

Removal of citric acid from water by tributyl amine in octyl acetate: equilibrium and optimization by central composite design

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ABSTRACT

Citric acid is one of the most important natural organic acid and extensively used in pharmaceuticals, foods, beverages, personal care products and mainly manufactured in the form of aqueous solutions by fermentation processes. In this study, the removal of citric acid from aqueous solutions was investigated by reactive extraction using an extractant namely tributylamine (TBA) in octyl acetate. The effects of different parameters on the removal such as initial extractant (TBA) concentration in octyl acetate (0–1.2 mol L⁻¹), initial citric acid concentration (0.26–0.78 mol L⁻¹) and, organic: aqueous phase ratio (0.2–1.0 v/v) were examined. In order to evaluate the performance of reactive extraction operation, extraction efficiencies (*E*%), distribution coefficients (*D*) and loading factors (*Z*) were calculated by using the experimental data. Furthermore, an optimization work was carried out for the reactive extraction process of citric acid. Response surface methodology was used to optimize the effect of input variables on the reactive extraction. In the variables examined, it was determined that the initial TBA concentration in the organic phase was the most effective parameter for the removal of citric acid from aqueous solutions. The optimum extraction conditions were found to be initial TBA concentration in the organic phase of 1.2 mol L⁻¹, the initial citric acid concentration of 0.26 mol L⁻¹ and organic: aqueous phase ratio of 1.0 (v/v), respectively. Under these optimum conditions, the predicted and experimental extraction efficiencies were obtained as 86.31% and 82.44%, respectively. The correlation coefficient values (*R*² and adjusted *R*² > 0.9) denoted that the obtained model equation represents the experimental data adequately.

Keywords: Citric acid; Reactive extraction; Octyl acetate; Tributyl amine; Central composite design

1. Introduction

Hydroxy acids are organic acids having one or more hydroxyl groups bonded directly to the carbon chain of an aliphatic or alicyclic carbon atom. Hydroxy acids mainly can be categorized into four groups: (1) α -hydroxy acids: (a) alkyl α -hydroxy acids, (b) aryl alkyl α -hydroxy acids, and (c) polycarboxy α -hydroxy acids; (2) β -hydroxy acids; (3) polyhydroxy acids/polycarboxy hydroxy acids; (4) aromatic hydroxy acids. Citric acid is a [C(OH)(COOH)

(CH₂COOH)₂/3-carboxy-3-hydroxypentane-1,5-dioic acid] polycarboxy α -hydroxy acid and can be classified both α -hydroxy and β -hydroxy acid at the same time [1].

Citric acid is one of the most important natural organic acids and synthesized through chemical or fermentative methods. It is mainly utilized in pharmaceuticals, foods, beverages, personal care products, cleaners, detergents and other usages like animal feed and industrial applications. About 70% of these consumption areas are food and beverages. In beverages and foods, citric acid is substantially used

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as a flavoring agent, preservative, acidifier, and chelating agent [2–4]. Recent studies denoted that citric acid was an efficient eluting medium in the application of the titanium type lithium-ion sieve [5]. The estimated world manufacture of citric acid for industrial uses was reported as about 2 million tons [6]. Having a wide range of versatile utilization and increasing market demand has made it inevitable to conduct scientific research on citric acid production and recovery.

Precipitation, extraction, and adsorption are the main separation methods for the uptake of citric acid from wastewaters, fermentation broths or aqueous solutions [4]. Among these methods, solvent extraction has important advantages of eliminating the usage of calcium hydroxide and sulfuric acid utilized in the precipitation process [7]. Besides these, reactive extraction is an emerging influential method for the removal of carboxylic acid. Reactive extraction involves the integration of the reaction and separation steps using specific extractants with different diluents. Carbon bonded oxygen donor extractants, phosphorus-bonded oxygen donor extractants, and aliphatic amines can be classified as main extractant groups [8]. Extractants are dissolved in diluents, thus its physical properties such as surface tension and viscosity were improved [9].

In the literature [7,10–26], various (extractant + diluent) systems have been tested for the citric acid removal from its dilute solutions. In this work, the reactive extraction of citric acid from dilute aqueous solutions was examined using tributylamine (TBA)-octyl acetate as an extractant-diluent system. The initial citric acid concentration, initial TBA concentration in the organic phase, and organic: aqueous phase ratio were investigated as parameters affecting the separation process. The experimental data were evaluated using the distribution coefficient (D), extraction efficiency ($E\%$), and loading factor (Z) values.

An experimental design is a detailed plan of experiments arranged to get desired information on the observed results. Response surface methodology (RSM) is used for understanding how the response of interest is influenced by a set of variables, and the objective is to optimize this response. It is possible with the RSM both to locate the optimum conditions, and to analyze how the input variables affect the optimum conditions. RSM includes several methods to design the experimental procedures and some of them are Box–Behnken design, central composite design, and D -optimal design [27].

The initial citric acid concentration (0.26–0.78 mol L⁻¹), initial TBA concentration in organic phase (0–1.2 mol L⁻¹), and organic: aqueous phase ratio (0.2–1.0 v/v) were selected as input variables (factors), and the extraction efficiency was selected as a response. Central composite design was performed to determine the influence of the factors and their interactions on the response. Among the factors investigated in the experimental and optimization studies, it was determined that the initial amine concentration in the organic phase was the most effective parameter for the removal of citric acid from aqueous solutions.

