Desalination and Water Treatment
www.deswater.com
doi: 10.1080/19443994.2013.796993

51 (2013) 3826–3831
May

Taylor & Francis
Taylor & Francis Group

Solvent extraction of phenol with cumene from wastewater

Junteng Liu, Jing Xie, Zhongqi Ren, Weidong Zhang*

State Key Laboratory of Chemical Resource Engineering, Beijing Key Laboratory of Membrane Science and Technology, Beijing University of Chemical Technology, P.O. Box 1#, No. 15, N. 3rd Ring Rd East, Beijing 100029, China
Tel. +86 10 6442 3628; Fax: +86 10 6443 6781; email: zhangwd@mail.buct.edu.cn

Received 8 August 2012; Accepted 10 April 2013

ABSTRACT

In this paper, the extraction of phenol from wastewater using cumene as an extractant is investigated. H_2SO_4 and HCl are used for the pH adjustment of the wastewater. The effects of extraction temperature, pH value, initial concentration, and phase ratio on the extraction performance are studied. The results show that the distribution coefficient *D* increases with the increase in extraction temperature (from 25 to 55˚C) and the decrease in pH value of the aqueous phase (from 13.0 to 0.0). The type of the acids and the initial concentration of phenol show a weak effect on the distribution coefficient. The stripping of loaded organic and the reuse of extractant are also discussed.

Keywords: Phenol; Solvent extraction; Cumene

---

1. Introduction

Phenol is a widely used commodity chemical in manufacturing process, such as synthetic resins, plastics, pharmaceuticals, intermediate of dyes, etc. Since 1952, the three-step Hock process (also called cumene peroxidation method) is the main commercial process for the production of phenol, which consists of three steps [1–3]: (1) reaction of benzene with propylene to produce cumene; (2) oxidization of cumene with air to produce cumene hydroperoxide; and (3) decomposition of cumene hydroperoxide with an acid to produce phenol along with acetone as a byproduct. A large amount of phenol wastewater is produced in this production process, which leads to a serious environmental problem because of its highly toxic and hazardous character [4]. Both, US Environmental Protection Agency and European Union regard phenol as hazardous substance that is discharged into the aquatic environments.

Several techniques have been developed to dephenolize the wastewater, such as solvent extraction [5], biological treatment [6], pyrolytic method [7], adsorption [8,9], and membrane separation [10,11]. Among them, solvent extraction is the most effective method to remove and recover phenol from the wastewater. Many extractants have been applied to the extraction of phenol and show excellent extraction performance, such as octanol [4], N-octanoylpyrrolidine [12], amines [5], Cyanex 923 [13], diethyl carbonate [14], MIBK [15], TBP [16], and ionic liquids [17], etc. As cumene is the intermediate material in cumene–phenol process, which can be circulated in

---

*Corresponding author.

Presented at the 2012 Qingdao International Desalination Conference June 26–29, 2012, Qingdao, China

the whole process, the reuse of cumene will not induce secondary pollutants. Besides, cumene shows many advantages as an extractant in terms of its low cost, low solubility, and excellent chemical stability. Consequently, cumene is the most widely used extractant in industry. It is of good importance to investigate its extraction performance systemically for design and optimization of a solvent extraction process.

Using cumene as an extractant, the extraction of phenol from wastewater is investigated in this paper. The following factors are considered, including pH value of the phenol solution, type of the inorganic acid used to adjust the pH of the feed phase, phenol initial concentration, phase ratio, and extraction temperature. Furthermore, the stripping and reuse of the extractant are also investigated.

2. Materials and methods

2.1. Chemicals and solutions

The chemicals used in this work, include C_6H_5OH (>99.0%), NaOH (>96.0%), H_2SO_4 (95%–98%), HCl (36%–38%), cumene (>98.5%), 4-amino antipyrine (>99.0%), and potassium hexacyanoferrate (>99.0%). All these chemicals are analytically pure and used without further purification. Physical properties of cumene and phenol are listed in Table 1. The simulated phenol wastewater is prepared with deionized water and weighed amount of phenol. The pH is adjusted to a desired value by adding different type of acids (H_2SO_4, HCl). Solutions of 0.1–1.0 mol/L sodium hydroxide are used as stripping reagents.

2.2. Experiments

Known volumes of extractant and phenol solution are shaken mechanically in a constant-temperature water bath with a vibrating rate of 200 rpm at the selected temperature for an appropriate time period. Then, the samples are allowed to stand for 20 min for phase separation. The faffinate sample is taken from the bottom layer for phenol concentration analyses. The phenol concentration in the extractant is calculated by mass balance. After extraction, the loaded organic phase is stripped with $0.1\,\mathrm{mol\,L^{-1}}$ of NaOH solution, and then the regenerated extractant is used for following cycles of extraction and stripping tests. All the stripping experiments are carried out using the same procedure and conditions as the extraction experiments.

