

Original Research

Complex Mechanism of Phenol Extraction of Coal Gasification Wastewater

Song Du^{1,2}, Jikun Wang², Wenbiao Jin^{1*}, Weimin Wu³

¹Harbin Institute of Technology, Shenzhen Graduate School, Shenzhen Engineering Laboratory of Microalgal Bioenergy, Shenzhen, China

²Beijing Research Institute of Coal Chemical, China Coal Research Institute, Beijing, China

³Department of Civil and Environmental Engineering, Stanford University, Stanford, California, USA

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Abstract

In this study, tri-butyl-phosphate (TBP)-kerosene is used as the extraction solvent to remove phenols from coal gasification wastewater, and the complex mechanism of the extraction is investigated. An effect experiment is conducted to determine the complex structures, the enthalpy change of reaction, and the effect of extraction solvent concentration and temperature on the distribution coefficient. To predict the extraction effect before the experiment, the distribution coefficient mathematical model of phenol extraction is established, which is based on a liquid-liquid extraction model and verified for accuracy by the experiment. The effect experiment result shows that with an increase in concentration of TBP and decrease in temperature, the extraction distribution coefficient increases and further determines the complex structures and the enthalpy change of the reaction. Meanwhile, a comparison of experimental and calculated values in the model experiment result shows that the average relative error of extraction distribution coefficient is 5.56% in different concentrations of TBP and 2.72% in different temperatures. Considering the error of the experiment, this work concludes that the distribution coefficient mathematical model of phenol extraction has a high predictive effect on the distribution coefficient and extraction rate of volatile phenol in actual wastewater.

Keywords: complex mechanism, phenol, TBP, distribution coefficient, mathematical model

Introduction

Coal gasification wastewater is a notorious toxic industrial effluent that urgently needs treatment because of its high concentration of pollution components, such as phenols, ammonia, carbon dioxide, hydrogen sulfide, and tar [1-2]. Phenols are considered priority pollutants [3] and have strong biological toxicity but

have high value as an important chemical raw material [4]. These pollutants are difficult to biologically degrade because of their toxicity and high concentration [5-7]. A considerably high concentration of phenols in water [8-9] is generated and discharged into the environment without effective treatment of wastewater, causing a significant effect on the ecosystem. Therefore, a pretreatment for removing phenols from wastewater is required to relieve the biological treatment burden and improve the recovery rate of phenols.

The physical extraction method, which is based on the solubility of phenol in different solvents, is the

*e-mail: 13828830095@139.com

Table 1. Basic water quality of wastewater.

Water quality	Volatile phenol	Nonvolatile phenol	Total phenol	BOD	COD	Ammonia
Content (ppm)	4100	1063	5163	2810	16200	142

main phenol extraction method [10]. At present, most gasification plants at home and abroad remove phenols from wastewater by physical extraction [11], such as at Harbin [12], Henan Yima [13], and United States Great Plains Gasification Plants [14], etc. However, this method has many problems [15-16], such as low extraction rate, significant solvent loss, and secondary pollution, which increase the biological treatment burden. In comparison with the physical extraction method, the complex extraction method [17-18], which is based on chemical reaction, is highly efficient and selective [19-21] in removing phenols. However, there has been little researches about it, especially its complex extraction mechanism.

Considering the extraction effect and economic cost, this work uses TBP [22-24] as the complexing solvent and kerosene as the diluent to investigate the mechanism of extracting phenol from coal gasification wastewater. First we analyzed the basic water quality of the wastewater. Then we researched the variety of main organic compounds in the wastewater by GC-MS and the complex mechanism of the extraction by IR. Meanwhile, we designed the effect experiment of the concentration of TBP and temperatures on distribution coefficient. Finally we validated the distribution coefficient model and compared the experimental and calculated values of distribution coefficients.

Materials and Methods

Materials

TBP, phenol, sulfuric acid, 4-aminoantipyrine, sodium thiosulfate, potassium iodide, bromine standard solution, kerosene

Ultraviolet spectrophotometer, infrared light metering instrument, Gas chromatography-mass spectrometry (GC-MS) (Agilent Technologies 7890A), ultrapure water meter, pH meter (Thermo Scientific Orion 4-Star, USA)

Experimental Methods

Equal volumes of the extraction solvent and the water sample were added into the liquid separating funnel and fully agitated for 10 min at constant temperature. Then they were statically separated (60 min). Finally, we obtained the equilibrium water phase and selected three samples to detect phenol content.