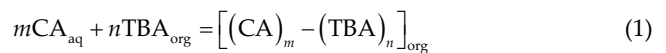
2. Experimental

The solutions of citric acid (Sigma-Aldrich, Germany, >99%) were prepared in different concentrations of 0.26, 0.52

and 0.78 mol L⁻¹ by using distilled water. The solutions of the organic phase were prepared by the dissolving of TBA (Merck, Germany, ≥99%) in octyl acetate (Merck, Germany, ≥99%). The initial TBA concentrations in octyl acetate were 0, 0.2, 0.4, 0.6, 0.8, 1.0 and 1.2 mol L⁻¹. The organic phase volume: aqueous phase volume ratios (phase ratios, v/v) were studied as 1:5 mL (phase ratio:0.2 v/v), 3:5 mL (phase ratio:0.6 v/v) and 5:5 mL (phase ratio:1.0 v/v). The experiments were performed by using a water bath shaker (NÜVE ST 402 model, Turkey) for predetermined equilibrium time (2 h) at 150 rpm and room temperature. After the extraction, the samples were centrifuged in a centrifuge device (NÜVE NS 200 model) at 4,000 rpm for 10 min. The concentration of citric acid in the aqueous phase was analyzed using Schott Titroline automatic titrator with 0.1 N NaOH. The concentration of citric acid in the organic phase was determined using the mass balance.

3. Theoretical

Reaction mechanism of citric acid (CA) with TBA can be described by following Eq. (1):



In this equation, CA implies the non-dissociated citric acid in an aqueous phase and $(\text{CA})_m - (\text{TBA})_n$ signifies citric acid-extractant complex in the organic phase.

The reactive extraction process was evaluated by using the parameters, namely distribution coefficient (D), extraction efficiency ($E\%$), and loading factor (Z). The ratio of the equilibrium concentration between organic and aqueous phases is called the distribution coefficient (D). This coefficient symbolizes as follows [28]:

$$D = \frac{C_{\text{CA,org}}}{C_{\text{CA,aq}}} \quad (2)$$

The extraction efficiency ($E\%$) is defined as the ratio of the concentration of extracted acid to initial acid concentration and it is calculated as below [28]:

$$E\% = \left[1 - \left(\frac{C_{\text{CA,aq}}}{C_{\text{CA,0}}} \right) \right] \times 100 \quad (3)$$

In the reactive extraction of carboxylic acids, the loading factor (Z) is used to specify the activity of amine in the organic phase. This parameter represents the ratio of the concentration of transported acid to TBA concentration in the organic phase. It is indicated as follows [28]:

$$Z = \frac{C_{\text{CA,org}}}{C_{\text{TBA,org}}} \quad (4)$$

4. Result and discussion

4.1. Reactive extraction equilibrium studies

Citric acid solutions of different initial concentrations were prepared to examine the separation of citric acid from

the aqueous medium by the reactive extraction method. However, the effects of initial amine concentration ($C_{\text{TBA,org}}$) in the organic phase, and organic:aqueous phase ratio (v/v) on the reactive separation process were investigated. The experimental conditions included initial citric acid concentrations of 0.26, 0.52 and 0.78 mol L⁻¹; TBA concentrations in the organic phase of 0, 0.2, 0.4, 0.6, 0.8, 1.0 and 1.2 mol L⁻¹; and phase ratio of 0.2, 0.6, and 1.0 (v/v). The equilibrium citric acid concentration in the aqueous phase ($C_{\text{CA,aq}}$) was determined experimentally. The citric acid concentration in the organic phase was calculated using mass balance. Using the obtained data, distribution coefficient (D), loading factor (Z), and extraction efficiency ($E\%$) were calculated. The obtained experimental results according to each initial citric acid concentration (0.26, 0.52 and 0.78 mol L⁻¹) were summarized in Tables 1–3. As can be seen in Tables 1–3, when the results of physical extraction experiments using different initial citric acid concentrations and organic phase contents without TBA were analyzed, the values of extraction efficiency ($E\%$) varied between 0.160% and 4.108%. When the reactive extraction experimental results were examined, the maximum extraction efficiency values reached above 80%. These results showed that reactive extraction is more effective than physical extraction.

