



ORIGINAL ARTICLE

# Study on the extraction kinetics of phenolic compounds from petroleum refinery waste lye



Yanbo Zhou <sup>\*</sup>, Feng Gao, Yin Zhao, Jun Lu

College of Resource and Environmental Engineering, East China University of Science and Technology, Shanghai 200237, China

Received 10 August 2011; accepted 22 November 2011

Available online 28 November 2011

## KEYWORDS

Waste lye;  
Extraction;  
Phenols;  
Kinetics

**Abstract** A large amount of waste lye is produced in petroleum refineries during alkali cleaning process, which consists of high concentration of phenols, sulfides, oils and other pollutants. In this study, tributyl phosphate (TBP) was used as extraction agent and the extraction kinetics of phenolic compounds was investigated by the constant interfacial cell method. The effects of stirring speed, temperature and specific area on extraction rate were studied. The experimental results show that the extraction of phenols by TBP is a first-order reaction, and the extraction process may be controlled by diffusion. The effects of stirring speed and specific area on extraction rate are significant.

© 2011 Production and hosting by Elsevier B.V. on behalf of King Saud University.  
Open access under [CC BY-NC-ND license](#).

## 1. Introduction

A large amount of waste lye is produced in petroleum refineries during alkali cleaning process, which contains high concentration of phenolic pollutants that is the most damaging to the environment. Therefore, we must adopt an effective method to eliminate phenols in waste lye to achieve the purpose of environmental protection.

Researches on the treatment of phenol wastewater are numerous, many scholars study and develop series of effective treatment technologies to reduce the phenol content, such as ion exchange, adsorption, extraction, advanced oxidation,

chemical precipitation, membrane separation and biological treatment methods (Cichy and Szymanowsky, 2002; Terzyk, 2007; Stavropoulos et al., 2008; Saravanan et al., 2008). The phenol removal performance of general physical extraction is not good due to the solvent that cannot be recycled; while the complex extraction provides high selectivity, high separation efficiency and it could be re-used (Guido et al., 2008). So the complex extraction is more suitable for engineering application. However, the majority of dynamic factors of extraction system are higher than the equilibrium separation factors. A thorough study on the extraction kinetics is very essential for the extraction equipments design or enlarging (Danesi et al., 1980). Among the above mentioned factors, determining the control type of complex extraction and its kinetics model is extremely important. Engineers could find corresponding methods to speed up the extraction process and increase the separation efficiency based on the kinetic information (Geist et al., 2000; Miyake and Baba, 2000; Biswas and Mondal, 2003). Constant interfacial cell with laminar flow developed by Zheng et al. (1998) is a kind of revised Lewis cell. Many studies demonstrated that it is a good

\* Corresponding author. Tel./fax: +86 21 64252876.

E-mail address: [zhouyanbo@ecust.edu.cn](mailto:zhouyanbo@ecust.edu.cn) (Y. Zhou).

Peer review under responsibility of King Saud University.



Production and hosting by Elsevier

instrument to investigate extraction kinetics because of its stable interface and efficient forced convection.

In this work, the extraction kinetics of phenolic compounds from waste lye with tributyl phosphate (TBP) in cyclohexane using constant interfacial cell with laminar flow was investigated. The purpose is to understand the reaction kinetics of the system, and provide useful information on developing more efficient and economical waste lye treatment process.

## 2. Materials and methods

### 2.1. Materials

Reagents: Tributyl phosphate (TBP) and cyclohexane (AR, Shanghai LingFeng Chemical Reagent Co., Ltd.). They are mixed in proper proportion to produce the organic phase for extraction; the waste lye used for extraction is provided by the Fushun Petrochemical Company (mainly phenol and other monophenol, the mixed phenol concentration of 15,500–25,000 mg/L).

### 2.2. Extraction experiments

The extraction kinetics was performed by using a homemade constant interfacial cell with laminar flow as previously described. Aqueous phase (the upper phase) and organic phase (the lower phase) are stirred simultaneously in order to realize adverse current extraction of phenols. Identical aliquots (200 mL) of aqueous phase containing phenols and the organic phase containing TBP are introduced into the cell without disturbing the interface. The stirring speed is controlled at 210 rpm in order to keep the interface stable and flat except in the study of stirring speed effects. Two milliliters of the aqueous phase samples are withdrawn from the cell for analysis at 10 min intervals. The phenolic compounds content was determined by the brominated titration method. The amount of phenols transferred into the organic phase is estimated from the phenols in aqueous phase. All experiments are carried out at  $303 \pm 1$  K, unless otherwise stated. In most of the experiments, the interfacial area is maintained at  $4.53 \times 10^3$  m<sup>2</sup> except the study on the effect of specific interfacial area on the extraction rate.