Table 1
Physical properties of the pure compounds

Chemical	Cumene	Phenol
Formula	$C_6H_5C_3H_5$	C_6H_5OH
Relative molecular	120.2	94.1
Boiling point, ℃	152.4	182
Flashing point	31	–
Relative density	0.86	1.07

The phenol concentration in the aqueous solution and the stripping reagent is measured by a UV-vis spectrophotometer setting the absorption wavelength at 510 nm and 4-amino antipyrine (4-AAP) used as the indicator. The pH value of the aqueous phase is determined with a pH meter (PXS-450 model) with a deviation of ± 0.01. Each experiment is repeated three times under each operating condition, and the results from same experiment agree with 5%.

The results are expressed as phase ratio α, distribution coefficient D, extraction efficiency E, and stripping efficiency R defined as

$$\alpha = \frac{V_e}{V_p} \tag{1}$$

$$D = \frac{C_{e,eq}}{C_{p,eq}} \tag{2}$$

$$E = \frac{C_{p,ini} - C_{e,eq}}{C_{p,ini}} \times 100\% \tag{3}$$

$$S = \frac{C_{s,eq}}{C_{e,ini}} \times 100\% \tag{4}$$

where C and V are the concentration (mg/L) and the volume (ml), the subscripts p, e, s, eq, and ini represent the phenol solution, extractant, and stripping reagent at equilibrium and initial state, respectively.

3. Results and discussion

3.1. Effect of the extraction time

The effect of the extraction time on distribution coefficient D is considered, and the results are shown in Fig. 1. The operation condition is 100 ppm and pH value 7 of phenol solution at 25℃. As shown in Fig. 1, the extraction efficiency remains constant after 20 min. These results indicate that the time required to achieve the extraction equilibrium is less than 30 min. So, 30 min is selected for the extraction in the following experiments.

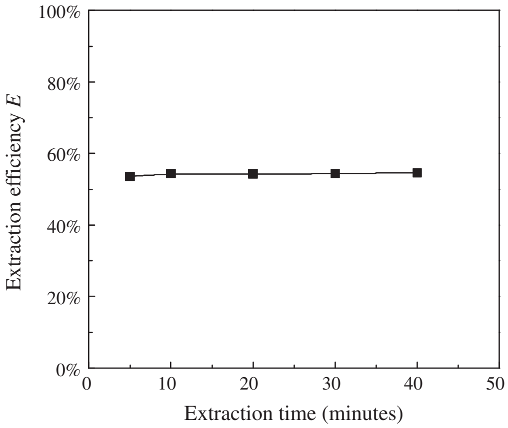

Fig. 1. Effect of time on the extraction of phenol from aqueous solution at 298.3 K; pH = 7; $C_{p,ini} = 100$ ppm.

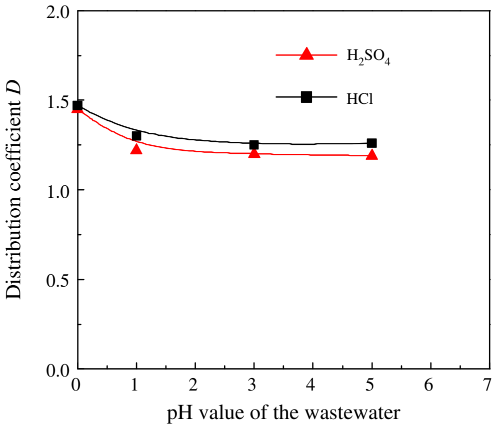

Fig. 2. Extraction of phenol from different inorganic acid aqueous phases using cumene at 298.3 K; $C_{p,ini} = 100$ ppm.

3.2. *Effect of the inorganic acid*

HCl and H_2SO_4 are used to adjust acidity of the phenol aqueous solution. No significant change on the distribution coefficient *D* is found from the results shown in Fig. 2. This fact ascertains that the effect of the kind of inorganic acid on the extraction can be ignored. Because of its non-volatility, H_2SO_4 is usually selected for the pH adjustment of the phenol solution in industries.