Moreover, the distribution coefficient (D), loading factor (Z), and extraction efficiency ($E\%$) values for the different initial acid concentrations are illustrated in Fig. 1. As can be seen from Fig. 1, the distribution coefficients (Figs. 1a1, 1b1 and 1c1) and extraction efficiencies (Figs. 1a3, 1b3 and 1c3) increased considerably with increasing TBA

concentration in octyl acetate. Because, with increasing TBA concentration in the organic phase, more TBA-acid complexes occur in the organic phase and the more citric acid molecules removed from the aqueous phase and so, the values of distribution coefficient (D) and extraction efficiency ($E\%$) increase. The results were consistent with the fact that similar reactive extraction studies reported in the literature [28,29]. When the results were discussed in terms of loading factor values (see Figs. 1a2, 1b2 and 1c2); it was seen that the loading factor values varied between 0–0.41. These values mean that the acid-amine complexes contain more than one amine per complex. When the loading factor values greater than unity, it is called overloading. Overloading indicates that the complexes with more than one acid molecule per amine are formed. The loading factor values were under unity at all experimental conditions, and this situation indicates that overloading does not occur [30,31]. From all plots illustrated in Fig. 1, as the organic:aqueous phase ratio, increased from 0.2 to 1.0 (v/v), the values of distribution coefficient, extraction efficiency, and loading factor had increased. Owing to using larger organic phase volume, the more acid was extracted into the aqueous phase from the organic phase. The observation was consistent with the fact that similar reactive extraction studies [32,33]. However, the values of distribution coefficient and extraction efficiency were decreased with increasing initial citric acid concentration from 0.26 mol L⁻¹ (Fig. 1a) to 0.78 mol L⁻¹ (Fig. 1c). It can be explained with the extraction power of TBA decreases with an increase in the initial acid concentration. Similarly, Eda et al. [34] examined the removal of levulinic acid by

Table 1
Results of reactive extraction experiments with initial citric acid concentration of 0.26 mol L⁻¹

Phase ratio (v/v)	$C_{\text{TBA,org}}$ mol L ⁻¹	$C_{\text{CA,org}}$ mol L ⁻¹	$C_{\text{CA,aq}}$ mol L ⁻¹	D	Z	$E\%$	pH
0.2	0.0	0.006	0.254	0.024	–	2.306	1.739
	0.2	0.019	0.241	0.080	0.096	7.411	3.250
	0.4	0.030	0.230	0.130	0.075	11.515	4.151
	0.6	0.046	0.214	0.217	0.077	17.821	3.750
	0.8	0.063	0.197	0.318	0.078	24.127	4.750
	1.0	0.079	0.181	0.437	0.079	30.433	5.105
	1.2	0.098	0.162	0.609	0.082	37.840	6.210
	0.6	0.0	0.004	0.256	0.017	–	1.706
0.2		0.047	0.213	0.221	0.236	18.121	2.981
0.4		0.091	0.169	0.539	0.228	35.038	3.721
0.6		0.131	0.129	1.022	0.219	50.553	4.400
0.8		0.166	0.094	1.767	0.208	63.865	5.093
1.0		0.191	0.069	2.770	0.191	73.475	5.539
1.2		0.208	0.052	4.035	0.174	80.141	5.899
1.0		0.0	0.011	0.249	0.043	–	4.108
	0.2	0.068	0.192	0.356	0.341	26.229	3.167
	0.4	0.127	0.133	0.951	0.317	48.751	4.258
	0.6	0.169	0.091	1.871	0.282	65.167	5.074
	0.8	0.199	0.061	3.251	0.249	76.477	5.641
	1.0	0.208	0.052	3.995	0.208	79.981	5.861
	1.2	0.214	0.046	4.696	0.179	82.443	6.072

Table 2
Results of reactive extraction experiments with initial citric acid concentration of 0.52 mol L⁻¹

Phase ratio (v/v)	C _{TBA,org} mol L ⁻¹	C _{CA,org} mol L ⁻¹	C _{CA,aq} mol L ⁻¹	D	Z	E%	pH
0.2	0.0	0.013	0.509	0.026	–	2.531	1.632
	0.2	0.025	0.497	0.050	0.123	4.725	2.360
	0.4	0.044	0.478	0.092	0.110	8.414	2.785
	0.6	0.051	0.471	0.108	0.084	9.710	3.950
	0.8	0.074	0.448	0.165	0.093	14.197	3.055
	1.0	0.095	0.427	0.222	0.095	18.136	2.956
	1.2	0.117	0.405	0.290	0.098	22.473	3.240
0.6	0.0	0.005	0.517	0.009	–	0.886	1.645
	0.2	0.057	0.465	0.122	0.283	10.857	2.426
	0.4	0.100	0.422	0.237	0.250	19.183	2.929
	0.6	0.135	0.387	0.349	0.225	25.864	3.057
	0.8	0.196	0.326	0.601	0.245	37.530	3.735
	1.0	0.232	0.290	0.797	0.232	44.360	3.984
	1.2	0.285	0.237	1.199	0.237	54.531	4.466
1.0	0.0	0.002	0.520	0.004	–	0.387	1.424
	0.2	0.073	0.449	0.161	0.363	13.898	2.422
	0.4	0.137	0.385	0.356	0.343	26.263	3.088
	0.6	0.196	0.326	0.602	0.327	37.580	3.599
	0.8	0.253	0.269	0.938	0.316	48.399	4.141
	1.0	0.304	0.218	1.396	0.304	58.270	4.583
	1.2	0.352	0.170	2.067	0.293	67.394	5.156

Table 3
Results of reactive extraction experiments with initial citric acid concentration of 0.78 mol L⁻¹

