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Separation of Succinic Acid from Aqueous Solution by Alumina Adsorption

İsmail İnci,[*,†] Şahika Sena Bayazit,[‡] and Yavuz Selim Aşçi[†]

[†]Engineering Faculty, Chemical Engineering Department, İstanbul University, 34320, İstanbul, Turkey

[‡]Engineering and Architecture Faculty, Department of Chemical Engineering, Beykent University, Ayazağa, Istanbul, Turkey

ABSTRACT: Attempts were made to recover succinic acid (IUPAC systematic name as ethane 1,2-dicarboxylic acid) from aqueous solutions by alumina adsorption. Experimental adsorption works were conducted with aqueous solutions containing succinic acid in four different concentrations: (0.13, 0.22, 0.32, and 0.45) $mol \cdot kg^{-1}$. Alumina were used in 10 different amounts: (0.2, 0.4, 0.6, 0.8, 1.0, 1.2, 1.4, 1.6, 1.8, and 2) g. Also adsorption experiments were carried out at three different temperatures: (298, 308, and 318) K. The equilibrium distributions of succinic acid were determined. The minimum equilibrium concentration of succinic acid was 0.28 $mol \cdot kg^{-1}$ for 0.45 $mol \cdot kg^{-1}$ initial succinic acid concentration with 2 g of alumina. The adsorption data fit well within the Langmuir, Freundlich, and Temkin isotherms. Isotherm parameters have been obtained. Also the kinetics of the adsorption for succinic acid were determined as the pseudosecond-order model.

INTRODUCTION

The recovery of biotechnological acids produced by fermentation from both aqueous solutions and fermentation broths, where it is present in dilute form, is always of interest to many researchers.[1] A number of methods have been studied to separate these acids from aqueous solutions.[2−5] Adsorption is operative in most natural systems including physical, biological, and chemical separation methods. Adsorption uses solids such as alumina, and different synthetic resins are widely used in industrial applications and for purification and separation.[6]

Mostly succinic acid, a dicarboxylic acid having the molecular formula of $C_4H_6O_4$, is produced by chemical method using petroleum as a starting material. However, there has recently been much interest in the production of succinic acid from renewable resources by fermentation because of the dramatic increase in petroleum price and ever-increasing environmental concerns. Succinic acid is produced in many organisms as an intermediate of tricarboxylic acid (TCA) cycle and also as one of the fermentation end products of anaerobic metabolism. Many different microorganisms have been studied for succinic acid production from various carbon sources. Among them, *Anaerobiospirillum succiniciproducens*[7,8] and *Actinobacillus succinogenes*[9,10] have been most studied because of their ability to produce a relatively large amount of succinic acid. More recently, a new succinic acid producing bacterium *Mannheimia succiniciproducens* MBEL55E was isolated from bovine rumen.[11] Also, there has been effort in developing recombinant *Escherichia coli* strains which are capable of enhanced succinic acid production under aerobic and anaerobic conditions.[12]

Robert Knock, the Nobel Prize winner, proved that succinic acid has a positive influence on human metabolism, and as there is no risk of its accumulation in the human body, it has been used in food industries for a long time. Succinic acid is an intermediate of the tricarboxylic acid (TCA) cycle and one of the fermentation end-products of anaerobic metabolism. Therefore, it is synthesized in almost all microbial, plant, and animal cells.[13,14]

The interaction between the carboxylic group of acid and hydroxyls on the surface has been investigated by a lot of researchers. Particularly, the adsorption of aromatic acids on alumina has been studied. It is generally recognized that both oxygen atoms in the carboxylic group are anchored on the alumina surface, but two models (bridging and chelating models) have been proposed for the interaction. The bridging model considers that both oxygen atoms of the carboxylic group involved in the interaction are linked to Al−O sites on the surface with hydrogen bonding. The chelating model considers that the carboxylic group is dissociated and forms a bidentate linkage with a single Al−O−H site. The adsorption of carboxylic acids from aqueous solution onto the alumina surface is a dissociative adsorption process.[15,16] The adsorbed carboxylic acids may interact with the alumina surface in such a way that a hydrogen atom is shared between each oxygen atom in the carboxylic group with an oxygen atom on the alumina surface forming a strong hydrogen bond.[17]

The subject of this study is to separate succinic acid from aqueous solutions by using adsorbent alumina. The Freundlich, Langmuir, and Temkin isotherms have been fitted to experimental data. The kinetics of the adsorption for succinic acid was determined as pseudosecond-order model.

