

# Extraction of phenol in wastewater with annular centrifugal contactors

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## Abstract

Solvent extraction is an effective way to treat and recover the phenolic compounds from the high content phenolic wastewater at present. The experimental study on treating the wastewater containing phenol has been carried out with QH-1 extractant (the amine mixture) and annular centrifugal contactors. The distribution ratio of phenol was 108.6 for QH-1–phenol system. The mass-transfer process of phenol for the system was mainly controlled by diffusion. When the flow ratio (aqueous/organic) was changed from 1/1 to 4/1, the rotor speed was changed from 2500 to 4000 r/min, and the total flow of two phases was changed from 20 to 70 mL/min, the mass-transfer efficiency  $E$  of the single-stage centrifugal contactor was more than 95%. When the flow ratio was changed from 4.4/1 to 4.9/1, the rotor speed was 3000 r/min, and the total flow of two phases was changed from 43.0 to 47.0 mL/min, the extraction rate  $\rho$  of the three-stage cascade was more than 99%. When 15% NaOH was used for stripping of phenol in QH-1, the stripping efficiency of the three-stage cascade was also more than 99% under the experimental conditions.

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**Keywords:** Phenol; Wastewater; Annular centrifugal contactor; QH-1; Extraction

## 1. Introduction

Phenol is a common pollutant discharged from petroleum and petrochemical, coal-conversion, and phenol-production industries. In general, two types of treatment processes are available, one based on the destructive process principle and the other based on a recovery or regenerative scheme. When the phenolic content in the wastewater exceeds 1000 ppm, the recovery scheme becomes an attractive proposition. Some methods were proposed to recover phenol from the high content phenolic wastewaters, such as adsorption [1,2], solvent extraction [3,4], membrane separation [5–7], biodegradation [8,9], and thermal decomposition [10,11]. The most effectively and widely practiced method for treating the high content phenolic wastewaters is based on solvent extraction using polar organic solvents with high distribution ratio of the solute. The common extractants for treating phenolic wastewaters are TBP (tributyl phosphate), 1-octanol, N-503, MIBK (methyl ketone), QH-1 and so on [12–15]. QH-1 is a high efficient complexing extractant, which is the amine mixture. It has been developed by Tsinghua Univer-

sity, China, and has been used for treating phenolic wastewaters successfully.

Compared with conventional contactors such as mixer-settlers and column extractors, annular centrifugal contactors are the efficient extraction equipments in extraction processes, and offer the following advantages:

- low liquid inventories;
- excellent phase separation;
- high mass transfer efficiency;
- compact and short therefore low capital costs;
- maintain steady-state when shut-down;
- rapid start-up, shut-down and wash out of the process liquors;
- direct interconnection of any desired number of contactors for multi-stage processes.

The primary centrifugal contactor, which was the paddle type, had been successfully developed and operated for many years at the Savannah River Plant (SRL). In the late 1960s, the paddle-type centrifugal contactor was modified to the annular type at Argonne National Laboratory (ANL). The ANL centrifugal contactor was reliable, easy to operate and maintain [16–18]. In the late 1970s, Institute of Nuclear and New Energy Technology

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Table 1  
Properties of QH-1

Density (kg/m <sup>3</sup> )	Viscosity (Pa s)	Interfacial tension (N/m <sup>3</sup> )	Solubility (kg/m <sup>3</sup> )	Flashing point (°C)	Boiling point (°C)
838	$2.12 \times 10^{-3}$	$1.1 \times 10^{-2}$	<0.1	68	191

(INET), Tsinghua University, China, developed its own annular centrifugal contactor. A series of INET centrifugal contactors have been developed with the rotor diameter from 10 to 230 mm, and have been successfully applied in some industrial fields [19–21].

In this paper, study on treating the phenolic wastewater was carried out with the 20-mm annular centrifugal contactors and QH-1 extractant.

## 2. Experimental

### 2.1. Materials

QH-1 was obtained from Department of Chemical Engineering, Tsinghua University, China, which was a mixed extractant. Its chemical formula was unpublished. Its main physical properties are shown in Table 1 [22].

