Separation and Purification Technology 173 (2017) 151–155

Contents lists available at ScienceDirect

Separation and Purification Technology

journal homepage: www.elsevier.com/locate/seppur

Evaluation of extractability of 2,4,6-trinitrophenol by secondary amine extractant in alcohols: Equilibrium and molecular dynamic study

Hasan Uslu

Istanbul Esenyurt University, Engineering & Architecture Faculty, Industrial Engineering Department, Esenyurt, Turkey

ARTICLE INFO

Article history:
Received 8 June 2016
Received in revised form 11 September 2016
Accepted 16 September 2016
Available online 17 September 2016

Keywords:
Reactive extraction
Picric acid
Amberlite LA-2
Alcohol

ABSTRACT

Extractive separation of 2,4,6-trinitrophenol (picric acid, PAH) from its aqueous solutions was examined at constant temperature of 298.2 K. The experiments were studied on the extraction of PAH (0.061 mol kg^{-1}) by Amberlite LA2, a secondary amine diluted in five different alcohols such as isopropyl alcohol, isoamyl alcohol, hexanol, heptanol, and decanol. In addition to reactive extraction, experiments on physical extraction were also performed by pure diluents. Experimental results obtained from batch extraction were evaluated in terms of distribution coefficients (K_D), extraction efficiency (E), and loading factors (Z). The highest synergistic effect was achieved with isopropyl alcohol in LA-2 at a concentration of 0.588 mol kg^{-1} as 98.36%. The highest value of probable equilibrium constants for the complex between acid and amine (1:1), K_{11} was calculated to be 11.62 for isopropyl alcohol at 0.588 mol kg^{-1} LA-2 concentration. Kinetic and potential energies of components during reactive extraction in the organic phase have been determined by molecular dynamic modeling for picric acid + isopropyl alcohol + secondary amine. The values of energy, per atom, for mixture picric acid + isopropyl + secondary amine were respectively: ~30,000 kcal/mol, ~15,000 kcal/mol, ~−50,000 kcal/mol and ~−60,000 kcal/mol.

1. Introduction

Wastewater is continuously produced from many chemical petrochemical plants such as production of pharmaceuticals, agricultural chemicals, and dyes [1,2], herbicides, fungicides, insecticides, explosives, and precursors for dyes and plasticizers [3]. 2,4,6-trinitrophenol (picric acid, PAH) is one of the nitro aromatic compounds in the wastewater that cause headache, nausea, dizziness, difficulty in swallowing, diarrhea, vomiting, shock, convulsions, or death. It can affect the central nervous system, liver, and kidneys [4–7]. Environmental Protection Agency (EPA) and European Union (EU) restrict the maximum concentration of total phenol to 10 ng/ml [8].

Nitro phenols removal was studied by many researchers using different techniques. Among the investigated technologies, the advanced oxidation [9,10], adsorption [11] and biological treatment [12–14] were some of them. Liquid membrane extraction process was used to remove nitro phenols from wastewater [15–18]. In this technique unsupported liquid membrane [19,20] or supported liquid membrane with hollow fiber [21] was also used to remove different types of nitrophenols [22–27]. The advantage of this process over other processes is its lower cost and no production of other toxic materials, and the flexibility of continuous operation in the industrial scale [28].

No enough information is available in the literature for the extraction of picric acid from wastewater. Amberlite LA2, a secondary amine with high molecular weight can be used in the removal of acids from aqueous solution forming water-insoluble amine salts [29]. Equilibrium study of the extraction of picric acid from wastewater using Amberlite LA2 in different alcohols were conducted and investigated in this work.

2. Materials and methods

2.1. Materials

The all chemical materials were used as purchased. Picric acid (2,4,6-trinitrophenol) (purity > 0.98 in mass) and alcohols (purity > 0.98 in mass) were purchased from Sigma-Aldrich. Amberlite LA-2, ((Sigma-Aldrich) > 0.99); with density of 0.83 g mL^{-1} anion exchange extractant, is a yellow liquid. Physical properties of chemicals are tabulated in Table 1.

E-mail address: hasanuslu@gmail.com

http://dx.doi.org/10.1016/j.seppur.2016.09.027

Table 1
Physical characteristics of chemicals used in the study.