The concentration of volatile phenols was detected by 4-aminoantipyrine spectrophotometric analysis before and after extraction. The minimum detectable concentration of the analysis method was 0.1 mg/L. The concentration of phenols in the equilibrium extraction phase was determined in accordance with the material balance calculation. The extraction distribution coefficient D is expressed in Equation (1).

$$D = \frac{C_e}{C_w} \quad (1)$$

...where C_e and C_w denote the concentrations of the extraction and water phases, respectively.

Results and Discussion

Water Quality Analysis

The water sample consists of wastewater after removing ammonia from the Henan Yima Gasification

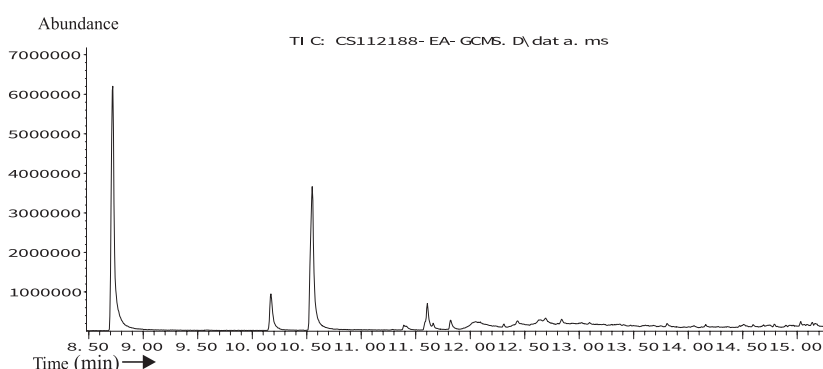


Fig. 1. Analysis of main organic compounds by GC-MS.

Table 2. Variety of main organic compounds in wastewater.

Number	Retention time/min	Component	Number	Retention time/min	Component
1	8.721	Phenol	8	12.050	2-Hydroxy-6-methoxyacetophenone
2	10.172	2-Methylphenol	9	12.310	2-Ethyl-4-methylphenol
3	10.550	3-Methylphenol	10	12.434	2,6-Bis(hydroxymethyl)-p-cresol
4	11.389	2,5-Dimethylphenol	11	12.629	6-Hydroxy-4- methyl group-2,3-two methyl benzene
5	11.590	4-Ethylphenol	12	12.694	5-Hydroxyhydrindene
6	11.606	2,3-Dimethylphenol	13	12.840	4-Allylphenol
7	11.817	3,4-Dimethylphenol	14	13.809	2-Naphthol

Plant. Table 1 shows the analysis result of the basic water quality of the wastewater.

Table 1 shows that the contents of total phenol, volatile phenol, and nonvolatile phenol reach 5163, 4100, and 1063 ppm, respectively. These values meet the characteristic of high phenolic content of gasification wastewater. Therefore, the treatment of phenols is necessary. Biodegradability (BOD/COD) is 0.17, which is less than 0.3 (when biodegradability is more than 0.3, the requirement of biological treatment is met). The water sample is the wastewater after removing ammonia; thus, the content of ammonia is reduced to 142 ppm.

Gas chromatography-mass spectrometry (GC-MS) is used to analyze the variety of main organic compounds in the wastewater [25]. Fig. 1 shows the result.

In combination with GC-MS spectrum data, the variety of the main organic compounds in the wastewater is shown in Table 2.

Fig. 1 and Table 2 show that the main organic compounds are phenols, benzene, and alcohol. Phenols

are the most prevalent organic compound, and its variety is complex.

To further investigate the variety and content of phenols in the wastewater, an Agilent Technologies 7890A GC is used as a gas chromatograph, a DB-Petro capillary column is used as a chromatographic column, and a flame ionization detector is used as a detector. The external standard method is used for analysis [26]. Fig. 2 shows the analysis result.

In combination with GC spectrum data, the variety and content of phenols are shown in Table 3.