3.3. *Effect of the pH value*

The effect of the pH value of the phenol solution on extraction behavior is investigated by adjusting a 100 ppm phenol solution to the desired pH by the addition of H_2SO_4. The results are listed in Table 2 and Fig. 3. It is shown that the extraction performance strongly depends on the pH value of the phenol solution. From 0 to 9.0 of the pH, phenol is effectively extracted from the aqueous solution and the pH value has a small effect on the distribution coefficient *D*. The distribution coefficient and the extraction efficiency reach maximum of 1.45 and 59.2%, respectively. However, the distribution coefficient, *D*, decreases sharply from 1.15 to a minimum value of 0.04 when pH value is kept increasing to 13.0. These results agree with similar work on the extraction of phenol with MIBK (methyl isobutyl ketone) from the coal gasification [18]. Li et al. also found that the distribution coefficient for phenol extracted with N-octanoylpyrrolidine begins to drop at pH > 8, and little phenol can be extracted at pH > 12 [12].

Table 2
Effect of pH value on the extraction of phenol from H_2SO_4 aqueous solution at 298.3 K

pH	$C_{p,ini}$/ppm	$C_{p,eq}$/ppm	$C_{e,ini\ i}$/ppm	D	E/%
0	100	40.97	59.03	1.45	59.22
1	100	45.26	54.74	1.22	54.95
3	100	45.60	54.4	1.20	54.61
5	100	45.77	54.23	1.19	54.44
7	100	45.77	54.23	1.19	54.44
9	100	46.80	53.2	1.15	53.41
10	100	61.89	38.11	0.62	38.39
11	100	95.34	4.66	0.05	5.10
12	100	96.37	3.63	0.04	4.07
13	100	96.54	3.46	0.04	3.90

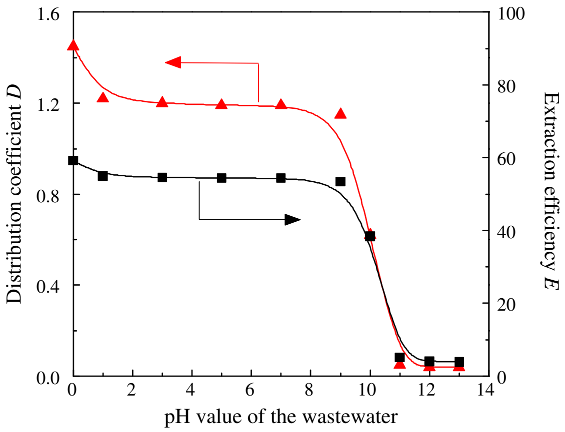

Fig. 3. Effect of pH value on the extraction of phenol from H_2SO_4 aqueous solution at 298.3 K, $C_{p,ini} = 100$ ppm.

This deterioration of the extraction performance can be explained by phenol-ionization at a high pH value. The acidic dissociation constant of phenol pKa is 10. When pH becomes higher than 9, the extraction efficiency decreases greatly due to phenol's dissociation. Therefore, to ensure the phenol removal efficiency in practical application, the pH value of the phenol solution should be adjusted and the best pH value should be kept at neutral or weak acid considering the operating cost.

3.4. Effects of the phenol initial concentration

The phenol initial concentration of the aqueous phase ranges between 50 and 5,000 ppm and the pH value are fixed at 1 or 7. The results reported in Fig. 4 show the relationship between the initial phenol concentration and the distribution coefficient, *D*. The distribution coefficient is independent of the initial concentration and pH value under this experimental condition.

3.5. Effects of the phase ratio

In this work, the extraction of phenol between water and solvent is measured over a range of initial phenol concentrations from 50 ppm to 2,167 ppm at a phase ratio between 0.5 and 4.0. The results are shown in Fig. 5. The extraction efficiency, *E*, increases with the increase of the phase ratio and higher phase ratio will facilitate the extraction performance. The separation of phenol relies on its different solubility in extractant and water. Higher phase ratio means more extractant in unit volume of the phenol solution, which significantly enhances the cumene extraction capability. Therefore, the degree of extraction for phenol can be improved with the addition of the cumene.

3.6. Effects of the temperature

At a constant phase ratio of one, the effect of the temperature on extraction process is studied. The plot of distribution coefficient *D* vs. temperature is depicted in Fig. 6. The distribution coefficient *D* increases with the increase of temperature, independent of the initial concentration of phenol. The linear relation between distribution coefficient *D* and temperature is found to be as described in Eq. (5).