Chemical	Molar mass (kg $kmol^{-1}$)	Molecular formula	Suppliers	Purity (%)
Picric acid (2,4,6-trinitrophenol)	229.10	$C_6H_3N_3O_7$	Sigma-Aldrich	>98.0
Isopropyl alcohol	60.10	C_3H_8O	Sigma-Aldrich	>98.0
Isoamyl alcohol	88.148	$C_8H_{12}O$	Fluka	>98.0
Decanol	158.28	$C_{10}H_{21}OH$	Sigma-Aldrich	>99.0
Hexanol	102.18	$C_6H_{13}OH$	Sigma-Aldrich	>98.0
Heptanol	116.20	$C_7H_{15}OH$	Sigma-Aldrich	>98.0
Amberlite La-2	353.68	$C_{24}H_{51}N$	Sigma-Aldrich	>98.0

2.2. Methods

The picric acid concentration was prepared as 0.061 mol kg^{-1} because of the maximum aqueous solubility. Both phases (organic and aqueous) were prepared so that determine effect of amine concentrations. Various concentrations of amine by dissolved in alcohols were prepared. The concentrations are 0.118 mol kg^{-1}, 0.235 mol kg^{-1}, 0.353 mol kg^{-1}, 0.470 mol kg^{-1}, and 0.588 mol kg^{-1}. This concentration range was chosen based on the preliminary experiments performed to achieve the best extraction efficiency. Alcohols with different molecular weight were considered as diluting solvents to prepare the organic phase. 20 mL each of the organic and aqueous phases were taken in an Erlenmeyer flask and shaking was performed for 2 h at 50 rpm and at the constant temperature (298.2 K) in a temperature controlled shaker. After the equilibrium was achieved, the phases were kept for 2 h to have a clear separation of the phases. Then the aqueous phase containing the PAH was analyzed by base titration (0.01 N NaOH) and using phenolphthalein as indicator to determine the concentration of PAH in the aqueous phase at equilibrium. PAH concentration after extraction in the organic phase was calculated by a mass balance. Equilibrium experiments and chemical analyses were done in duplicate, and the average values were used for the calculation. In maximum circumstances, the deviation in analyzing the concentration in each experiment did not exceed beyond ±3%.

3. Discussion of results

This part has been investigated in terms of calculated parameters and experimental results.

3.1. Distribution coefficient (K_D)

K_D value can be calculated from Eq. (1). The parameter indicates the mass transfer between two phases. $\overline{C}_{PAH}$ is the concentration of picric acid in the organic phase and C_{PAH} is the concentration of picric acid in the aqueous phase [29,30].

$$K_D = \frac{\overline{C}_{PAH}}{C_{PAH}} \tag{1}$$

The experimental and calculated results that of reactive extraction of PAH by LA-2 diluted in 5 different alcohols such as isopropyl alcohol, isoamyl alcohol, hexanol, heptanol, and decanol was tabulated in Table 2. As seen from Table 2 the organic phase LA-2 concentrations were changed from 0.118 mol kg^{-1} to 0.588 mol kg^{-1} by using alcohols. The initial aqueous PAH concentration was

Table 2
Equilibrium data for the reactive extraction of picric acid with Amberlite LA2 in 5 different alcohols at 298.2 K.

Solvents	$\overline{C}_{LA2}$	C_{aq}	C_{org}	K_D	Z	E
iso-propyl alcohol	0.118	0.030	0.031	1.033	0.264	50.82
	0.235	0.021	0.040	1.905	0.170	65.57
	0.353	0.013	0.048	3.692	0.136	78.69
	0.470	0.007	0.054	7.714	0.115	88.52
	0.588	0.001	0.060	60.000	0.102	98.36
Isoamyl alcohol	0.118	0.033	0.028	0.848	0.238	45.90
	0.235	0.024	0.037	1.542	0.157	60.66
	0.353	0.015	0.046	3.067	0.130	75.41
	0.470	0.009	0.052	5.778	0.111	85.25
	0.588	0.002	0.059	29.5	0.100	96.72
Hexanol	0.118	0.035	0.026	0.743	0.221	42.62
	0.235	0.026	0.035	1.346	0.149	57.38
	0.353	0.018	0.043	2.389	0.122	70.49
	0.470	0.012	0.049	4.083	0.104	80.33
	0.588	0.004	0.057	14.25	0.097	93.44
Decanol	0.118	0.043	0.018	0.419	0.153	29.51
	0.235	0.034	0.027	0.794	0.115	44.26
	0.353	0.025	0.036	1.44	0.102	59.02
	0.470	0.017	0.044	2.588	0.094	72.13
	0.588	0.012	0.049	4.083	0.083	80.33
Heptanol	0.118	0.045	0.016	0.356	0.136	26.23
	0.235	0.038	0.023	0.605	0.098	37.70
	0.353	0.033	0.028	0.848	0.079	45.90
	0.470	0.029	0.032	1.103	0.068	52.46
	0.588	0.025	0.036	1.44	0.061	59.01

$\overline{C}_{LA2}$ = amine concentration (Amberlite LA2) in the organic phase (mol/kg).
C_{aq} = picric acid concentration in the aqueous phase after extraction (mol/kg).
C_{org} = picric acid concentration in the organic phase after extraction (mol/kg).
$K_D = C_{org}/C_{aq}$, distribution coefficient; $Z = C_{org}/C_e$, loading factor; E = extraction efficiency.