EXPERIMENTAL SECTION

Alumina and succinic acid were purchased from Merck Company (acid purities > 99.0 %). We prepared four different concentrations for succinic acid: 0.13 $mol \cdot kg^{-1}$, 0.22 $mol \cdot kg^{-1}$, 0.32 $mol \cdot kg^{-1}$, and 0.45 $mol \cdot kg^{-1}$. Mixtures of a known amount of adsorbent and 5 mL of 0.45 $mol \cdot kg^{-1}$ succinic acid solution

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Table 1. Effect of Initial Acid Concentration on the Adsorption of Succinic Acid

C_o	Amberlite IRA-67	C_e	Q_e	T
$mol \cdot kg^{-1}$	g	$mol \cdot kg^{-1}$	$g \cdot mg^{-1}$	K
0.13	0.6	0.10	0.029	298
0.22	0.6	0.18	0.038	298
0.32	0.6	0.26	0.052	298
0.45	0.6	0.39	0.056	298
0.13	0.6	0.10	0.022	308
0.22	0.6	0.18	0.035	308
0.32	0.6	0.27	0.047	308
0.45	0.6	0.39	0.051	308
0.13	0.6	0.11	0.020	318
0.22	0.6	0.18	0.032	318
0.32	0.6	0.28	0.038	318
0.45	0.6	0.41	0.040	318

were prepared, and equilibration was carried out in a thermostatted shaker. All solutions were left in a temperature-controlled shaking bath at (298, 308, and 318) K. In every 0.25 h, a sample was taken out and titrated with 0.1 N NaOH, and phenolphthalein was used as an indicator (relative uncertainty: 1 %). So, the period of achieving to the equilibrium state was determined as 1.5 h. The samples were shaken for 1.5 h, and an optimum amount of adsorbent was determined as 0.6 g. The effect of initial acid concentration was investigated at (298 ± 1) K by using this optimum amount of alumina. Adsorption isotherms depended on the initial acid concentration.

■ RESULTS AND DISCUSSION

Adsorption experiments were studied at four different initial succinic acid concentrations by alumina to see the effect of initial acid concentration on adsorption. It was observed from Table 1 and shown in Figure 1 that increasing the initial acid concentration from 0.13 $mol \cdot kg^{-1}$ to 0.45 $mol \cdot kg^{-1}$ adsorbed acids decreased in the efficiency for acids. In this respect, equilibrium concentrations increased from 0.10 $mol \cdot kg^{-1}$ to 0.41 $mol \cdot kg^{-1}$ for succinic acid. This may be explained by the saturation of accessible exchangeable sites of these adsorbents.

Tables 2 and Figure 2 present the results of the effect of the adsorbent dose on the extent of solute adsorption which was investigated by varying the dose from (0.2 to 2) g for alumina with a 0.45 $mol \cdot kg^{-1}$ initial succinic acid concentration at the temperature 298 K, respectively. It was observed that, as the dose increases, the amount of adsorbed solute increases. In the maximum alumina dose, 2 g, the maximum adsorption was reached and the minimum equilibrium concentration, 0.28 $mol \cdot kg^{-1}$.

Table 3 and Figure 3 show that the results of effect of contact time on the removal of succinic acid. The effect of contact time for the adsorption of succinic acid by alumina was studied for a period of 1.5 h for an initial succinic acid concentration of 0.45 $mol \cdot kg^{-1}$ at 298 K,; the alumina dosage was 0.6 g. The adsorbent uptakes of adsorbate species are fast at the initial stages of the contact period, and thereafter, it becomes slower near the equilibrium. In between these two stages of the uptake, the rate of adsorption is found to be nearly constant. This is obvious from the fact that a large number of vacant surface sites are available for adsorption during the initial stage, and after a lapse of time, the remaining vacant surface sites are

