efficiency decreased as pyridine content further increased to 20%. This deterioration of the extraction performance can be explained by the fact that the extraction capacity of extractant for phenol has reached saturation. On the other hand, the volume of the organic phase decreased with further increasing the pyridine content, resulting in the decrease in the phenol solubility in the extractant. In addition, the emulsification of pyridine–coal tar may be appeared during stripping process when the pyridine content become exorbitant (such as 20%). In general, these results indicated that the content of pyridine bases should be optimized to 8%.

3.5.5. Extraction temperature

Appropriate temperature can accelerate the movement rate of the molecules in solution and mass

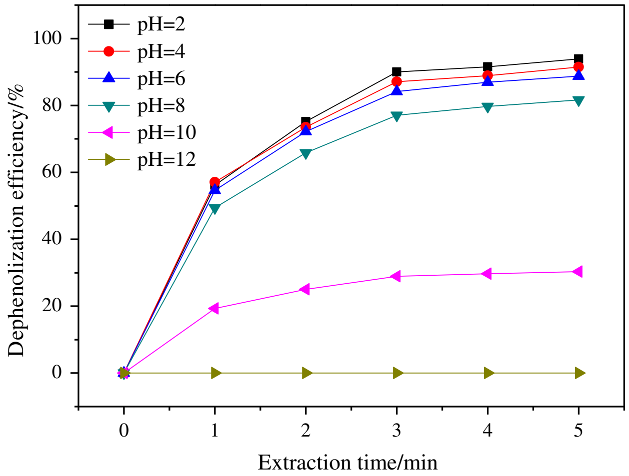


Fig. 5. Effect of pH on dephenolization efficiency (pyridine/coal tar = 8%, R = 1.4:1 (organic/aqueous), rotary speed = 160 rpm, extraction temperature = 50˚C, and extraction time = 5 min).

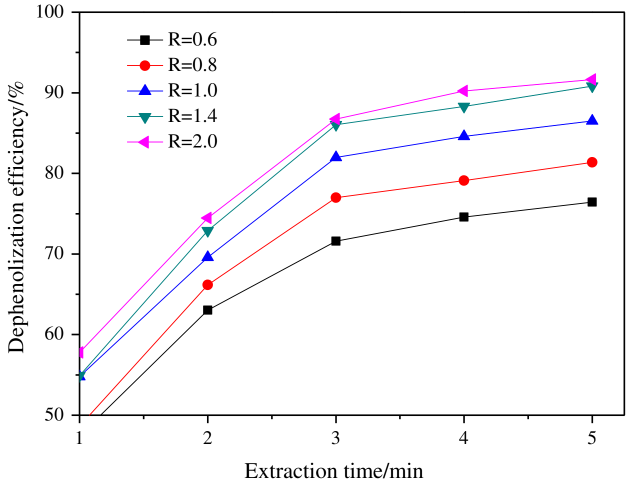


Fig. 6. Effect of solvent ratio R on dephenolization efficiency (pyridine/coal tar = 8%, extraction temperature = 50˚C, pH 7, rotary speed = 160 rpm, and extraction time = 5 min).

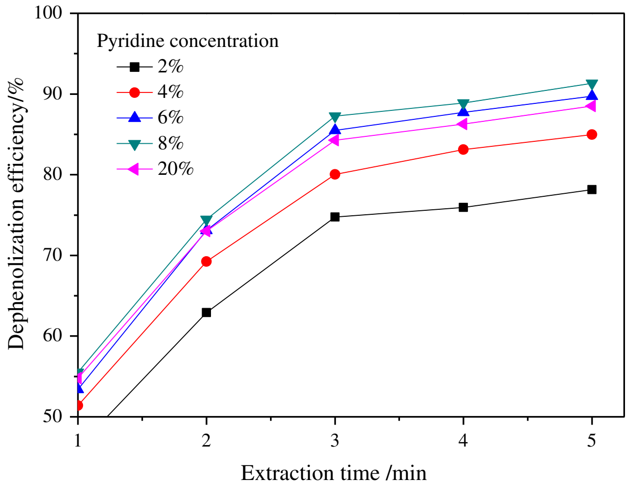


Fig. 7. Effect of pyridine content on dephenolization efficiency (pH 7, R = 1.4:1 (organic/aqueous), rotary speed = 160 rpm, extraction temperature = 50℃, and extraction time = 5 min).