It was reported that when QH-1 was used to extract phenol, acid solution was required, namely, when pH of the aqueous phase was less than 3, the extraction efficiency of QH-1 was excellent. And it was also reported that when QH-1 was used to extract phenol, the higher temperature was, the worse the extraction efficiency of QH-1 was [23]. H<sub>2</sub>SO<sub>4</sub> was usually used to adjust acidity of the aqueous phase. However, the main material of experimental apparatus (annular centrifugal contactors, controlled volume pumps, etc.) was the stainless steel, which can be corroded by H<sub>2</sub>SO<sub>4</sub>. So, in our work, we chose pH 2 and  $T=25\text{ }^{\circ}\text{C}$  (ambient temperature), and HNO<sub>3</sub> was used to adjust acidity of the aqueous phase, which did not affect the extraction efficiency.

Phenol was obtained from Beijing Chemical Plant, China, and was used to compound the simulated phenolic wastewater.

### 2.2. Apparatus

The 20-mm annular centrifugal contactor was developed and manufactured by INET. Its hold-up volume was approximately 20 mL. The HP8452A UV-spectrophotometer and the SA-520 acidometer were obtained from HP Co., USA and ORION Co., USA, respectively.

The main structures of the 20-mm annular centrifugal contactor made of stainless steel are shown in Fig. 1. Two immiscible liquids are fed from the opposite sides into the annular mixing zone between the spinning rotor and the stationary housing, and are mixed by skin friction as they flow down the annular space. Four radial vanes in the bottom of the housing inhibit the rotation of the mixture and direct it through the inlet in the bottom and into the inside of the rotor. Here the emulsion breaks rapidly under the high centrifugal force. The separated phases flow separately through the heavy phase weir and the light phase

weir of the rotor into their collector rings in the housing. Then each liquid leaves its collector ring through a tangential exit, and flows into an adjacent stage respectively. The extraction cascade is formed by linking the exit to its corresponding inlet of the neighbor contactor in the opposite direction.

### 2.3. Analytical methods

The HP8452A UV-spectrophotometer was used to measure the phenol concentration of the aqueous phase. The SA-520 acidometer was used to measure pH of the aqueous phase.

## 3. Procedures

### 3.1. The mass transfer rate test

The mass transfer rate of phenol in the QH-1–phenol (pH 2.0) system was determined through the following process: 20.0 mL QH-1 and 20.0 mL simulated phenolic wastewater were magnetically stirred for 3 s in a test tube, and then two phases were separated by centrifugation and were analyzed, and the extraction stage efficiency  $E$  was calculated. The same processes were carried out when the mixing time was 5, 10, 20, 40 s, respectively.

The extraction stage efficiency of phenol was calculated by Murphree equation as follows [24]:

$$E_A(\%) = \frac{(C_{A,\text{in}} - C_{A,\text{out}})}{(C_{A,\text{in}} - C_{A,\text{eq}})} \times 100 \quad (\text{for the aqueous phase})(1)$$

$$E_O(\%) = \frac{(C_{O,\text{out}} - C_{O,\text{in}})}{(C_{O,\text{eq}} - C_{O,\text{in}})} \times 100 \quad (\text{for the organic phase})(2)$$

where  $E_A$  and  $E_O$  are the extraction stage efficiency of the aqueous phase and the organic phase, respectively (%),  $C_{A,\text{in}}$  and  $C_{A,\text{out}}$  the inlet and the outlet concentrations of phenol in the

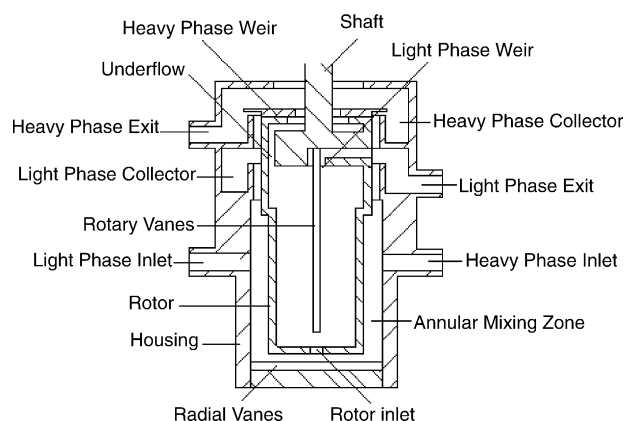


Fig. 1. Schematic diagram of the 20-mm annular centrifugal contactor.