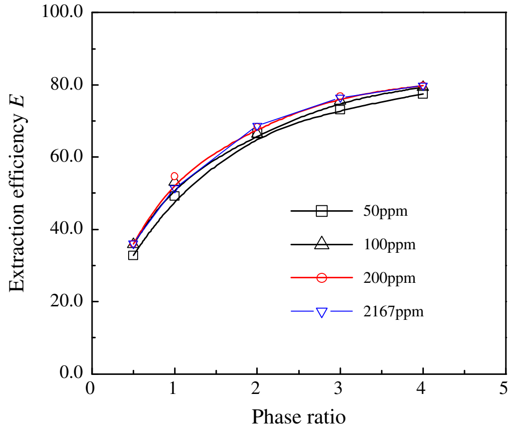

Fig. 5. Effect of phase ratio on the distribution coefficient, *D*, of phenol from phenol aqueous solution at 298.3 K.

$$D = 7.2 \times 10^{-3}T - 0.9878 \quad (5)$$

3.7. The stripping and reuse of extractant

In industry, it is of important to reuse the extractant without significant loss in extraction ability. Cumene-free phenol is required to recycle for the use of extraction. For the assessment of recycling behavior of cumene, the feed aqueous phase is equilibrated with the organic phase at 1:1 phase ratio. Sodium

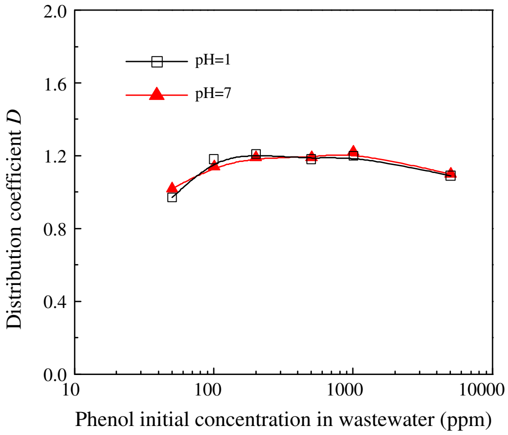

Fig. 4. Effects of the initial concentration of phenol from H_2SO_4 aqueous solution at 298.3 K.

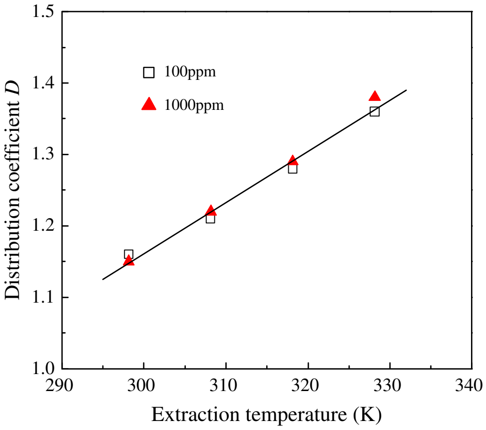

Fig. 6. *D* vs. *T* for the extraction of phenol by cumene from aqueous solution at various initial concentrations.

Table 3
Effect of NaOH concentration on stripping of phenol from loaded organic at 298.3 K

C_{NaOH}/mol L^{-1}	$C_{e,ini}$/ppm	$C_{s,eq}$/ppm	S
0	1169.53	627.27	53.63
0.1	1169.53	1165.85	99.68
0.5	1169.53	1169.28	99.98
1.0	1169.53	1169.28	99.98

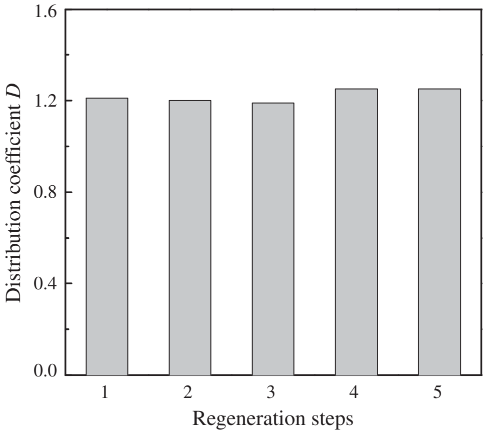

Fig. 7. D vs. the number of used times of cumene for the extraction of phenol by cumene from aqueous solution at 298.3 K; $C_{p,ini} = 1004$ ppm; phase ratio 1:1.

hydroxide is used as the stripping reagent. In the stripping process, the transfer of phenol from the organic phase back to the aqueous phase involves the following chemical reaction [19]:

$$C_6H_5OH + NaOH \rightarrow C_6H_5ONa + H_2O \qquad (6)$$

The equilibrium data on the recovery of phenol is given in Table 3. For an initial feed concentration of 1,169 ppm in organic phase, more than 99% of the phenol could be stripped with a 0.1 mol L^{-1} NaOH solution. It means, almost all the phenol is recovered. Increasing the NaOH concentration further has no significant improvement on the stripping efficiency. The ability of cumene to be reused for the extraction of phenol from aqueous solution is investigated (Fig. 7). No obvious decrease in the percent extraction or recovery of phenol is observed within five regeneration steps.