transfer process, which is beneficial to separate the extractant from phenolic wastewater. However, lower temperature is unfavorable for the two-phase contact leading to incomplete complexation reaction, and heightening of the temperature would result in flooding phenomenon and extractant wastage. As can be seen from Fig. 8, the dephenolization efficiency largely depends on the temperature. When the extraction temperature ranged from 40 to 50℃, phenol was effectively extracted from the simulated wastewater. In general, for phenolic effluent discharged by most of factories with the temperature ranging from 45 to 50℃, pyridine–coal tar extractant can be used for dephenolization without further adjustment in temperature.

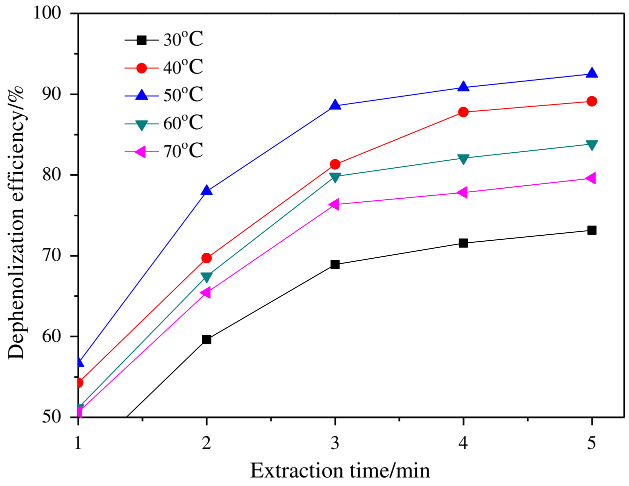


Fig. 8. Effect of temperature on dephenolization efficiency (pH 7, R = 1.4:1 (organic/aqueous), pyridine/coal tar = 8%, rotary speed = 160 rpm, and extraction time = 5 min).

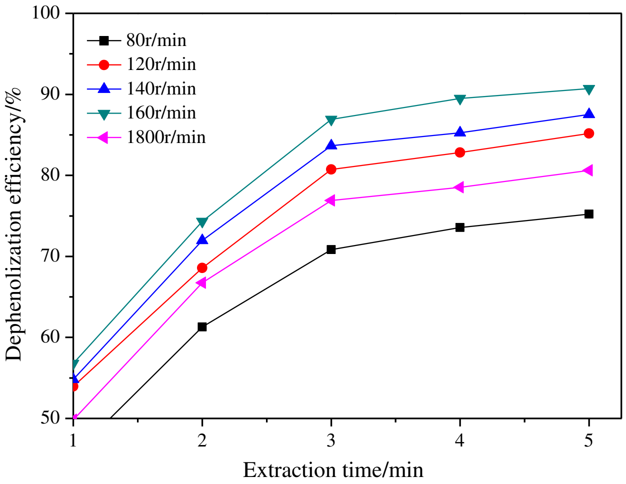


Fig. 9. Effect of rotary speed on dephenolization efficiency (pyridine/coal tar = 8%, pH 7, R = 1.4:1 (organic/aqueous), extraction temperature = 50℃ and extraction time = 5 min).

