



Solid/liquid extraction equilibria of phenolic compounds with trioctylphosphine oxide impregnated in polymeric membranes



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HIGHLIGHTS

- A model based on law of mass action was developed to predict equilibrium.
- Bivariate analysis was performed to examine factors affecting extraction degree.
- Effects of ring substitution on extraction equilibrium was studied.
- High membrane mass transfer resistance affected equilibrium distribution.
- Hydrophobicity was the dominant factor affecting distribution coefficient.

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ABSTRACT

Trioctylphosphine oxide based extractant impregnated membranes (EIM) were used for extraction of phenol and its methyl, hydroxyl and chloride substituted derivatives. The distribution coefficients of the phenols varied from 2 to 234, in the order of 1-naphthol > *p*-chlorophenol > *m*-cresol > *p*-cresol > *o*-cresol > phenol > catechol > pyrogallol > hydroquinone, when initial phenols loadings was varied in 100–2000 mg/L. An extraction model, based on the law of mass action, was formulated to predict the equilibrium distribution of the phenols. The model was in excellent agreement ($R^2 > 0.97$) with the experimental results at low phenols concentrations (<800 mg/L). At higher phenols loadings though, Langmuir isotherm was better suited for equilibrium prediction ($R^2 > 0.95$), which signified high mass transfer resistance in the EIMs. Examination of the effects of ring substitution on equilibrium, and bivariate statistical analysis between the amounts of phenols extracted into the EIMs and factors affecting phenols interaction with TOPO, indicated the dominant role of hydrophobicity in equilibrium determination. These results improve understanding of the solid/liquid equilibrium process between phenols and the EIMs, and these will be useful in designing phenol recovery process from wastewater.

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1. Introduction

Phenol and its derivatives are common pollutants in wastewater from many industrial processes, which include refineries, coking operations, coal gasification and manufacturing of disinfectants, biocides, dyes, pharmaceuticals and cosmetics (Michałowicz and Duda, 2007). Most phenols, including, chlorophenol, methylphenol and catechols are characterized by acute toxicity, and exposure to even a relatively low amount of these compounds may be detrimental for living beings (Yang et al., 2013). Therefore,

removal of phenols from industrial effluents is of utmost importance.

Phenols can be removed from wastewater through solvent extraction using organophosphorus extractants (Chang et al., 2012). These extractants are characterized by the presence of a phosphoryl group on long alkyl chains, which imparts them high Lewis basicity and hydrophobicity (Flett, 2005; Hasan et al., 2009), and makes them suitable in extraction of weak organic acids. The organophosphorus extractants offer the advantages of low water solubility, high stability, low cost and easy regeneration (Hong et al., 2001), and they are widely used in wastewater treatment (Alguacil et al., 2004; Zidi et al., 2010), fermentation (Hossain and Maisuria, 2008; Blanch, 2009) and hydrometallurgy (Alguacil et al., 2004; Navarro et al., 2009).

One of the most commonly used organophosphorus extractant

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in phenol removal is trioctylphosphine oxide (TOPO) (Reis et al., 2007). Unlike most of the other organic extractants, TOPO is a greasy solid and requires dissolution in a non-volatile carrier solvent (Navarro et al., 2008). When TOPO containing organic solvent is contacted with the aqueous phase, the extractant reacts reversibly with the solute (Lux and Siebenhofer, 2013) and enhances the mass transfer rate of the solute (González-Muñoz et al., 2003). The advantages of high partitioning capacity of TOPO is also apparent in the use of supported liquid membranes (Zidi et al., 2010) and solvent impregnated polymeric microcapsules (Kamio et al., 2002), where high extraction capacities and rapid mass transfer rates are achieved, even with a very small volume of the organic phase. Recently, TOPO has been used to develop extractant impregnated membranes (EIM) for solventless extraction of phenols (Praveen and Loh, 2013b). The EIMs were prepared by impregnating solid TOPO into the walls of hydrophobic semi-permeable membranes. They have the advantages of high distribution coefficient, high mass transfer rate and prolonged stability, which have been demonstrated in effective and sustainable treatment of phenolic wastewater (Praveen and Loh, 2014).