4. Conclusion

In this work, the extraction of phenol using cumene as the extractant is investigated. Cumene shows excellent extraction performance on phenol in acidic solution. The extraction efficiency has slight difference between H_2SO_4 and HCl for pH value adjustment. Cumene has an excellent extraction capability on phenol. When 0.1 mol/L NaOH is used for stripping of phenol from loaded cumene, the stripping efficiency is above 99% under the current experimental conditions.

Acknowledgements

We gratefully acknowledge the financial support for this project from the National Natural Science Foundation of China (Nos. 21006001 and 21076012) and the Research Fund for the Doctoral Program of Higher Education (Nos. 200800100001 and 20100010120001).

References

[1] R.J. Schmidt, Industrial catalytic processes-phenol production, Appl. Catal. A 280 (2005) 89–103.
[2] M.R. Mafra, M.A. Krähenbühl, Liquid–liquid equilibrium of (water + acetone) with cumene or α-methylstyrene or phenol at temperatures of (323.15 and 333.15) K, J. Chem. Eng. Data 51 (2006) 753–756.
[3] G.D. Yadav, S.S. Salgaonkar, Loss prevention and waste minimization with cascade-engineered green synthesis of bisphenol-a from cumene hydroperoxide and phenol using heteropoly acid-supported clay catalysts, Org. Process Res. Dev. 13 (2009) 501–509.
[4] H. Jiang, Y. Fang, Y. Fu, Studies on the extraction of phenol in wastewater, J. Hazard. Mater. 101 (2003) 179–190.
[5] J.Q. Xu, W.H. Duan, X.Z. Zhou, Extraction of phenol in wastewater with annular centrifugal contactors, J. Hazard. Mater. 131 (2006) 98–102.
[6] Y. Jiang, J.P. Wen, H.M. Li, The biodegradation of phenol at high initial concentration by the yeast Candida tropicalis, Biochem. Eng. J. 24 (2005) 243–247.
[7] A. Fortuny, C. Bengoa, J. Font, Bimetallic catalysts for continuous catalytic wet air oxidation of phenol, J. Hazard. Mater. 64 (1999) 181–193.
[8] Y.H. Shen, Removal of phenol from water by adsorption flocculation using organobentonite, Water Res. 36 (2002) 1107–1114.
[9] M. Akcay, G. Akcay, The removal of phenolic compounds from aqueous solutions by organophilic bentonite, J. Hazard. Mater. 113 (2004) 189–193.
[10] J.Y. Luan, A. Plaisier, Study on treatment of wastewater containing nitrophenol compounds by liquid membrane process, J. Membr. Sci. 229 (2004) 235–239.
[11] W. Kujawski, A. Warszawski, W. Ratajczak, Removal of phenol from wastewater by different separation techniques, Desalination 163 (2004) 287–296.
[12] Z. Li, M. Wu, Z. Jiao, B. Bao, S. Lu, Extraction of phenol from wastewater by N-octanoylpyrrolidine, J. Hazard. Mater. 114 (2004) 111–114.
[13] M.T.A. Reisa, O.M.F. Freitasa, M.R.C. Ismael, J.M.R. Carvalho, Recovery of phenol from aqueous solutions using liquid membranes with Cyanex 923, J. Membr. Sci. 305 (2007) 313–324.
[14] J. Olejniczak, J. Staniewski, J. Szymanowski, Extraction of phenols and phenyl acetates with diethyl carbonate, Anal. Chim. Acta 535 (2005) 251–257.
[15] M.S.A. Palma, J.L. Paiva, M. Zilli, A. Converti, Batch phenol removal from methyl isobutyl ketone by liquid–liquid extraction with chemical reaction, Chem. Eng. Prog. 46 (2007) 764–768.

[16] N. Messikh, M.H. Samar, L. Messikh, Neural network analysis of liquid–liquid extraction of phenol from wastewater using TBP solvent, Desalination 208 (2007) 42–48.

[17] J. Fan, Y. Fan, Y. Pei, K. Wua, J. Wang, M. Fan, Solvent extraction of selected endocrine-disrupting phenols using ionic liquids, Sep. Purif. Technol. 61 (2008) 324–331.

[18] C. Yang, Y. Qian, L. Zhang, J. Feng, Solvent extraction process development and on-site trial-plant for phenol removal from industrial coal-gasification wastewater, Chem. Eng. J. 117 (2006) 179–185.

[19] K. Trivunac, S. Stevanovic, M. Mitrovic, Pertraction of phenol in hollow-fiber membrane contactor, Desalination 162 (2004) 93–101.