## 3. Results and discussion

### 3.1. Demonstration of first-order reaction for extracting phenols by TBP

In this experiment, the initial phenol concentration in the water phase is 19,841.7 mg/L, the TBP concentration in the organic phase (using cyclohexane as solvent) is 30%. The stirring speed was controlled at 210 rpm to keep the interface stable; it can be considered that the effect of diffusion on mass transfer is almost constant. The hypothesis that the extraction of phenols by TBP was first-order reaction, mass transfer of phenol in two phases is shown as follows:



Fixing the relative interfacial area ( $V/A$ ) as  $e$ , the phenol extraction rate  $k$  is calculated as follows:

$$k = -\frac{d[\text{ArOH}_{(w)}]}{dt} = k_f[\text{ArOH}_{(w)}] - k_b[\text{ArOH}_{(o)}] \quad (2)$$

where  $V$  is the volume of water phase and organic phase, cm<sup>3</sup>;  $A$  is the interfacial area, cm<sup>2</sup>; ArOH denotes the phenols;  $w$  represents the water phase,  $o$  represents the organic phase;  $k_f$  is the positive apparent extraction rate constant,  $k_b$  is the negative apparent extraction rate constant.

Suppose the initial concentration of phenol in organic phase is zero, the phase ratio is 1:1, integrated Eq. (2) as follows:

$$\frac{a_0 - a_e}{a_e} \ln \frac{a_0 - a_e}{a_t - a_e} = k_f t \quad (3)$$

$$\frac{a_e}{a_0} \ln \frac{a_0 - a_e}{a_t - a_e} = k_b t \quad (4)$$

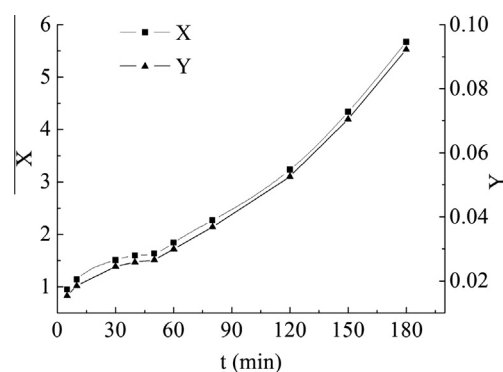
where  $a$  is the concentration of phenol, mg/L;  $t$  is the reaction time, min;  $a_0$  is the initial concentration of phenol;  $a_e$  is the equilibrium concentration of phenol and  $a_t$  is the concentration of phenol at  $t$ .

Suppose  $\frac{a_0 - a_e}{a_e} \ln \frac{a_0 - a_e}{a_t - a_e} = X$  and  $\frac{a_e}{a_0} \ln \frac{a_0 - a_e}{a_t - a_e} = Y$ , according to  $X$ ,  $Y$  plot of  $t$  (as shown in Fig. 1) we may calculate the  $k_f$  and  $k_b$ .

Fig. 1 shows that two-phase has not been fully reacted at the initial extraction stage, the positive and negative apparent extraction rate constant changed little, and extraction rate was slower. But with time increasing water and organic phase has been fully mixed and reacted, the extraction rate also increases linearly, and the slopes of  $X$  and  $Y$  versus  $t$  are approximately equal to 1. These curves pass the origin, which indicates that the extraction of phenols by TBP was a first-order reaction. In Fig. 1, we can see that the positive apparent extraction rate constant was larger than the negative apparent extraction rate constant, so the apparent extraction rate constant can be substituted by the positive apparent extraction rate constant ( $k = k_f$ ).

### 3.2. Effect of stirring speed on the extraction rate constant

The effect of the stirring speed on extraction rate was investigated by the constant interfacial cell method, so kinetic model can be initially understood. The interfacial area was maintained at  $4.53 \times 10^3$  m<sup>2</sup>, and then the stirring speed of two phases was changed. The phenol concentration in water phase was measured along with time.



**Figure 1** Experimental demonstration of first-order reaction for extraction of phenols by TBP (30 °C).

Download English Version:

<https://daneshyari.com/en/article/229499>

Download Persian Version:

<https://daneshyari.com/article/229499>

[Daneshyari.com](https://daneshyari.com)