Phase ratio (v/v)	C _{TBA,org} mol L ⁻¹	C _{CA,org} mol L ⁻¹	C _{CA,aq} mol L ⁻¹	D	Z	E%	pH
0.2	0.0	0.001	0.781	0.002	–	0.160	1.425
	0.2	0.031	0.751	0.042	0.156	3.987	2.150
	0.4	0.050	0.732	0.069	0.125	6.417	1.955
	0.6	0.063	0.719	0.087	0.104	8.014	2.562
	0.8	0.076	0.706	0.108	0.095	9.711	2.876
	1.0	0.098	0.684	0.143	0.098	12.507	3.126
	1.2	0.133	0.649	0.204	0.111	16.966	3.258
0.6	0.0	0.008	0.774	0.010	–	0.992	1.440
	0.2	0.058	0.724	0.080	0.291	7.448	2.215
	0.4	0.108	0.674	0.160	0.269	13.771	2.289
	0.6	0.155	0.627	0.246	0.258	19.762	2.617
	0.8	0.211	0.571	0.370	0.264	26.984	3.158
	1.0	0.256	0.526	0.485	0.256	32.674	3.408
	1.2	0.327	0.455	0.718	0.272	41.793	3.728
1.0	0.0	0.005	0.777	0.007	–	0.692	1.228
	0.2	0.083	0.699	0.119	0.416	10.643	2.190
	0.4	0.163	0.619	0.264	0.408	20.860	2.654
	0.6	0.219	0.563	0.389	0.365	28.015	3.088
	0.8	0.287	0.495	0.580	0.359	36.701	0.000
	1.0	0.332	0.450	0.737	0.332	42.426	3.721
	1.2	0.416	0.366	1.136	0.347	53.175	4.253

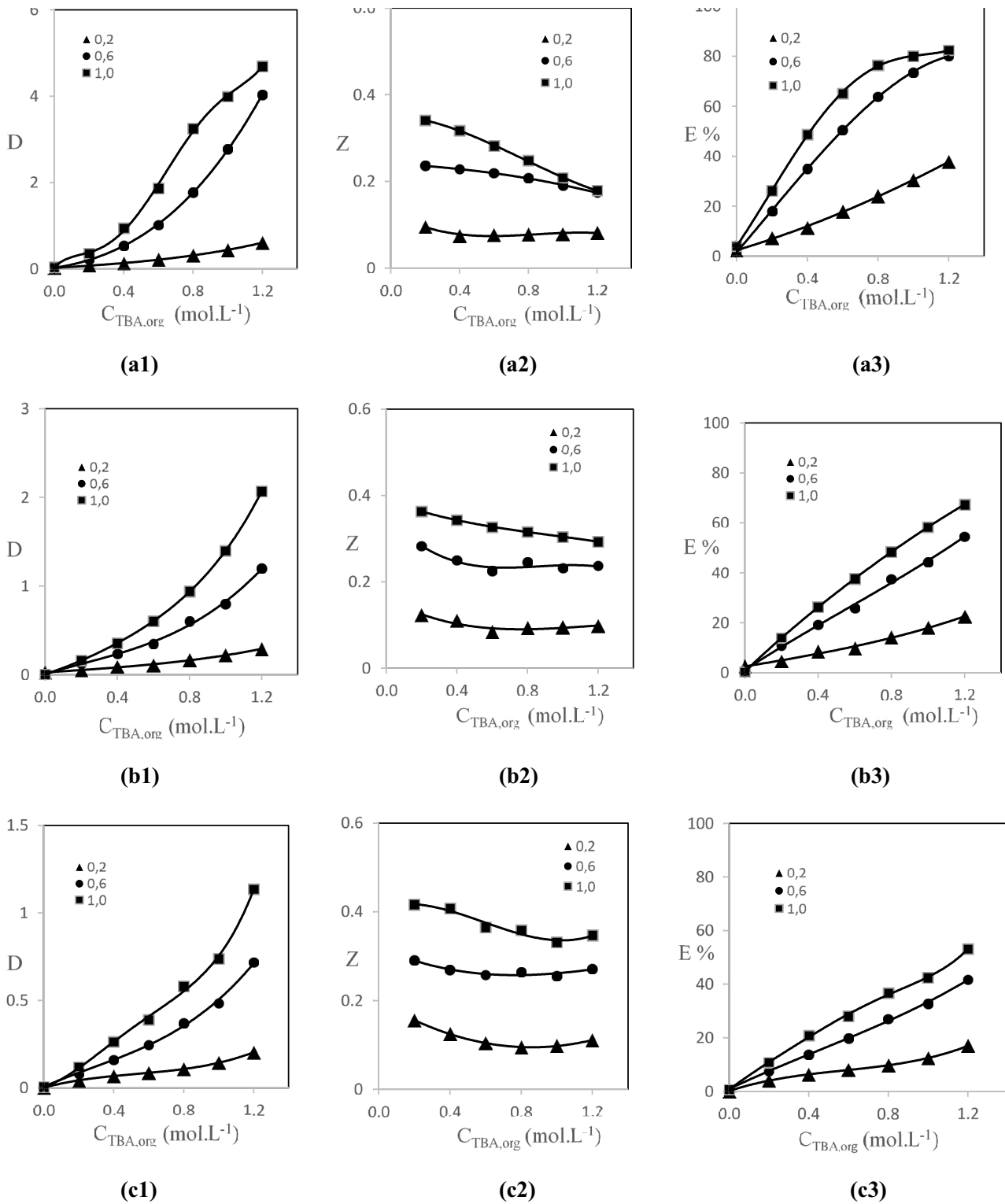


Fig. 1. Effect of initial TBA concentration ($C_{TBA,org}$) on the distribution coefficient (D), loading factor (Z), and extraction efficiency ($E\%$) (initial citric acid concentration (a) 0.26 mol L⁻¹, (b) 0.52 mol L⁻¹, and (c) 0.78 mol L⁻¹).