3.5.6. Oscillation strength

Fig. 9 depicts the effect of oscillation strength on the dephenolization efficiency. It is evident that the dephenolization efficiency increased as the rotary speed increased. With a rotary speed of 160 rpm, the phenol concentration in aqueous solution decreased to 0.362 mg/L, and the corresponding dephenolization efficiency achieved the highest value of 90.72%. However, the dephenolization efficiency declined significantly as the rotary speed continued to increase. This might be ascribed to the emulsification of pyridine–coal tar extraction system resulted from excessive oscillation intensity. In addition, for industrial energy consumption concern, 160 rpm was selected as the optimum rotary speed in the whole extraction experiment.

3.6. Multistage cross-flow extraction

Multistate cross-flow extraction of 4,000 mg/L simulated phenolic wastewater was conducted to investigate the effect of the number of extraction stages on dephenolization efficiency, and the experimental processes are as follows: the aqueous raffinate from one extraction unit is fed to the next unit as the aqueous feed, while fresh extractant needs to be added into each unit to enhance the mass transfer driving force.

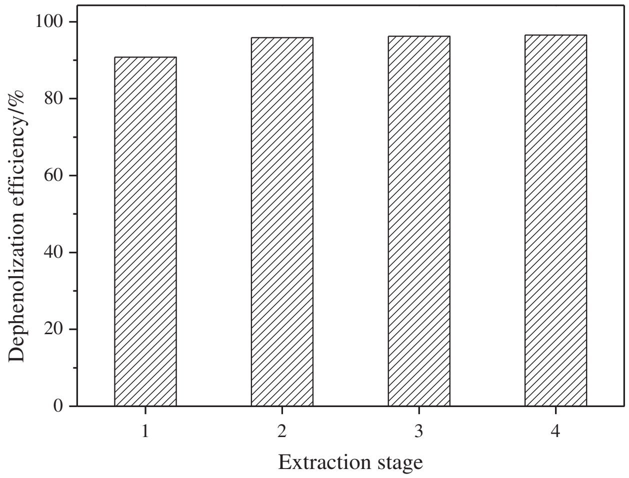


Fig. 10. Condition of multistage cross-flow extraction ($C_{\mathrm{ph,ini}}$ = 4,000 mg/L, pyridine/coal tar = 8%, pH 7, rotary speed = 160 rpm, R = 1.4:1 (organic/aqueous), extraction temperature = 50℃, and extraction time = 5 min).

Hence, in this way, as the number of extraction stages increased, the extraction efficiency increased significantly at first and then the rate of increase tended to slow down. As shown in Fig. 10, dephenolization efficiency achieved with 1-stage, 2-stage, 3-stage and 4-stage extraction were 90.79, 95.85, 96.24, and 96.56%, respectively. In comparison with 2-stage extraction, the dephenolization efficiencies of 3-stage and 4-stage were increased slightly. This result implies that higher cross-flow extraction is ineffective for improving dephenolization efficiency because of the poor performance of extractant in low-concentration phenolic wastewater treatment. Furthermore, plenty of extractant would be consumed during multistage cross-flow extraction, and the phenol concentration is extremely low in the organic phase after completion of the reaction, which would increase the cost of extractant recovery and the energy consumption of industrial operation. Therefore, the single-stage extraction is recommended for the industrial dephenolization process using pyridine–coal tar complexation system.

3.7. Practical phenolic wastewater extraction test

The discharged phenolic effluent was collected from a coal gasification plant of Yunnan Jiehua Group with the outlet temperature 45–50℃, pH value of 8.50. The pH value of samples was immediately acidified to 4 with phosphoric acid, followed by adding proper amount of copper sulfate to inhibit the biological oxidation of micro-organisms on phenols. Because the components of practical phenolic wastewater are quite complex, it required distillation process prior to determination of volatile phenol concentrations. In order to investigate the possibility of phenol removal from practical phenolic wastewater, the pyridine–coal tar extractant was mixed with 50 ml of pretreated sample (after alkali washing; 4258.3 mg/L volatile phenol content) via single-stage extraction process under the optimal experiment conditions. The results show that the phenol concentration in wastewater was decreased to 566.0 mg/L with the corresponding dephenolization efficiency of 86.7%, indicating that the proposed method has the potential to remove phenol from industrial wastewater. The corresponding flowchart of actual industrial effluent dephenol process is presented in Fig. 11.