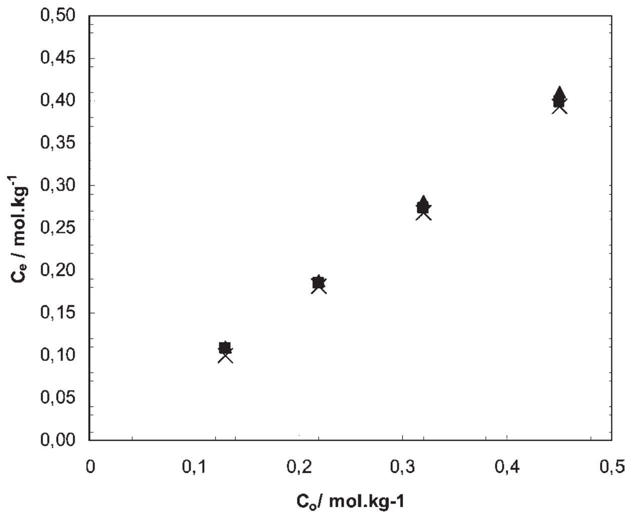

Figure 1. A plot of the effect of initial acid concentration on the adsorption of succinic acid. ×, 298 K; ■, 308 K; ▲, 318 K.

difficult to be occupied due to repulsive forces between the solute molecules on the solid and bulk phases.[18]

The effect of temperature on the adsorption of acids onto the alumina was studied at 298 K, 308 K, and 318 K. Table 4 shows the results of adsorption efficiency at different temperatures. It can be seen from the experimental results in Table 4 that the adsorption capacity of the alumina decreases with increasing temperature. This situation shows that the reaction is an exothermic reaction.

Adsorption Isotherms. Langmuir isotherm and Freundlich isotherm were studied to find equilibrium characteristics of adsorption.

The Langmuir equation,[17,18]

$$Q_e = \frac{K_A \cdot Q_o \cdot C_e}{1 + K_A \cdot C_e} \tag{1}$$

Q_e and Q_o denote the adsorbent-phase concentrations of succinic acid and saturation capacity.

The values of K_A and Q_e are determined by the following equation to which eq 2 is transformed.

$$\frac{C_e}{Q_e} = C_e \frac{1}{Q_o} + \frac{K_L}{Q_o} \qquad K_L = \frac{1}{K_A} \tag{2}$$

The results show that the Langmuir isotherm obeys to experimental data for succinic acid standart deviation (SD) values of 5.26, at 298 K; 11.48, at 308 K; and 8.43 at 318 K, respectively.

The values of K_L and Q_o are determined from the intercept and slope of the straight line in Figure 4. Calculated parameters of Langmuir equation was presented in Table 5.

The second isotherm used in this study is Freundlich isotherm[19,20]

$$Q_e = K_f \cdot C_e^{1/n} \tag{3}$$

A logarithmic plot linearizes the equation enabling the exponent n and the constant K_f to be determined,

$$\log Q_e = \log K_f + (1/n) \log C_e \tag{4}$$

The values of K_f and $1/n$ at different concentrations were determined from the slope and intercept of the linear plots of log Q_e and log C_e.

Table 2. Effect of Amount of Adsorbents on the Adsorption of Succinic Acid

C_o	Amberlite IRA-67	C_e	Q_e	T
$mol \cdot kg^{-1}$	g	$mol \cdot kg^{-1}$	$g \cdot mg^{-1}$	K
0.45	0.2	0.42	0.091	298
0.45	0.4	0.41	0.061	298
0.45	0.6	0.39	0.056	298
0.45	0.8	0.39	0.048	298
0.45	1	0.38	0.042	298
0.45	1.2	0.36	0.046	298
0.45	1.4	0.34	0.048	298
0.45	1.6	0.33	0.046	298
0.45	1.8	0.30	0.048	298
0.45	2	0.28	0.050	298