Table 4
Factors and actual and coded levels used in FCCCD

Factors	Levels					
	Actual	Coded	Actual	Coded	Actual	Coded
X_1 Phase ratio (v/v)	0.2	-1	0.6	0	1.0	+1
X_2 Initial citric acid concentration (mol L ⁻¹)	0.26	-1	0.52	0	0.78	+1
X_3 TBA concentration (mol L ⁻¹)	0	-1	0.6	0	1.2	+1

reactive extraction using trioctylamine in methyl isobutyl ketone and they also reported that the distribution coefficient decreased with increasing initial acid concentration.

4.2. Face-centered central composite design

In order to analyze and optimize the reactive extraction process factors affecting the extraction efficiency, face-centered central composite design (FCCCD) was employed in the Design-Expert® Software Version 11 Trial, (Stat-Ease, Inc., Minneapolis, USA). Based on the aforementioned the experimental results, phase ratio (X_1 , organic phase volume/ aqueous phase volume, v/v), initial citric acid concentration (X_2) and initial TBA concentration in the organic phase (X_3) were chosen as three factors affecting on the extraction efficiency (Y , response). These factors and actual and coded levels were given in Table 4. The factors and their levels were entered into Design-Expert® Software, the experimental layout and results were acquired as shown in Table 5.

Table 5
Experimental layout and results for the extraction efficiency (Y)

Run	Factors			Response
	X_1	X_2	X_3	Y (%)
1	0	0	0	25.91
2	-1	+1	+1	16.97
3	-1	0	0	9.71
4	0	0	0	25.86
5	+1	0	0	37.58
6	+1	+1	-1	0.69
7	+1	-1	-1	4.11
8	0	+1	0	19.76
9	+1	-1	+1	82.44
10	-1	-1	-1	2.31
11	0	-1	0	50.55
12	0	0	0	25.86
13	+1	+1	+1	53.18
14	-1	+1	-1	0.16
15	0	0	0	25.85
16	0	0	0	25.88
17	0	0	-1	0.89
18	0	0	+1	54.53
19	0	0	0	25.83
20	-1	-1	+1	37.84

The obtained experimental data were analyzed by analysis of variance (ANOVA). ANOVA data were given in Table 6. The significance of the model is evaluated by model F -value and p -value in ANOVA table [35]. As can be seen from Table 6, the model F -value (51.72) and model p -value (<0.0001) denoted that the model for extraction efficiency was significant. Besides, the significance of model terms can be analyzed with a p -value. The p -values of model terms <0.05 represent these model terms are important and they have an important effect on the response. ANOVA results indicated that five model terms (X_1 , X_2 , X_3 , X_1X_2 , X_2X_3) were significant (p -value < 0.05). The effects that were not important (p -value > 0.05) were excluded from the model equation. In this way, the following regression model Eq. (5) in terms of coded factors representing the extraction efficiency (Y) was acquired as:

$$Y = 26.30 + 11.10X_1 - 8.65X_2 + 23.68X_3 + 9.81X_1X_3 - 5.57X_2X_3 \quad (5)$$

As can be seen in the model equation, all factors (X_1 , X_2 , X_3) have an important effect on the extraction efficiency. Because of the highest coefficient in the model, the most significant factor affecting the extraction efficiency is TBA concentration (X_3).

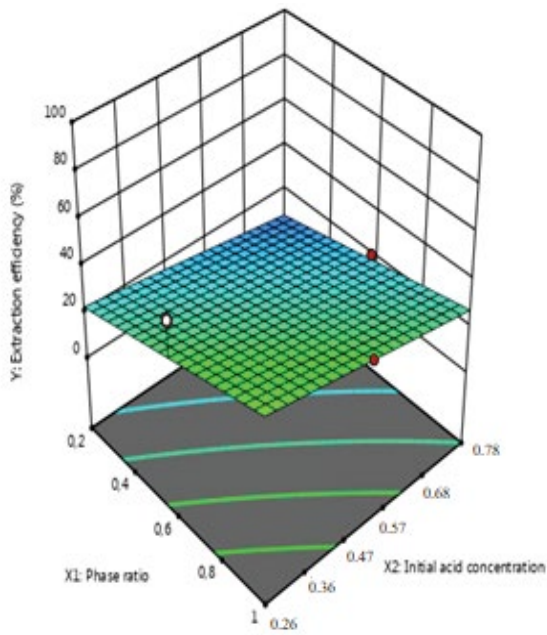
Table 6
ANOVA results for the extraction efficiency