3.8. Stripping and recycling of extractant

It is very crucial to separate out phenol from loaded organic phase in the pyridine–coal tar

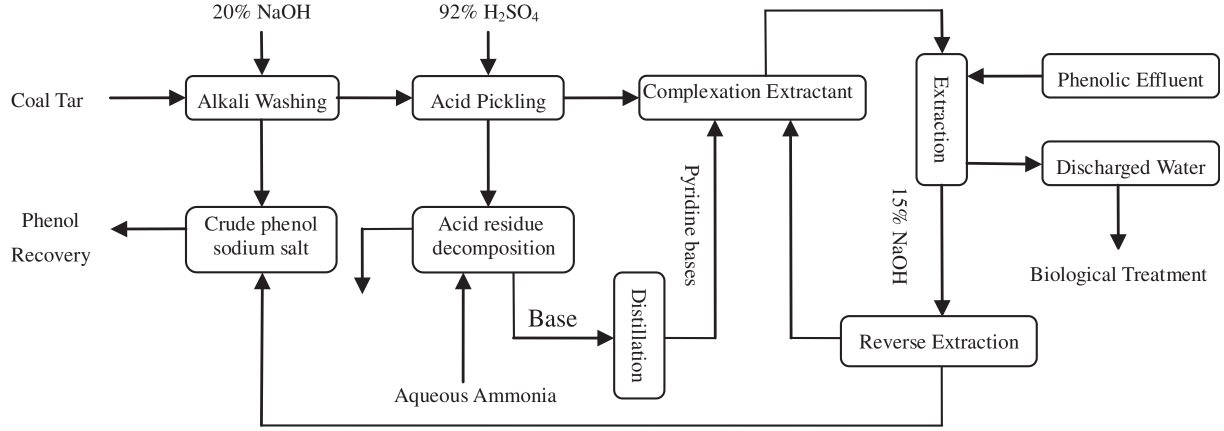


Fig. 11. Flow diagram of phenol removal process.

Table 7
Effect of NaOH concentration, alkali–coal tar phase ratio, reaction temperature, shaking speed, and reaction time on stripping of phenol from loaded extractant

C_{NaOH} (%)	*S* (%)	Phase ratio	*S* (%)	Reaction temperature (℃)	*S* (%)	Shaking speed (rpm)	*S* (%)	Reaction time (min)	*S* (%)
5	41.63	5	55.6	25	50.3	100	80	1	87.13
10	88.93	10	74.24	35	69.3	120	88.8	2	97.54
15	92.93	15	93.84	45	94.5	140	99.7	3	99.23
20	91.81	20	95.88	55	99.5	160	93.5	4	99.37
25	89.71	60	96.05	65	91.3	180	63.7	5	99.54
30	85.17	–	–	–	–	200	30.3	10	99.73

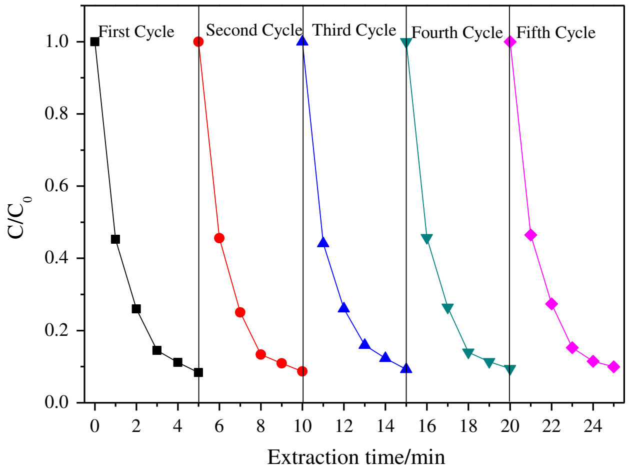


Fig. 12. Dephenolization efficiency vs. regeneration cycle (pyridine/coal tar = 8%, pH 7, extraction temperature = 50℃, rotary speed = 160 rpm, *R* = 1.4:1 (organic/aqueous), and extraction time = 5 min).