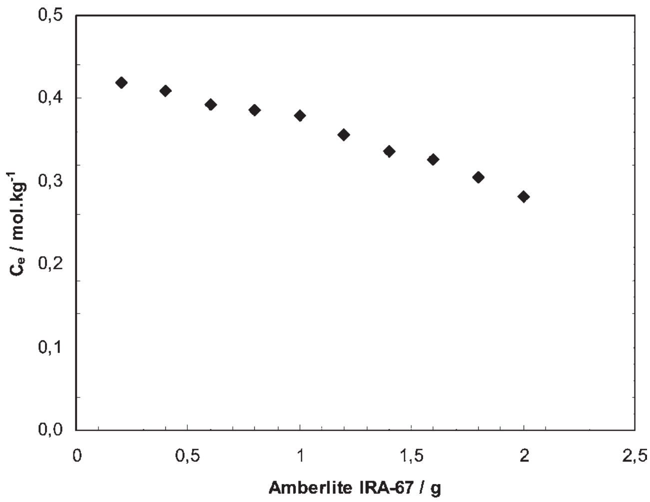

Figure 2. A plot of the effect of the amount of adsorbents on the adsorption of succinic acid, at 298 K.

Table 3. Effect of Contact Time on the Adsorption of Succinic Acid

C_o	Amberlite IRA-67	C_e	Q_e	t	T
$mol \cdot kg^{-1}$	g	$mol \cdot kg^{-1}$	$g \cdot mg^{-1}$	h	K
0.45	0.6	0.41	0.038	0.25	298
0.45	0.6	0.40	0.045	0.50	298
0.45	0.6	0.40	0.047	0.75	298
0.45	0.6	0.40	0.049	1	298
0.45	0.6	0.40	0.049	1.25	298
0.45	0.6	0.40	0.049	1.5	298

The results shows that the Freundlich isotherm obeys the experimental data for succinic acid standard deviation (SD) values of 0.19, at 298 K; 0.25, at 308 K; and 0.29, at 318 K, respectively.

The values of K_f and $1/n$ at different concentrations were determined from the slope and intercept of the linear plots of log Q_e and log C_e. Figure 5 shows the plot of the Freundlich equation isotherm for succinic acid adsorption for both

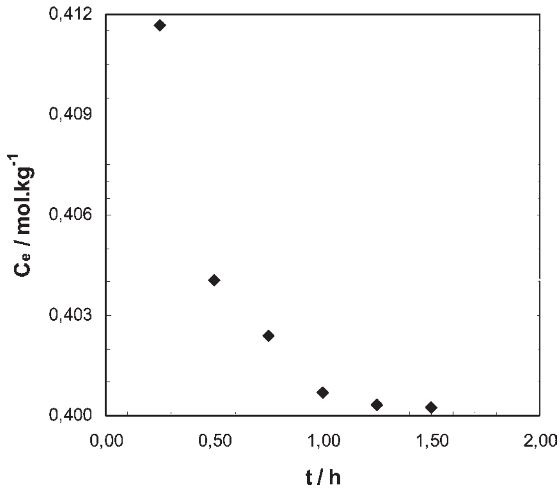

Figure 3. A plot of the effect of contact time on the adsorption of succinic acid, at 298 K.

Table 4. Effect of Temperature on the Adsorption of Succinic Acid

C_o	Amberlite IRA-67	C_e	Q_e	T
$mol \cdot kg^{-1}$	g	$mol \cdot kg^{-1}$	$g \cdot mg^{-1}$	K
0.45	0.6	0.39	0.056	298
0.45	0.6	0.40	0.051	308
0.45	0.6	0.41	0.040	318

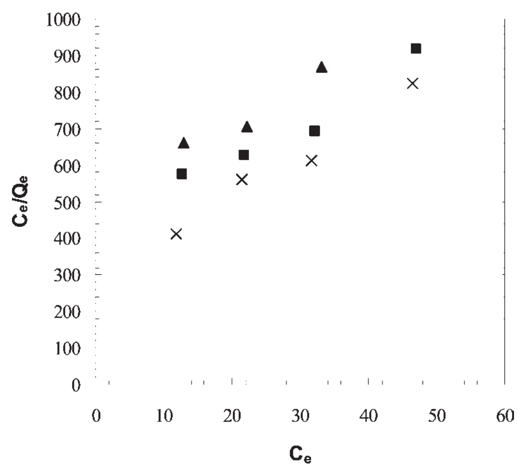

Figure 4. A plot of the Langmuir isotherm equation for the adsorption of succinic acid. ×, 298 K; ■, 308; ▲, 318 K.

adsorbents. Results of the Freundlich equation are presented in Table 6.