Source	Sum of squares	df	Mean square	F -value	p -value Prob > F
Model	8,617.55	6	1,436.26	51.72	<0.0001
X_1	1,232.32	1	1,232.32	44.37	<0.0001
X_2	748.05	1	748.05	26.94	0.0002
X_3	5,607.42	1	5,607.42	201.91	<0.0001
X_1X_2	11.66	1	11.66	0.4200	0.5282
X_1X_3	769.89	1	769.89	27.72	0.0002
X_2X_3	248.20	1	248.20	8.94	0.0104
X_1^2	361.03	13	27.77		
X_2^2	361.03	8	45.13	60,171.41	<0.0001
X_3^2	0.0038	5	0.0008		
Residual	8,978.58	19			
Lack of Fit	8,617.55	6	1,436.26	51.72	<0.0001
Pure Error	1,232.32	1	1,232.32	44.37	<0.0001
Cor. total	748.05	1	748.05	26.94	0.0002

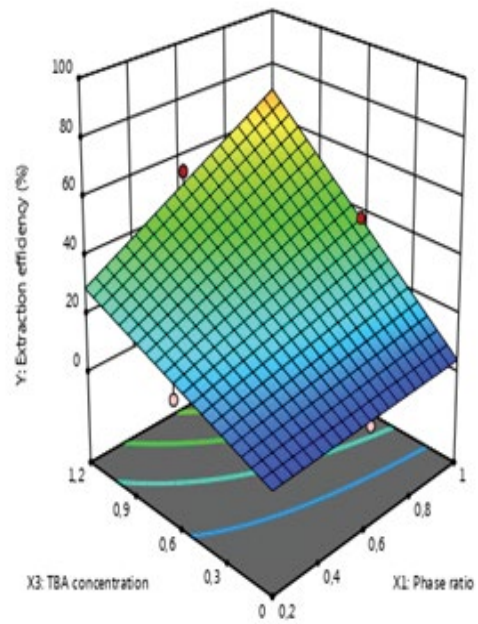
The validity of the model was verified by analyzing various statistical parameters given in Table 7. As shown in Table 7, the model correlation coefficients (R^2 and adjusted R^2) were obtained very higher (>0.9). These results indicated that the model had a good fit for the experimental data. The value of predicted R^2 was in reasonable agreement with the value of adjusted R^2 due to the difference is less than 0.2. Adequate precision (AP) which measures the ratio of signal to noise is desirable greater than 4. AP value was found to be 27.8602 and it demonstrated an adequate signal

Table 7
Statistical parameters obtained in FCCCD

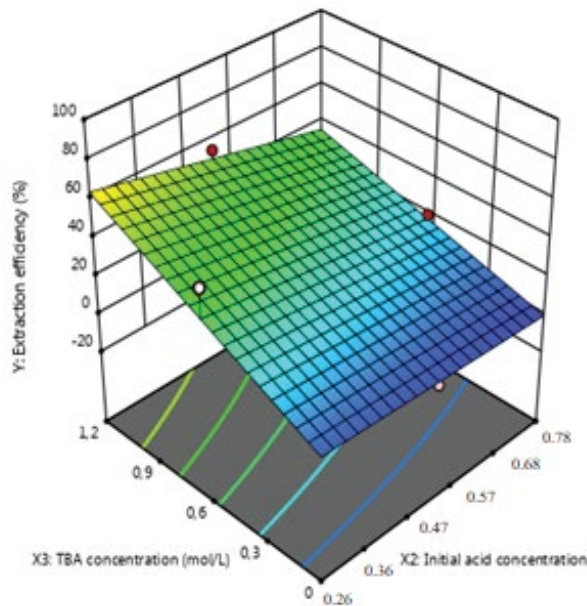
R^2	0.9598
Adjusted R^2	0.9412
Predicted R^2	0.8678
Adequate precision (AP)	27.8602
Standard deviation (SD)	5.27



(a) TBA concentration: 0.6 mol.L⁻¹



(b) Initial acid concentration: 0.52 mol.L⁻¹



(c) Phase ratio: 0.6 (v/v)

Fig. 2. Effect of (a) phase ratio (X_1) and initial acid concentration (X_2), (b) phase ratio (X_1) and TBA concentration (X_3), and (c) initial acid concentration (X_2) and TBA concentration (X_3) on the extraction efficiency (Y).

[36]. As a result, the obtained model equation can be used to design this system.

3D response surface plots of model equation (Fig. 2) were depicted to explain the effect of factors on the extraction efficiency. Fig. 2a and b clearly showed that the extraction efficiency increased with increasing the organic:aqueous phase ratio. Due to using larger organic phase volume, the more acid was embodied in the aqueous phase from the organic phase. Similar reactive extraction studies has confirmed this result [32,33,37]. Fig. 2a also indicated that the extraction efficiency values decreased with an increase in the initial citric acid concentration. Likewise, it can be observed in Fig. 2c. It can be explained with the extraction power of TBA decreases with an increase in the initial acid concentration [28]. Moreover, Fig. 2b and c demonstrated that as increasing TBA concentration, the extraction efficiency was increased considerably. Similarly, as amine concentration increases, more amino-acid complexes forms in the organic phase and so, the more acid molecules extracted from the aqueous phase [37].