The kinetics of extractive separation of phenol using EIMs has been studied in detail in previous studies (Praveen and Loh, 2013b, 2014), but little is known about the extraction equilibria between EIMs and phenols, and the factors affecting the equilibria. In addition, it is difficult to predict the equilibrium due to the involvement of both sorption and solvation in the solid/liquid extraction, and the difficulty in accessing the binding sites due to high diffusion resistance within the membranes. Being weak acids, the uptake of phenols by the EIMs may be considered analogous to the solvent extraction of phenols/carboxylic acids by TOPO, which is based on solvation and hydrogen bonding between P=O of TOPO and OH of the phenol (Chang et al., 2012). The equilibrium parameters in this reactive extraction can be affected mainly by the hydrophobicity and the acid strength of the phenols (Lux and Siebenhofer, 2013). However, interactions between the phenols and TOPO during solid/liquid extraction may be very different from that in conventional solvent extraction due to immobile extractants and high mass transfer resistance in the membranes pores (Praveen and Loh, 2014).

In this research, a detailed and systematic study was performed to understand the solid/liquid extraction equilibria of phenol and its substituted derivatives by the EIMs. An equilibrium model based on the law of mass action was used in conjugation with the Langmuir isotherm to predict the distribution coefficients over a wide concentration range. The novelty of this research lies in elucidating the mechanism of EIM-based solid/liquid extraction and in identifying the factors affecting the equilibrium.

2. Material and methods

2.1. Chemicals and analytical methods

All the chemicals used in this research were of analytical grade and were used as received from the supplier. TOPO was dissolved in dichloromethane (DCM) to prepare a 400 g/L stock solution.

The aqueous concentrations of phenol and its derivatives were determined by measuring absorbance using an ultraviolet-visible spectrophotometer (UV-1240, Shimadzu, Japan). The wavelengths used to analyze phenol, *p*-chlorophenol and *p*-cresol were 270, 280 and 260 nm, whereas all other compounds investigated were measured at 220 nm. Table 1 shows the physical properties of the phenolic compounds used in this study.

Phenol concentration in the solid phase (EIMs) was calculated by mass balance. The adsorption capacity calculations were made based on the total weight of TOPO in the EIMs used in the

experiments, which was 0.688 g. The total volume of TOPO in the EIMs was 0.782 cm³. The initial concentration of TOPO in the EIMs was calculated by dividing the total amount of TOPO in EIMs by the aqueous phase volume. The initial TOPO concentration was obtained as 44.5 mM.

2.2. EIM preparation

Commercial polypropylene hollow fiber membranes (Accurel PP 50/280, Membrana GmbH, Germany) were used for the immobilization. Membrane specification is described elsewhere (Praveen and Loh, 2013a). The fibers were cut into small pieces of 6 cm each and bundles of.

20 pieces were prepared using epoxy resins (Araldite, England). For immobilization, TOPO/DCM stock solution was diluted with DCM to the desired concentration and the bundles were added to it. The contents were stirred on a shaking water bath for 1 h at 150 rpm to allow the TOPO solution to penetrate the fibers. The solution wetted fibers were then removed and rinsed twice with ultrapure water to remove DCM present on the outer surfaces of the fibers. Finally, the fibers were air dried for 24 h to evaporate the DCM, leaving solid TOPO inside the fibers. The resulting EIMs were washed thoroughly to remove loosely held extractant on the outer surfaces of the fibers. Although the tube side of the hollow fibers was not used during extraction, the empty space in the tube side was used to maximize TOPO packing in the membranes.

2.3. Extraction/stripping

The extraction experiments were carried out in batch mode in a 50 mL Falcon tube with 40 mL of phenolic solution on a thermomixer (HLC Biotech, Germany) operating at 25 °C and 200 rpm. A total of 15 bundles of EIMs were used during the solid/liquid extraction. Samples were collected periodically to measure phenols concentrations in the aqueous and the solid phases. Phenol stripping from the EIMs was carried out in 40 mL of 0.2 M sodium hydroxide solution. Each experiment was repeated three times for reproducibility. In all the experiments, the standard deviations between triplicates were less than 5%.

3. Theory

Being a solid/liquid mass transfer process, extraction of phenols by the EIMs could be considered a sorption process. Therefore, both extraction and adsorption based approaches were used to examine the distribution equilibrium.

3.1. Isotherm

In a solid/liquid mass transfer process involving adsorption, the equilibrium can be modeled using Langmuir isotherm which is given by Foo and Hameed (2010):

$$Q_e = Q_{max} \left[\frac{k_L C_e}{1 + k_L C_e} \right] \quad (1)$$

where C_e is the equilibrium aqueous phenol concentration (mg/L), k_L is the Langmuir adsorption constant (L/mg) and Q_{max} is the maximum adsorption capacity (mg/g). The parameters k_L and Q_{max} can be calculated from the slope and intercept, respectively, of a double-reciprocal plot of $1/Q_e$ against $1/C_e$.

3.2. Extraction equilibrium modeling

In the extraction of weak organic acid, phenol, by the strong

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