The last isotherm for this work is the Temkin isotherm. This isotherm contains a factor that explicitly takes into account adsorptive−adsorbent interactions. This isotherm assumes that the heat of adsorption of all the molecules in the layer decreases linearly with coverage due to adsorbent−adsorbate interactions and that the adsorption is characterized by a uniform distribution of binding energies, up to some maximum binding energy.[17,18]

Table 5. Results of Langmuir Isotherms for the Adsorption of Succinic Acids by Alumina

Langmuir isotherm					
K_L/Q_o	Q_o	K_L	$1/Q_o$	SD	T/K
285.42	0.088	25.12	11.40	5.26	298
418.22	0.100	41.82	9.98	11.48	308
389.82	0.062	24.17	16.24	8.43	318

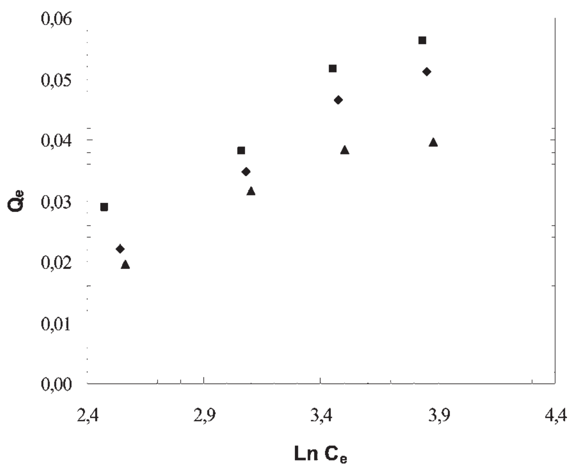

Figure 5. A plot of the Freundlich isotherm equation for the adsorption of succinic acid. ×, 298 K; ■, 308; ▲, 318 K.

Table 6. Results of Freundlich Isotherms for the Adsorption of Succinic Acids by Alumina

Freundlich isotherm					
$\log K_f$/mg·g^{-1}	$1/n$	K_f	n	SD	T/K
−2.09	0.52	0.0081	1.92	0.19	298
−2.36	0.66	0.0044	1.67	0.25	308
−2.28	0.54	0.0052	1.85	0.29	318

The Temkin isotherm for adsorption is given as

$$Q_e = \frac{RT}{b}\ln(K_T C_e) \tag{5}$$

which can be linearized as;

$$Q_e = B_1 \ln(K_T) + B_1 \ln(C_e) \tag{6}$$

where

$$B_1 = \frac{RT}{b} \tag{7}$$

A plot of Q_e versus $\ln(C_e)$ enables the determination of the isotherm constants B_1 and K_T from the slope and the intercept, respectively. K_T is the equilibrium binding constant (mol^{-1}) corresponding to the maximum binding energy, and constant B_1 is related to the heat of adsorption. Figure 6 shows the Temkin isotherm plot for alumina. The Temkin isotherm quantities listed in Table 7 alumina.

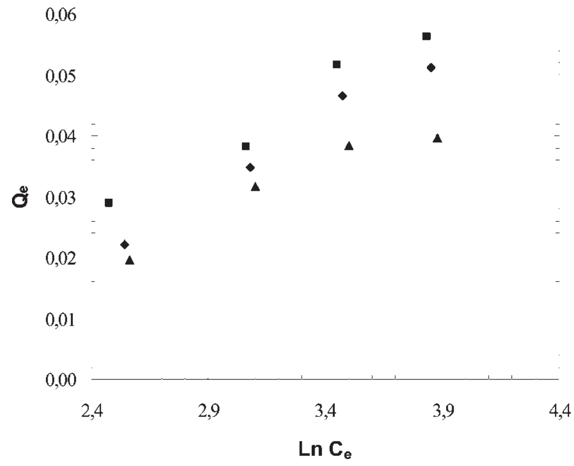

Figure 6. A plot of the Temkin isotherm equation for the adsorption of succinic acid. ×, 298 K; ■, 308; ▲, 318 K.