Eventually, an optimization study was enforced in Design-Expert® Software. The optimal reactive extraction conditions were determined as the phase ratio of 1.0 (v/v), the initial citric acid concentration of 0.26 mol L⁻¹ and initial TBA concentration of 1.2 mol L⁻¹. Under the optimal conditions, the predicted and experimental extraction efficiencies were obtained as 86.31% and 82.44%, respectively. It indicated that the model was fitted to the experimental values.

5. Conclusion

In this study, in order to investigate the effects of some variable parameters on reactive extraction, the removal of citric acid from aqueous solutions was tested. In the experimental studies, three different parameters were gradually changed, initial acid concentration, initial TBA concentration in the organic phase and organic: aqueous phase ratio. The highest *E*% was obtained as 82.44% for 1.2 mol L⁻¹ initial TBA concentration, an equal volume of each phase, and with 0.26 mol L⁻¹ initial citric acid concentration. The mathematical model equation representing the extraction efficiency was obtained by the RSM. The higher correlation coefficients (*R*² and adjusted *R*² > 0.9) showed that the obtained model fits well with experimental studies. From the experimental and model results it can be concluded that the reactive extraction process was affected by the examined parameters, in the order of initial TBA concentration in organic phase > organic:aqueous phase ratio > initial acid concentration. As a result of the general evaluation of the study, it was seen that the successful separation efficiency was achieved when the organic phases obtained by using the reactive and solvent mixtures were used optimally.

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References

- [1] T. Bhalla, V. Kumar, S. Bhatia, Hydroxy Acids: Production and Applications, Advances in Industrial Biotechnology, IK International Publishing House Pvt. Ltd., India, 2013, pp. 56–76.
- [2] B. Kristiansen, J. Linden, M. Matthey, Citric Acid Biotechnology, CRC press, 1998.
- [3] C.R. Soccol, L.P. Vandenberghe, C. Rodrigues, A. Pandey, New perspectives for citric acid production and application, Food Technol. Biotechnol., 44 (2006) 141–149.
- [4] G.S. Dhillon, S.K. Brar, M. Verma, R.D. Tyagi, Recent advances in citric acid bio-production and recovery, Food Bioprocess Technol., 4 (2011) 505–529.
- [5] S. Wang, M. Zhang, Y. Zhang, Y. Zhang, S. Qiao, S. Zheng, Application of citric acid as eluting medium for titanium type lithium-ion sieve, Hydrometallurgy, 183 (2019) 166–174.
- [6] E. Cavallo, H. Charreau, P. Cerrutti, M.L. Foresti, Yarrowia lipolytica: a model yeast for citric acid production, FEMS Yeast Res., 17 (2017) 1–16.
- [7] E.M.R. Araújo, F.E.B. Coelho, J.C. Balarini, T.L.S. Miranda, A. Salum, Solvent extraction of citric acid with different organic phases, Adv. Chem. Eng. Sci., 7 (2017) 304–324.
- [8] A. Kertes, C.J. King, Extraction chemistry of fermentation product carboxylic acids, Biotechnol. Bioeng., 28 (1986) 269–282.
- [9] A. Keshav, S. Chand, K.L. Wasewar, Reactive extraction of acrylic acid using tri-*n*-butyl phosphate in different diluents, J. Chem. Eng. Data, 54 (2009) 1782–1786.
- [10] V. Bizek, J. Horacek, R. Rericha, M. Kousova, Amine extraction of hydroxycarboxylic acids. 1. Extraction of citric acid with 1-octanol/*n*-heptane solutions of trialkylamine, Ind. Eng. Chem. Res., 31 (1992) 1554–1562.
- [11] P. Vaňura, L. Kuča, Extraction of citric acid by the toluene solutions of trilaurylamine, Collect. Czech. Chem. Commun., 41 (1976) 2857–2877.
- [12] V. Bizek, J. Horáček, M. Koušová, Amine extraction of citric acid: effect of diluent, Chem. Eng. Sci., 48 (1993) 1447–1457.
- [13] J. Prochazka, A. Heyberger, V. Bizek, M. Kousova, E. Volaufova, Amine extraction of hydroxycarboxylic acids. 2. Comparison of equilibria for lactic, malic, and citric acids, Ind. Eng. Chem. Res., 33 (1994) 1565–1573.
- [14] V. Bizek, M. Kousova, A. Heyberger, J. Prochazka, J. Horacek, Mathematical model of extraction of citric acid with amine, Chem. Eng. Sci., 47 (1992) 1433–1440.
- [15] U. Bauer, R. Marr, W. Rückl, M. Siebenhofer, Reactive extraction of citric acid from an aqueous fermentation broth, Ber. Bunsen Ges. Phys. Chem., 93 (1989) 980–984.
- [16] F.A. Poposka, K. Nikolovski, R. Tomovska, Kinetics, mechanism and mathematical modeling of extraction of citric acid with isodecanol/*n*-paraffins solutions of trioctylamine, Chem. Eng. Sci., 53 (1998) 3227–3237.
- [17] J. Prochazka, A. Heyberger, E. Volaufova, Amine extraction of hydroxycarboxylic acids. 3. Effect of modifiers on citric acid extraction, Ind. Eng. Chem. Res., 36 (1997) 2799–2807.
- [18] G. Malmayr, J. Albet, A. Putranto, J. Molinier, Recovery of carboxylic acids from aqueous solutions by liquid-liquid extraction with a triisooctylamine diluent system, Braz. J. Chem. Eng., 18 (2001) 441–447.
- [19] R. Canari, A.M. Eyal, Temperature effect on the extraction of carboxylic acids by amine-based extractants, Ind. Eng. Chem. Res., 43 (2004) 7608–7617.
- [20] A. Keshav, P. Norge, K.L. Wasewar, Reactive extraction of citric acid using tri-*n*-octylamine in nontoxic natural diluents: part 1-equilibrium studies from aqueous solutions, Appl. Biochem. Biotechnol., 167 (2012) 197–213.
- [21] D. Datta, Y.S. Aşçı, A.F. Tuyun, Intensification of citric acid extraction by a mixture of trioctylamine and tridodecylamine in different diluents, J. Chem. Eng. Data, 60 (2015) 960–965.
- [22] N. Thakre, A.K. Prajapati, S.P. Mahapatra, A. Kumar, A. Khapre, D. Pal, Modeling and optimization of reactive extraction of citric acid, J. Chem. Eng. Data, 61 (2016) 2614–2623.
- [23] N. Thakre, D. Datta, A. Prajapati, P. Chaudhari, D. Pal, Reactive extraction of citric acid using different extractants: equilibrium, kinetics and modeling, Chem. Biochem. Eng. Q., 31 (2017) 437–446.
- [24] M. Djas, M. Henczka, K. Potocka, J. Wawer, Reactive extraction of citric acid using supercritical CO₂ and trioctylamine, Chall. Mod. Technol., 6 (2015) 27–30.