Fig. 2 and Table 3 show that the proportions of identified and unidentified phenols are up to 61.55% and 38.55%, respectively.

Effect of TBP Concentration on Extraction Distribution Coefficient D

The concentration of TBP is the main factor in the extraction process [27]. With an increase in the concentration of TBP, the extraction distribution

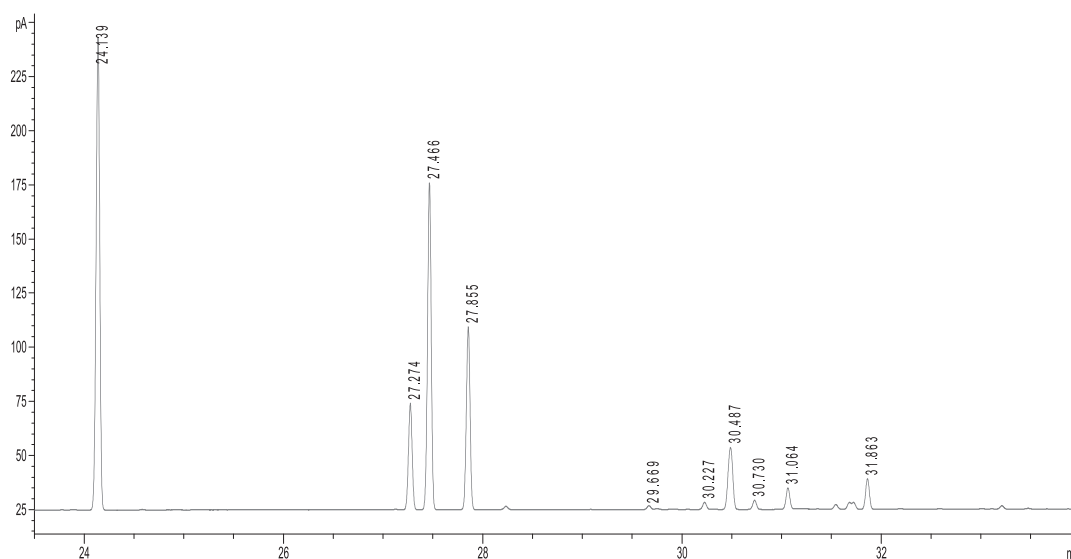


Fig. 2. Analysis of phenols by GC.

Table 3. Variety and content of phenols.

Number	Component	Proportion/%	Number	Component	Proportion/%
1	Phenol	21.39	9	p-Ethylphenol	0.89
2	o-Cresol	4.85	10	2,6-Dimethylphenol	1.97
3	m-Cresol	15.33	11	2,3-Dimethylphenol	0.33
4	p-Cresol	8.52	12	3,4-Dimethylphenol	1.44
5	o-Ethylphenol	1.87	13	2-Naphthol	0.76
6	2,5-Dimethylphenol	0.77	Identified phenols		61.45
7	m-Ethylphenol	2.75	Unidentified phenols		38.55
8	2,4-Dimethylphenol	0.58	Total		100

coefficient increases, leading to the consumption of a large amount of extraction solvent. To obtain the high extraction distribution coefficient and to reduce the consumption of extraction solvent, the effect of concentration on the extraction distribution coefficient must be investigated. To accurately analyze the effect of concentration on removing phenols, simulated water with a phenol content of 4100 ppm (the content of volatile phenol in the wastewater is 4100 ppm.) is used to investigate the change of distribution coefficient with TBP concentration (25°C). Fig 3 presents the results.

Fig. 3 shows that with an increase in concentration, the distribution coefficient increases significantly. When the concentration of TBP is 0, the distribution coefficient is merely 1.94. When the concentration of TBP increases to 10%, the distribution coefficient significantly increases to 17.6. When the concentration of TBP is up to 50%, the distribution coefficient reaches a maximum of 61.4. However, 30% TBP–kerosene is the best extraction solvent when the extraction effect and solvent consumption are considered.

To investigate the association mechanism of complex reaction, FT-IR is used to analyze the wave number change of the characteristic functional groups in the extraction phase [28]. Fig. 4 presents the graph.

