Reactive extraction of phenol from aqueous solution using tri-octylamine dissolved in alkanes and alcohols

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ARTICLE INFO

ABSTRACT

Extraction of phenol ($0.053 \text{ mol} \cdot \text{kg}^{-1}$) from wastewater is performed with trioctylamine (TOA: 0.023–0.091 $\text{mol} \cdot \text{kg}^{-1}$) dissolved in four solvents (decane, octane, decan-1-ol, and octan-1-ol) at a constant temperature of 298 K. The effect of TOA concentration and type of diluent on the removal efficiency of phenol have been derived. Results show that the neutral phenol molecule is effectively extracted by TOA into the organic phase at higher concentration of TOA than lower one. The equilibrium extraction results are presented in terms of distribution coefficient (D), degree of extraction ($\%E$) and loading ratio (Z). Maximum value of D ($= 12.25$) with $\%E = 92.45\%$ is observed at the highest concentration of TOA ($0.091 \text{ mol} \cdot \text{kg}^{-1}$) with octan-1-ol. A mathematical expression for the determination of D at equilibrium is presented by applying the mass action law. This model equation is used to graphically determine the equilibrium constant (K_E) and the stoichiometric coefficient (n) of extraction. Also, the individual equilibrium constants (K_{11}, K_{21} and K_{12}) for the phenol–TOA complexes formed are estimated from the regression of the experimental results. The highest value of complexation constant ($K_E = 2.3$) is found with TOA in octan-1-ol. Phenol molecules are extracted by TOA + decane or octane with simultaneous formation of 1:1 and 2:1 solvates, and by TOA + decan-1-ol or octan-1-ol by making 1:1 and 1:2 complexes in the organic phase. The extraction power of TOA in terms of D decreases in the order of octan-1-ol > decan-1-ol > octane > decane.

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1. Introduction

Phenols and/or phenolic compounds are significant families of chemicals used in many chemical industries such as petrochemical, plastics, dyes, pesticides, and preservative industries. These compounds are highly water-soluble, and toxic for living organisms. Therefore, they definitely originate in the groundwater which is one of the highest sources of consumption of water assembly. Among the phenolic compounds, phenol is the artless structure of phenolic compound and it has the maximum solubility. So, it is necessary to remove phenol from polluted water as it creates public health problems. Several technologies such as adsorption, biological treatment and photocatalytic degradation are used to treat phenol contained aqueous stream but not sufficient for the total removal of this contaminant [1–4].

Extraction method is more effective than the above-mentioned processes. Many studies related to the extraction can be found in the literature. Fan et al. [5] studied extraction of phenols from aqueous media using functionalized ionic liquids. They synthesized ionic liquids having hydroxyl-, benzyl-, and dialkyl-functionalized groups. These ionic liquids were used for the removal of phenol, and some phenolic compounds and to determine their extraction efficiencies. Li et al. [6] investigated extraction of phenol by toluene in the presence of NaOH. The effect of pH and NaOH on the extraction efficiency of phenol had been studied. Also, phase equilibrium model (NRTL) was applied to experimental results. Datta and Uslu [7] focused on the extraction of phenol from model wastewater solution using N,N-didodecyl-1-dodecanamine (tridodecylamine) diluted with benzene. The effect of pH (3 to 11) and tridodecylamine composition (5 vol.%, 15 vol.% and 20 vol.%) was investigated on the distribution of phenol. According to the results, phenol was successfully extracted by tridodecylamine from the aqueous solution to the organic media. The highest extraction efficiency of 83.41% was observed at an equilibrium pH of 5, and at a maximum composition of tridodecylamine (20 vol.%). Cumene was used as a solvent for the extraction of phenol from aqueous solution by Liu et al. [8]. Parameters such as extraction temperature, aqueous pH, initial phenol concentration, and phase-ratio were considered and their effect on the phenol extraction was studied. According to the experimental results, distribution coefficient increased with an increase in the temperature from 298 K to 328 K. Chasib [9] used five solvents [ethylene glycol, diethylene glycol,

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poly(ethylene glycol), dimethylsulfoxide and tetramethylenesulfolone] for the extraction of phenol from aqueous media. Bachman, Hand, and Othmer, and Tobias correlation was applied to the experimental data for the consistency of the tie-line. Lakshmi et al. [10] prepared new solution from imidazolium based ionic liquids for the extraction of phenol. 1-Butyl-3-methyl imidazoliumtetrafluoroborate [bmim] + [BF4] mixture was used with tributylphosphate. It was found that 97.5% of phenol was removed from the aqueous solution with 0.5 vol.% of ionic liquid [bmim] + [BF4] in TBP.

In this present study, investigation on the extraction of phenol from aqueous solution was aimed by using trioctylamine (TOA) in different diluents (alcohols: octan-1-ol, decan-1-ol, and alkanes: octane, decane). Equilibrium parameters such as distribution ratio (D), extraction degree (%E) and loading ratio (Z) were calculated using the experimental results. There is no study available in the literature by using these extractant–diluent systems. In this respect, this study will fill an important lack of the literature.

2. Chemicals and methods

2.1. Chemicals

All chemicals were used without any further purification. Physical properties of chemicals are tabulated in Table 1.