- [25] E. Hasret, Ş.İ. Kırbaşlar, H. Uslu, Extraction of citric acid and maleic acid from their aqueous solutions using a phosphorus-bonded extractant, tri-n-octylphosphineoxide, and a secondary amine, dioctylamine, *J. Chem. Eng. Data*, 63 (2017) 39–48.
- [26] E. Abraham, G.N. Mukunthan Sulochana, B. Soundarajan, S. Narayanasamy, Experimental investigation on microfluidic reactive extraction of citric acid using trioctylamine/1-decanol system in uniform and nonuniform circular microchannels, *Ind. Eng. Chem. Res.*, 56 (2017) 10845–10855.
- [27] K.A.M. Said, M.A.M. Amin, Overview on the response surface methodology (RSM) in extraction processes, *J. Appl. Sci. Process Eng.*, 2 (2015) 8–17.
- [28] Y.S. Aşçı, İ. İnci, Extraction of glycolic acid from aqueous solutions by Amberlite LA-2 in different diluent solvents, *J. Chem. Eng. Data*, 54 (2009) 2791–2794.
- [29] İ. İnci, A. Aydın, Extraction of hydroxycarboxylic acids with MIBK/toluene solutions of amines, *J. Sci. Ind. Res.*, 62 (2003) 926–930.
- [30] A.F. Tuyun, H. Uslu, Extraction of d-(–)-quinic acid using an amine extractant in different diluents, *J. Chem. Eng. Data*, 57 (2011) 190–194.
- [31] İ. İnci, Liquid-liquid equilibria of gluconic acid between water and trin-octylamine in various diluents, *Asian J. Chem.*, 14 (2002) 1711–1718.
- [32] E. Ayan, N. Baylan, S. Çehreli, Optimization of reactive extraction of propionic acid with ionic liquids using central composite design, *Chem. Eng. Res. Des.*, 153 (2020) 666–676.
- [33] K. Chawong, P. Rattanaphanee, n-Butanol as an extractant for lactic acid recovery, *World Acad. Sci. Eng. Technol.*, 80 (2011) 239–242.
- [34] S. Eda, A. Borra, R. Parthasarathy, S. Bankupalli, S. Bhargava, P.K. Thella, Recovery of levulinic acid by reactive extraction using tri-n-octylamine in methyl isobutyl ketone: equilibrium and thermodynamic studies and optimization using Taguchi multivariate approach, *Sep. Purif. Technol.*, 197 (2018) 314–324.
- [35] C.-C. Chen, K.-T. Chiang, C.-C. Chou, Y.-C. Liao, The use of D-optimal design for modeling and analyzing the vibration and surface roughness in the precision turning with a diamond cutting tool, *Int. J. Adv. Manuf. Technol.*, 54 (2011) 465–478.
- [36] Q.K. Beg, V. Sahai, R. Gupta, Statistical media optimization and alkaline protease production from *Bacillus mojavensis* in a bioreactor, *Process Biochem.*, 39 (2003) 203–209.
- [37] F.M. Antony, K.L. Wasewar, Reactive separation of protocatechuic acid using Tri-n-octyl amine and Di-(2-ethylhexyl) phosphoric acid in methyl isobutyl ketone, *Sep. Purif. Technol.*, 207 (2018) 99–107.