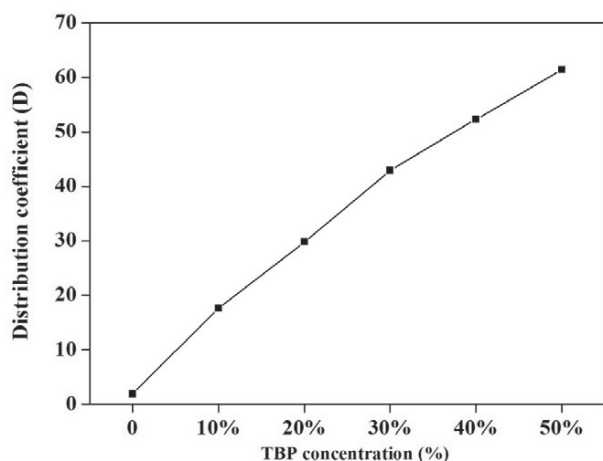


Fig. 3. Effect of concentration of TBP on distribution coefficient.

Fig. 4 shows that when TBP is loaded with phenols, a large wave number shift occurs on the characteristic peak of the P = O bond of TBP. The wave number of the P = O characteristic peak changes from 1272 cm⁻¹ to 1239 cm⁻¹. The wave number of the hydroxyl characteristic peak of phenol shifts from 3352 cm⁻¹ to 3258 cm⁻¹. However, the wave number of the methyl and methylene peak in TBP, which is in the range of 2870 cm⁻¹ to 2960 cm⁻¹, shows nearly no change. According to the wave number change of the characteristic functional groups, the association method of TBP and phenol is hydrogen bonding.

To further investigate the structure and composition of the complex formed by the complex reaction between TBP and phenol, the complexation ratio is assumed to be 1:n. ArOH is used to represent phenol. The complex extraction equation is expressed in Equation (2).



The extraction equilibrium constant K is presented in Equation (3).

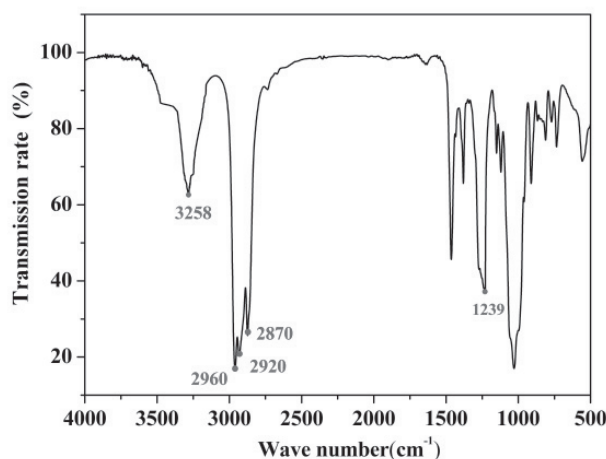


Fig. 4. IR spectra of TBP and phenol extracts.

$$K = \frac{[\text{ArOH} \cdot n\text{TBP(o)}]}{[\text{ArOH}][\text{TBP(o)}]^n} \quad (3)$$

...where $[\text{ArOH} \cdot n\text{TBP(o)}]$ is the concentration of the complex and $[\text{TBP(o)}]$ represents the concentration of TBP after extraction equilibrium.

The dissociation equilibrium equation of phenol is expressed in Equation (4):



The dissociation equilibrium constant K_a is presented in Equation (5):

$$K_a = \frac{[\text{H}^+][\text{ArO}^-]}{[\text{ArOH}]} \quad (5)$$

...where $[\text{ArOH}]$ is the concentration of phenol and $[\text{ArO}^-]$ denotes the concentration of negative ions in the water after the dissociation of phenol.

By combining Equations (2) and (4), the extraction distribution coefficient of phenol by complex extraction is expressed in Equation (6):

$$D = \frac{[\text{ArOH} \cdot n\text{TBP}]}{[\text{ArOH}] + [\text{ArO}^-]} = \frac{[\text{ArOH} \cdot n\text{TBP}]}{[\text{ArOH}](1 + \frac{[\text{ArO}^-]}{[\text{ArOH}]})} = \frac{[\text{ArOH} \cdot n\text{TBP}]}{[\text{ArOH}](1 + 10^{\text{pH} - \text{p}K_a})} \\ = \frac{K[\text{TBP}]^n}{1 + 10^{\text{pH} - \text{p}K_a}} \quad (6)$$

By converting Equation (6) into a logarithmic equation, we can obtain Equation (7):

$$\lg D = n \lg[\text{TBP}](o) + \text{constant} \quad (7)$$

In accordance with the relationship between $\lg D$ and $\lg[\text{TBP}](o)$ in Equation (7), the equilibrium distribution coefficient D is determined in different concentrations of TBP and the equilibrium concentration of TBP is measured after extraction equilibrium. Table 4 shows the result.