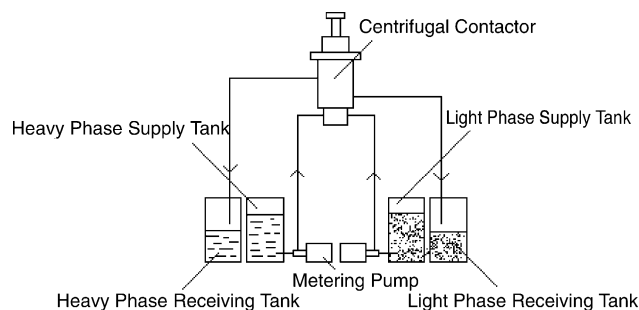


Fig. 2. Flowsheet of the single-stage contactor test.

aqueous phase, respectively (mg/L),  $C_{O,in}$  and  $C_{O,out}$  the inlet and outlet concentrations of phenol in the organic phase, respectively (mg/L),  $C_{A,eq}$  and  $C_{O,eq}$  the equilibrium concentrations of phenol in the aqueous phase and in the organic phase, respectively (mg/L).

### 3.2. The distribution ratio test

The distribution ratio of phenol in the QH-1–phenol (pH 2.0) system was determined through the following process: 20.0 mL QH-1 and 20.0 mL simulated phenolic wastewater were magnetically stirred for 5 min in a test tube, then two phases were separated by centrifugation and were analyzed. It was known from results of the mass transfer rate test that the system reached equilibrium after stirring 5 min. The distribution ratio was calculated by the following equation:

$$D = \frac{C_{O,eq}}{C_{A,eq}} \quad (3)$$

where  $D$  is the distribution ratio of phenol,  $C_{O,eq}$  and  $C_{A,eq}$  the equilibrium concentrations of phenol in the organic phase and in the aqueous phase, respectively (mg/L).

### 3.3. The single-stage test

The mass transfer tests of the single stage centrifugal contactor were carried out with the QH-1–phenol (pH 2.0) system to determine variation of the stage efficiency  $E$  with the total flow  $Q$  of two phases, the rotor speed  $\omega$  and the flow ratio  $R$  (aqueous/organic). The flowsheet of the single-stage contactor tests is shown in Fig. 2.

### 3.4. The three-stage test

The mass transfer tests and the stripping tests of the three-stage cascade were carried out, respectively. The flowsheet of

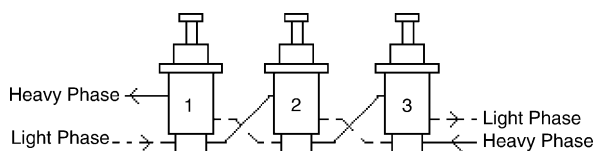


Fig. 3. Flowsheet of the three-stage contactor test.

the cascade tests is shown in Fig. 3. The back-extractant was 15% NaOH.

The extraction rate of the cascade was described as follows [24]:

$$\rho(\%) = \frac{(C_{O,out} - C_{O,in})V_O}{C_{A,in}V_A} \times 100 \quad (4)$$

where  $\rho$  is the extraction rate (%),  $V_O$  and  $V_A$  the volume of the organic phase and the aqueous phase, respectively (L), the definition of  $C_{O,in}$ ,  $C_{O,out}$  and  $C_{A,in}$  the same as above.

## 4. Results and discussion

### 4.1. Mass transfer rate of phenol

Experimental results are presented in Table 2, and show when the mixing time is more than 3 s,  $E$  is more than 99%, and the extraction process reaches equilibrium. It was obtained that the mass-transfer process of phenol for the experimental system was mainly controlled by diffusion.

The mixing time of two phases in the 20-mm annular centrifugal contactor is more than 4.5 s when the rotor speed is changed from 2000 to 4000 r/min, and the total flow is changed from 35 to 80 mL/min. Moreover, the degree of mixing for two phases in the annular centrifugal contactor is stronger than in the test-tube. So the annular centrifugal contactor can be used in treating the phenolic wastewater.

### 4.2. Distribution ratio of phenol

The experimental result is presented in Table 2, and indicates that the distribution ratio of phenol is 108.6 in the QH-1–phenol (pH 2.0) system (Table 3). So phenol is easy to be extracted by QH-1.