2.2. Method

Different concentrations of organic phase were prepared with mixing certain amount of TOA and diluent (octane, decane, octan-1-ol, and decan-1-ol). TOA concentrations were kept constant at 0.023 mol·kg^{-1}, 0.046 mol·kg^{-1}, 0.069 mol·kg^{-1}, and 0.091 mol·kg^{-1} in each of the diluent. Aqueous phase was prepared with a phenol concentration of 0.053 mol·kg^{-1}. This concentration was chosen as average phenol concentration for determination of its solubility in the reactive extraction. Two phases were mixed in a 50 ml Erlenmeyer flask, and then was kept for 3 h in a temperature controlled shaker at 298 K. This 3 h time was sufficient to reach equilibrium, and found from preliminary tests. After equilibrium was achieved, the samples were kept for another 2 h for settling and complete separation of phases. At equilibrium, the aqueous phase concentration was analyzed by a UV visible spectrophotometer according to method for phenol determination explained by Folin–Ciocalteu phenol reagent [11]. Phenol concentration in the organic phase was calculated by subtracting the value in aqueous phase at equilibrium from initial total amount.

3. Results and discussion

The equilibrium experiments were performed in batch mode at 298 K. The results obtained i.e. the measured values of aqueous and organic phase concentrations of phenol were utilized to calculate the distribution coefficient (D), degree of extraction (%E) and loading ratio (Z) and expressed by Eqs. (1), (2) and (3), respectively. Distribution coefficient of phenol (HP) by TOA between extract and aqueous water phases can be obtained from the ratio of total

concentration of phenol in the organic phase ($\overline{C}_{HP}$) to the aqueous phase (C_{HP}) at equilibrium.

$$D = \frac{\overline{C}_{HP}}{C_{HP}} \tag{1}$$

The degree of extraction (%E) at equilibrium can be calculated from the expression as shown in Eq. (2).

$$\%E = \frac{D}{1+D} \times 100 \tag{2}$$

The expression of loading ratio, Z is given as Eq. (3), where $[\overline{TOA}]_0$ is the total initial extractant concentration.

$$Z = \frac{\overline{C}_{HP}}{[\overline{TOA}]_0} \tag{3}$$

3.1. Physical extraction

Fig. 1 shows the physical extraction results of phenol using decane, octane, decan-1-ol and octan-1-ol, and the values of distribution coefficient were found to be 0.178, 0.233, 0.359 and 0.472, respectively with pure diluents. To increase the efficiency of the organic phase, amine based extractants can be used. The physical extraction values were compared with the chemical extraction values for 0.091 mol·kg^{-1} of TOA concentration.

3.2. Effect of diluent

The experimental results for the reactive extraction of phenol with different initial TOA concentrations (0.023 to 0.091 mol·kg^{-1}) dissolved in four solvents like octane, decane, octan-1-ol and decan-1-ol are shown in Table 2. Generally, the low molecular weight diluents lean to be miscible with water while high molecular weight ones shows poor extraction efficiency due to their lower polarity. Thus, the intermediate molecular weight diluents are generally preferred in the reactive extraction process. Also, alcohols as solvents showed better performance in the recovery of solutes from the aqueous solutions. Their high polarity makes them the most appropriate solvent among the diluent types tested by previous researchers. In the present study, octan-1-ol and decan-1-ol were used as active polar solvents having higher dipole moment, μ (5.60 × 10^{-30} Cm, and 5.34 × 10^{-30} Cm,

Table 1
Physical characteristics of chemicals used in the study.

Chemical	Molar mass (kg·kmol^{-1})	Molecular formula	Suppliers	Purity (%)
Phenol	94.11	C_6H_5OH	Merck	>99.0
Decane	142.29	$C_{10}H_{22}$	Sigma-Aldrich	>99.0
Octane	114.23	C_8H_{18}	Fluka	>99.7
Decan-1-ol	158.28	$C_{10}H_{21}OH$	Sigma-Aldrich	>99.0
Octan-1-ol	130.23	$C_8H_{17}OH$	Sigma-Aldrich	>99.0
Trioctylamine	353.68	$C_{24}H_{51}N$	Sigma-Aldrich	>98.0

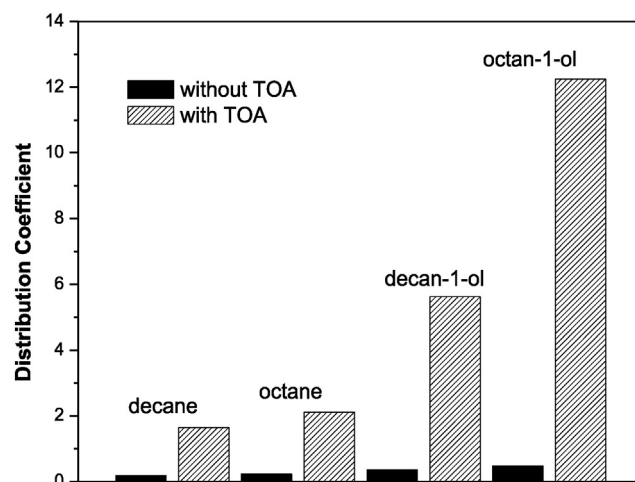**Fig. 1.** Comparison of physical extraction data with chemical extraction for TOA concentration of 0.091 mol·kg^{-1} at 298 K.