The relationship of $\lg D$ and $\lg[\text{TBP}]$ is formulated on the basis of the data in Table 4. Fig. 5 presents the results.

Table 4. Distribution coefficient of phenol in different concentrations of TBP.

Volume fraction of TBP/%	Volume fraction of kerosene/%	Concentration of TBP/mol/L	D
10	90	0.3657	17.6
20	80	0.7314	29.8
30	70	1.0970	42.9
40	60	1.4627	52.3
50	50	1.8284	61.4

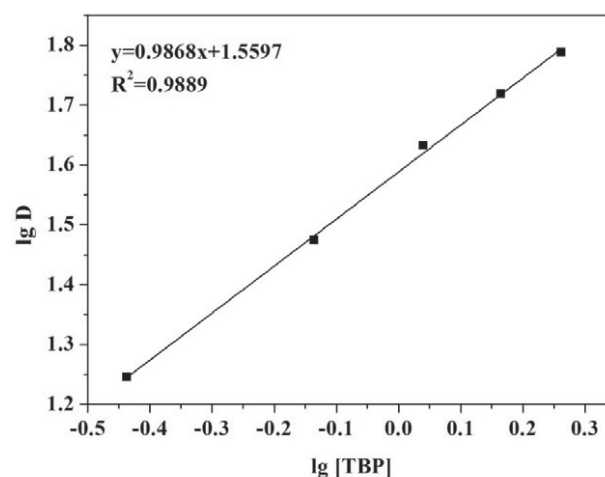
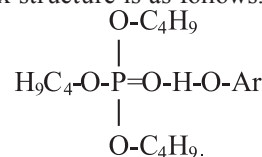


Fig. 5 Relationship of $\lg D$ and $\lg[\text{TBP}]$.

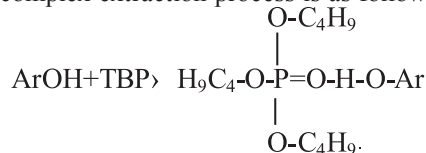
Fig. 5 shows that the linear slope is 0.9868, which is close to 1. Thus, the complexation ratio of the complex composed of TBP and phenol is 1:1.

By combining the association mechanism of the complex reaction and the complexation ratio of the complex, the complex structure of TBP and phenol is determined.

The complex structure is as follows:



The complex extraction process is as follows:



Effect of Temperature on Extraction Distribution Coefficient D

The temperature is the main factor affecting the extraction process [29]. When the temperature rises, it not only leads to a great loss of energy, but also to the reduction of distribution coefficient. To obtain a high extraction distribution coefficient and reduce the loss of energy, the effect of temperature on the extraction distribution coefficient must be investigated. Moreover, the content of volatile phenol in the wastewater is 4100 mg/L. Therefore, to accurately analyze the effect of temperature on the extraction of phenol, we select a simulated water sample with a phenolic content of 4100 mg/L to investigate the effect of temperature on the extraction distribution coefficient. Fig. 6 presents the results.

Fig. 6 shows that temperature has a significant influence on the distribution coefficient. When the temperature is 20°C, the distribution coefficient