### 4.3. Mass transfer efficiency of the single-stage contactor

When the initial phenol concentration of the aqueous phase was 5005 mg/L, the flow ratio  $R$  (aqueous/organic) was changed from 1/1 to 4/1, the rotor speed  $\omega$  was changed from 2500 to 4000 r/min, and the total flow  $Q$  of two phases was changed

Table 2  
Variation of  $E$  with the mixing time (25 °C)

$t$ (s)	3	5	10	20	40
$C_{A,in}$ (mg/L)	5005.0	5005.0	5005.0	5005.0	5005.0
$C_{A,out}$ (mg/L)	46.06	47.07	45.57	44.37	44.77
$C_{A,eq}$ (mg/L)	45.65	45.65	45.65	45.65	45.65
$E$ (%)	99.99	99.97	100.0	100.0	100.0

Table 3  
Distribution coefficient of phenol (25 °C)

Aqueous phase	Organic phase	$C_{A,eq}$ (mg/L)	Distribution ratio
5005.0 mg/L phenol–HNO <sub>3</sub> solution	QH-1	45.65	108.6

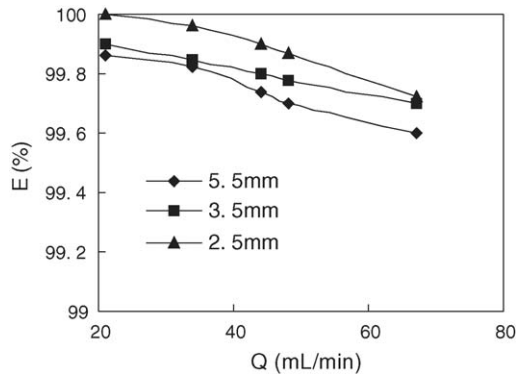


Fig. 4. Variation of  $E$  with  $Q$  for various widths of annular mixing zone (25 °C)  $\omega$ , 3000 r/min;  $R$ , 1/1.

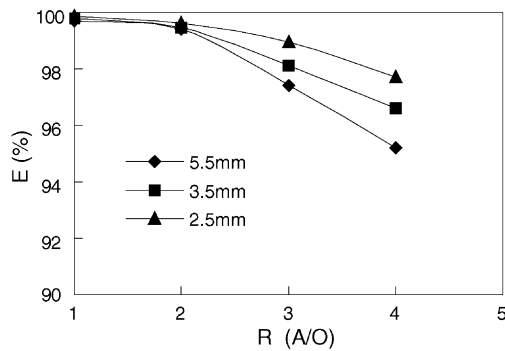


Fig. 5. Variation of  $E$  with  $R$  for various widths of annular mixing zone (25 °C)  $\omega$ , 3000 r/min;  $Q$ , 50 mL/min.

from 20 to 70 mL/min, and the width  $b$  of annular mixing zone was changed from 2.5 to 5.5 mm, the experimental results of the single stage contactor are presented in Figs. 4–6 which show the mass transfer efficiency is more than 95%, and the mass transfer efficiency decreases with increase of the width of annular mixing zone. When the width of annular mixing zone was increased, mixing of two phases was not strong.

As shown in Fig. 4, the mass transfer efficiency increased with decreasing the total flow of two phases at the given rotor speed and the flow ratio. From Fig. 5, it can be seen that the mass transfer efficiency decreased with increasing the flow ratio (aqueous/organic) at the given rotor speed and the total flow. From Fig. 6, it can be seen that the mass transfer efficiency

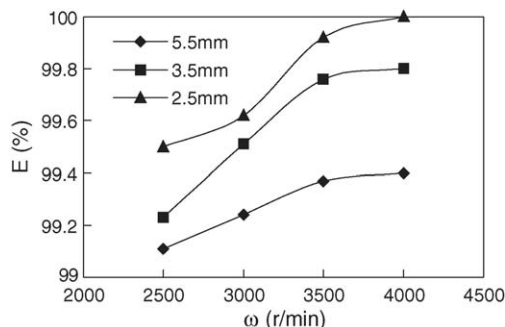


Fig. 6. Variation of  $E$  with  $\omega$  for various widths of annular mixing zone (25 °C)  $R$ , 2/1;  $Q$ , 40 mL/min.

increased with increasing the rotor speed at the given flow ratio and the total flow.

In industrial extraction equipment, the overall mass-transfer rate is given as [24–27]:

$$N = k_O a V (y^* - y) = k_A a V (x - x^*) \quad (5)$$

where  $N$  is the overall mass-transfer rate (kmol/h or mol/s),  $k_O$  and  $k_A$  the overall mass-transfer coefficients of the organic phase and the aqueous phase respectively (m/h or cm/s),  $a$  the specific interfacial area per unit volume in the extraction equipment ( $m^{-1}$  or  $cm^{-1}$ ),  $V$  the effective volume of the extraction equipment ( $m^3$  or  $cm^3$ ),  $(y^* - y)$  and  $(x - x^*)$  the mass transfer driving forces of the organic phase and the aqueous phase, respectively (kmol/ $m^3$  or mol/ $cm^3$ ).