Table 7. Results of Temkin Isotherms for the Adsorption of Succinic Acids by Alumina

Temkin isotherm			
K_T	B_1	SD	T/K
0.32	0.021	0.22	298
0.21	0.023	0.40	308
0.30	0.016	0.29	318

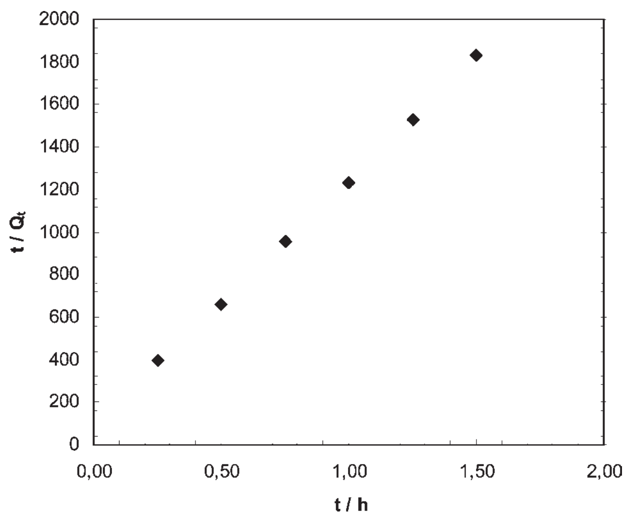

Figure 7. Linear plot of the pseudosecond-order kinetic model at 298 K.

The results shows that the Temkin isotherm obeys experimental data for succinic acid SD values of 0.22, at 298 K; 0.40, at 308 K; and 0.29, at 318 K, respectively.

Pseudosecond-Order Equation. Another model for the analysis of sorption kinetics is the pseudosecond-order equation. The rate law for this system is expressed as

$$\frac{dQ}{dt} = k_2 \cdot (Q_e - Q)^2 \tag{8}$$

Table 8. Obtained Constants for Pseudosecond-Order Kinetic Models

pseudosecond-order equation		
Q_e	k_2	
$mg \cdot g^{-1}$	$mg \cdot g^{-1} \cdot min^{-1}$	SD
0.052	3.89	3.20

Integrating eq 5, for the boundary conditions $t = 0$ to $t = t$ and $Q = 0$ to $Q = Q$, gives

$$\frac{1}{(Q_e - Q)} = \frac{1}{Q_e} + k_2 \cdot t \qquad (9)$$

where k_2 is the pseudosecond-order rate constant of sorption. Equation 6 can be rearranged to obtain a linear form,

$$\frac{t}{Q} = \frac{1}{k_2 \cdot Q_e^2} + \frac{1}{Q_e} \cdot t \qquad (10)$$

The plot of t/Q versus t gives a straight line with an intercept of $1/k_2 \cdot Q_e^2$ and slope of $1/Q_e$. So the gram of solute sorbed per gram of sorbent at equilibrium (Q_e) and sorption rate constant (k_2) could be evaluated from the slope and intercept, respectively. The pseudosecond-order model was recently applied for analysis of sorption kinetics from liquid solutions by Ho et al.[19−23]

The values of Q_e and k_2 were obtained from the slopes and intercepts of plots in Figure 7. These constants and also the correlation coefficients are listed in Table 8. As it can be seen in Figure 7 this model was fitted to these experimental results very well.

CONCLUSIONS

In this experimental investigation, the adsorption of succinic acid on alumina has been examined. The effects of contact time, amount of adsorbent, initial acid concentrations, and temperature on succinic acid adsorption by alumina have been investigated. It has been observed that the recovery of succinic acid increases with an increasing amount of alumina. But, initial acid concentration does not have a similar effect. Removal of succinic acid has decreased with increasing initial acid concentration. It has been found that adsorption decreases with increasing temperature. The results show that the adsorption process of succinic acid by alumina could be described well with both Freundlich and Langmuir isotherms. The experimental equilibrium data fitted well to all equations used with Langmuir, Freundlich, and Temkin equations could be recommended for succinic acid adsorption by alumina. The results show that alumina is an effective adsorbent for the removal of succinic acid from aqueous solutions.

AUTHOR INFORMATION

Corresponding Author

*E-mail: isminci@istanbul.edu.tr.

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