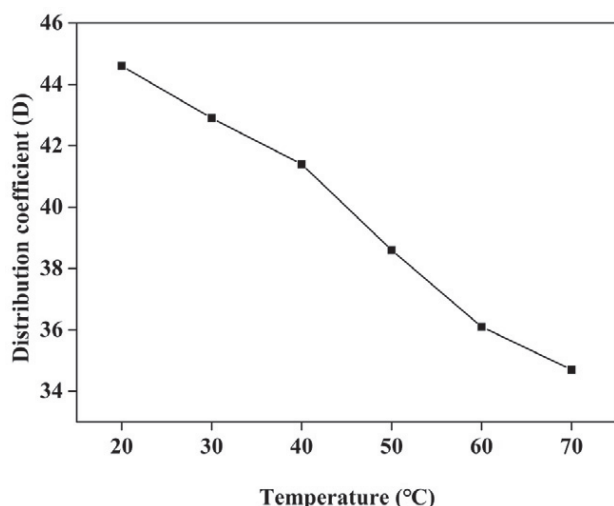


Fig. 6. Effect of temperature on distribution coefficient.

reaches the maximum of 44.6. While the temperature is increased to 70°C, the distribution coefficient decreases to 34.7. With an increase in temperature, the distribution coefficient significantly decreases. Considering the extraction effect and loss of energy, we select 20°C as the best experiment temperature.

The enthalpy change (ΔH) of the complex reaction of TBP with phenol can be obtained in terms of the relationship curve between $\lg K$ and $1/T$ by introducing the Van't Hoff equation:

$$\lg K = -\frac{\Delta H}{RT} + C \quad (8)$$

By integrating Equation (8), we can obtain Equation (9):

$$K = \exp \left(-\frac{\Delta H}{RT} + C \right) \quad (9)$$

In addition, due to the same extraction conditions, distribution coefficient (D) and equilibrium constant (K) satisfy the linear relationship. Hence, we can obtain Equation (10):

$$\lg D = -\frac{\Delta H}{RT} + C \quad (10)$$

Table 5. Distribution coefficient of phenol in different temperatures.

Extraction solvent	Temperature/°C	D
30% TBP-kerosene	30	42.9
	40	41.4
	50	38.6
	60	36.1
	70	34.7

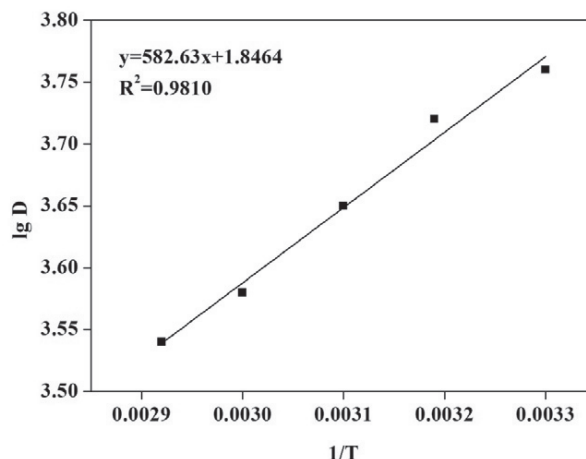


Fig. 7. Relationship of $\lg D$ and ΔH .

In accordance with the relationship between $\lg D$ and ΔH in Equation (10), the extraction distribution coefficient is determined at 30°C to 70°C with 30% TBP-kerosene as the extraction solvent. Table 5 presents the result.

The relationship of $\lg D$ and ΔH is formulated on the basis of the data in Table 5. Fig. 7 presents the results.

Fig. 7 shows that the linear slope is 582.63. Therefore, the enthalpy change is -4843.98 J/mol. The complex reaction of TBP with phenol is an exothermic reaction, and heating is not conducive to the extraction of the reaction.

Complex Extraction Equilibrium Model of Phenol

Description of Complex Extraction Equilibrium

To establish the extraction equilibrium model, the assumptions need to be formulated on the basis of the law of conservation of mass:

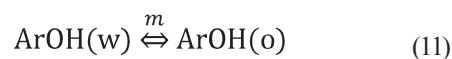
The activity of phenol in water and complex is proportional to its concentration.

The concentration of TBP is greater than that of phenol in water.

The total distribution coefficient is the sum of the distribution coefficients of the complex and physical extractions when the effect of kerosene on the physical extraction of phenol is considered.

Establishing the Distribution Coefficient Model

In addition to the complex equilibrium extraction and the dissociation equilibrium of phenol, the effect of kerosene on the physical extraction of phenol is also considered. The physical extraction of phenol is expressed in Equation (11).