The specific interfacial area based on unit volume of two-phase dispersion is given by:

$$a = \frac{6\phi_d}{d_m} \quad (6)$$

where  $\phi_d$  is the holdup of dispersed phase,  $d_m$  the Sauter mean drop diameter (m or cm).

The Sauter mean drop diameter ( $d_m$ ) based on the average volume-to-area ratio for  $N$  drops is given as:

$$d_m = \frac{\sum_{i=1}^N d_i^3}{\sum_{i=1}^N d_i^2} \quad (7)$$

where  $d_i$  is the drop diameter (m or cm).

It can be summarized from Eqs. (5)–(7) that the rate of attainment of equilibrium is proportional to the concentration difference (driving force) and to a physical rate constant ( $k_O 6\phi_d/d_m$  or  $k_A 6\phi_d/d_m$ ). The physical rate constant can be increased operationally by maintaining a high holdup and a small Sauter mean droplet diameter. Increase of the rate of attainment of equilibrium means increase of the mass transfer efficiency for the same extraction system and equipment.

When  $Q$  was increased, the degree of mixing and the mixing time of two phases decreased. So  $k_O$ ,  $k_A$  and  $a$  decreased, the mass transfer efficiency decreased accordingly. When  $R$  (aqueous/organic) was increased, the holdup of dispersed phase ( $\phi_d$ ) decreased (here the aqueous phase was the continuous phase, and the organic phase was the dispersed phase). So  $a$  decreased, the mass transfer efficiency also decreased accordingly. When the rotor speed was increased, the degree of mixing of two phases was stronger. So  $k_O$ ,  $k_A$  and  $a$  increased, the mass transfer efficiency increased accordingly.

#### 4.4. Mass transfer efficiency of the three-stage cascade

Experimental results of the three-stage cascade are presented in Table 4. It is shown that the extraction rate  $\rho$  can reach 99% under experimental conditions.

#### 4.5. Stripping efficiency of the three-stage cascade

The experimental results of the three-stage cascade for stripping are presented in Table 5. It is shown that the stripping rate  $\rho$

Table 4  
Results of the three-stage cascade tests (25 °C)

Aqueous phase	Organic phase	$Q$ (mL/min)	$R$	$\omega$ (r/min)	$b$ (mm)	$C_{A,out}$ (mg/L)	$\rho$ (%)
5434.4 mg/L phenol-HNO <sub>3</sub> solution	QH-1	43.0	4.4/1	3000	5.5	12.24	99.77
5434.4 mg/L phenol-HNO <sub>3</sub> solution	QH-1	47.0	4.9/1	3000	5.5	15.81	99.71

Table 5  
Results of stripping with the three-stage cascade (25 °C)

Organic phase	Aqueous phase	$Q$ (mL/min)	$R$	$\omega$ (r/min)	$b$ (mm)	$C_{O,out}$ (mg/L)	$\rho$ (%)
18727 mg/L phenol-QH-1 solution	15% NaOH	52.6	1/4.0	3000	5.5	10.20	99.95
18727 mg/L phenol-QH-1 solution	15% NaOH	51.8	1/5.1	3000	5.5	25.90	99.87

can reach 99% at experimental conditions. The extractant after stripping can be used for extraction again, and the extraction efficiency was the same as the new extractant. The emulsification had not happened when annular centrifugal contactors were used for stripping.

## 5. Conclusions

Liquid-liquid extraction is a means available to remove phenol from wastewater. The experimental study on treating the wastewater containing phenol has been carried out with QH-1. The distribution ratio of the phenol was 108.6 for QH-1-phenol system. The mass-transfer process of phenol for QH-1-phenol system was mainly controlled by diffusion. Annular centrifugal contactors are the high efficient liquid-liquid extraction equipments, and can be used to treat phenolic wastewaters. The mass-transfer efficiency  $E$  of the single-stage contactor can reach more than 95% at the experimental conditions. Both the extraction rate  $\rho$  and the stripping efficiency of the three-stage cascade can also reach more than 99% at the experimental conditions.

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