complexation system for the industrial purpose of circulating extraction using the regenerated extractant. In this study, sodium hydroxide was used as an efficient stripping reagent to recover the extractant under the following experimental conditions: alkali–oil phase ratio is 1:2, 15% of NaOH concentration, reaction temperature 55℃, shaking speed 140 rpm, and reaction time 5 min (detailed data associated with stripping process are provided in Table 7).

In order to determine the dephenolization efficiency of regenerated extractant, the same experiments were repeated 5 times under the same experimental conditions (Fig. 12), and the dephenolization efficiencies of each cycle were 91.65, 91.31, 90.76, 90.54, and 90.03%, respectively, which means that the recycled extractant still exhibited good extraction capacity after 5 cycles. Thus, the excellent extraction performance and easy recycling property of the pyridine–coal tar extractant enable it to have great potential for practical application.

3.9. Compared with other extractants

To further assess the effectiveness of pyridine–coal tar, a comparison between different extractants has been performed in Table 8. As can be seen, the dephenolization efficiency of pyridine–coal tar was relatively low compared with bis(2-ethylhexyl) sulfoxide (BESO), 1-butylimidazole (BIMZ), and octanol under optimal experimental conditions. But a similar stripping efficiency (>99%) for the pyridine–coal tar, cumene, and BESO was observed, indicating that the pyridine–coal tar has potential application in practical

Table 8
Comparison of different extractants with dephenolization efficiency and key operating parameters

Extractants	Dephenolization efficiency (%)	Solution pH	Extraction time (min)	Extraction temperature (℃)	Phase ratio (organic/aqueous)	Stripping efficiency (%)	Refs.
Pyridine–coal tar	91.65	≤7	5	50	1.4:1	>99	–
Cumene	54.44	≤7	30	25	0.5:1	>99	[20]
BESO	97.26	<8	10	25	1:1	>99	[19]
BIMZ	95	–	30	RT	1.2:1	76	[18]
Octanol	>99	3	3	RT	3:1	–	[21]

extraction process of the phenols. Interestingly, the maximum dephenolization efficiencies of all extractants are achieved at pH ≤ 7. This may be attributed to phenol ionization when the pH value becomes higher than phenol pK_a (see Table 8).

4. Conclusion

The pyridine–coal tar was prepared and its performance was investigated for treatment of phenol wastewater with 4,000 mg/L concentration. The results show that the dephenolization efficiency could be up to 90% in 5 min at 50°C when the pyridine content in the extractant was 8% with 1.4:1 of phase ratio, 160 rpm of rotary speed at weak acid or neutral pH. The extracted phenol in pyridine–coal tar could be recovered by 15% NaOH, and the dephenolization efficiency maintained at more than 90% during 5 recycle processes. The pyridine–coal tar could be used to extract phenol in real phenolic effluent from the coal gasification plant, and dephenolization efficiency was about 86.7%. This work provided a promising method with strong pertinence and theoretical basis, which not only can effectively reduce the phenol concentration from industrial effluent for recycling the useful phenols, but also provide new feasible way for the comprehensive utilization of coal tar and improving its economic value that has a big potential in environmental application.

Acknowledgments

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Symbol list

B — constant
C — concentration (mg/L)
D — distribution coefficient
E — dephenolization efficiency
K — apparent extraction equilibrium constant
S — stripping efficiency
V — volumes (ml)
RT — room temperature (°C)
pK_H — common logarithm of dissociation equilibrium constants

Subscripts

ex — extractant
ph — phenol solution
eq — equilibrium state
ini — initial state

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