...where $[ArOH](o)$ represents the concentration of phenol in the extraction phase after extraction, and $[ArOH](w)$ is the concentration of phenol in the water phase after extraction. Thus, the physical distribution coefficient (m) is expressed in Equation (12):

$$m = \frac{[ArOH](o)}{[ArOH](w)} \quad (12)$$

The total distribution coefficient ($D(total)$) is expressed in Equation (13):

$$D(total) = \frac{[ArOH \cdot nTOA] + \phi[ArOH](o)}{[ArOH] + [ArO^-]} \quad (13)$$

...where ϕ represents the volume fraction of kerosene. By combining Equations (7), (9), and (10), we can obtain Equation (14):

$$D(total) = \frac{K[TBP]^n + \phi m}{1 + 10^{pH - pKa}} \quad (14)$$

Equation (15) is derived by combining Equations (9) and (14)

$$D(total) = \frac{\exp\left(-\frac{\Delta H}{RT} + C\right)[TBP]^n + \phi m}{1 + 10^{pH - pKa}} \quad (15)$$

In accordance with one hydroxyl of phenol, the negative logarithm (pKa) of the dissociation constant of phenol is 9.98. In accordance with the complexation ratio of the complex, n of the equation is 1. In accordance with the relationship between $\lg D$ and ΔH , ΔH of the reaction is -4843.98 J/mol, and n of the equation is 1.8464. When the volume fraction of kerosene is 100%, the distribution coefficient (m) is 1.94. Therefore, we can derive Equation (16):

$$D(total) = \frac{(\exp\left(-\frac{-4843.98}{RT} + 1.8464\right))[TBP] + 1.94\phi}{1 + 10^{pH - 9.98}} \quad (16)$$

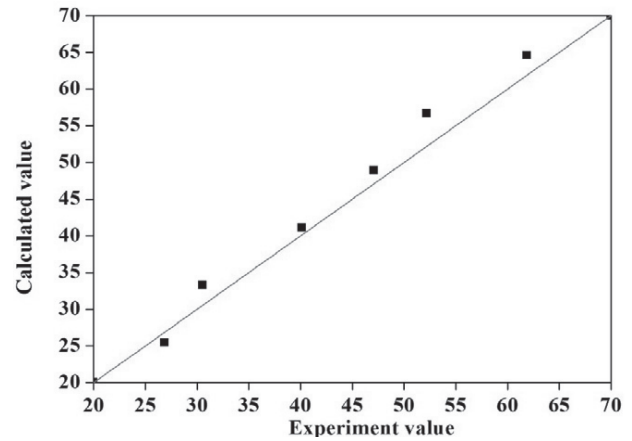


Fig. 8. Relationship of experimental and calculated values of distribution coefficient in different concentrations of TBP.

Equation (16) expresses the distribution coefficient model of extracting phenol.

Validating the Distribution Coefficient Model

To ensure the accuracy of the distribution coefficient model, the calculation value of the model needs to be validated by the experimental value of the distribution coefficient, which is extracted from the actual wastewater. Two variables of TBP concentration and temperature exist in the model; thus the model is validated from two sides.

First, the model is validated in different concentrations of TBP. The experimental condition is that the solvent water ratio is 1:1 at 23°C and single-stage cross-flow extraction. Moreover, the experimental values of the volatile phenol in the wastewater are collectively called phenols because of the complex types of phenol in the wastewater. Table 6 shows the result.

The relationship of the experimental and calculated values of the distribution coefficient is formulated on the basis of the data in Table 6. Fig. 8 presents the results.

Table 6 and Fig. 8 show that the average relative error of the experimental and calculated values of the distribution coefficient is 5.56% in different

Table 6. Comparison of experimental and calculated values of distribution coefficient in different concentrations of TBP.

Volume fraction of TBP (%)	Concentration of TBP (mol/L)	Volume fraction of kerosene (%)	Extraction rate (%)	pH of equilibrium water phase	D (experimental value)	D (calculated value)	Relative error (%)
15%	0.5486	85	96.41	6.47	26.86	25.42	5.35
20%	0.7314	80	96.83	5.56	30.55	33.26	8.86
25%	0.9143	75	97.57	6.32	40.15	41.08	2.32
30%	1.097	70	97.92	5.98	47.08	48.91	3.88
35%	1.279	65	98.12	6.35	52.19	56.69	8.62
40%	1.463	60	98.41	6.12	61.89	64.57	4.34

Table 7. Comparison of experimental and calculated values of distribution coefficient at different temperatures.

Temperature (°C)	Extraction rate (%)	pH of equilibrium water phase	D (experimental value)	D (calculated value)	Relative error (%)
10	98.18	6.47	53.95	55.82	3.46
20	98.06	5.56	50.55	52.13	3.14
30	97.92	6.32	47.08	48.90	3.87
40	97.9	5.98	46.67	46.07	1.28
50	97.79	6.35	44.37	43.56	1.82
60	97.57	6.12	40.22	41.34	2.79

concentrations of TBP. The model has a high prediction accuracy of the distribution coefficient, considering the error of the experimental process.

Second, the model is validated in different temperatures. The experimental condition is that the extraction solvent is 40% TBP-kerosene at a 1:1 solvent:water ratio and single-stage cross-flow extraction. The experimental values of the volatile phenol in the wastewater are collectively called phenols because of the complex types of phenol in the wastewater. Table 7 shows the results.

The relationship of the experimental and calculated values of the distribution coefficient is formulated on the basis of the data in Table 7. Fig. 9 presents the results.

Table 7 and Fig. 9 show that the average relative error of the experimental and calculated values of the distribution coefficient is 2.72% at different temperatures. The model has a high prediction accuracy of the distribution coefficient, considering the error of the experimental process.

The model is suitable for the prediction of the actual wastewater distribution coefficient and the extraction rate when the solvent water ratio is 1:1 and extraction

is single-stage cross-flow, considering the error of the experimental process.

Conclusions

We investigated the complex mechanism of phenol extraction of coal gasification wastewater. The following conclusions were obtained by using TBP to remove phenol:

With an increase in TBP concentration, the distribution coefficient significantly increased. Considering the extraction effect and solvent consumption, we selected 30% TBP-kerosene as the best extraction solvent.

The association method of TBP and phenol was hydrogen bonding by FT-IR.

The complexation ratio of the complex composed of TBP and phenol was 1:1, as determined by the slope method. The complex structure and extraction process were further studied.

With an increase in temperature, the distribution coefficient significantly decreased. The complex reaction of TBP with phenol was exothermic, and the enthalpy change of the complex reaction of TBP with phenol was -4843.98 J/mol.

The complex extraction equilibrium model of phenol was established considering that the total distribution coefficient was the sum of the distribution coefficients of the complex and physical extractions:

$$D(\text{total}) = \frac{(\exp(-\frac{-4843.98}{RT} + 1.8464))[\text{TBP}] + 1.94\varphi}{1 + 10^{\text{pH} - 9.98}}$$

By using the distribution coefficient model for validation, the average relative error of the experimental and calculated values of the distribution coefficient were 5.56% in different concentrations and 2.72% in different temperatures of TBP. With the error of the experimental process considered, the model was suitable for predicting the actual wastewater distribution coefficient and the extraction rate when the solvent water ratio was 1:1 and the extraction was single-stage cross-flow.

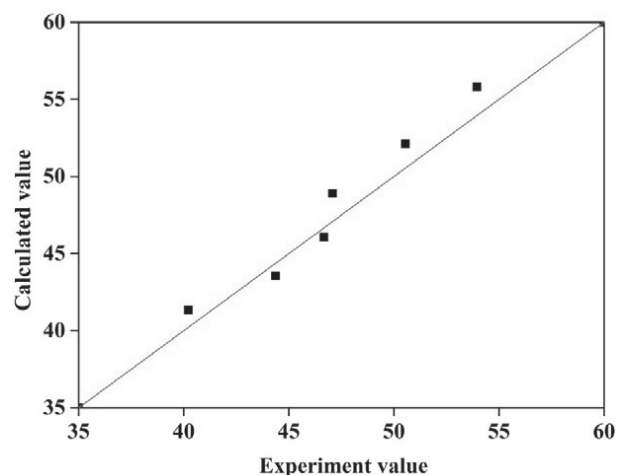


Fig. 9. Relationship of experimental and calculated values of distribution coefficient at different temperatures.

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Conflict of Interest

The authors declare no conflict of interest.

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