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Investigation of Adsorption Equilibrium and Kinetics of Propionic Acid and Glyoxylic Acid from Aqueous Solution by Alumina

İsmail İnci,*,† Şahika Sena Bayazit,‡ and Hasan Uslu‡

†Engineering Faculty, Chemical Engineering Department, Istanbul University, 34850, Istanbul, Turkey

‡Engineering and Architecture Faculty, Chemical Engineering Department, Beykent University, Ayazağa, 34396, Istanbul, Turkey

ABSTRACT: The adsorption equilibria of propionic acid and glyoxylic acid on alumina are investigated experimentally and theoretically in this study. Alumina was used as the adsorbent. The period of achieving the equilibrium state and the effects of the amount of adsorbent, temperature, and initial acid concentration were investigated experimentally. Langmuir, Freundlich, and Temkin adsorption isotherm equations are fitted well with the experimentally measured data. It was found that the equilibrium isotherms depended on the initial acid concentration significantly. The Langmuir isotherm was found to best represent the data for both of the acids. The pseudosecond-order model, intraparticle diffusion model, and Elovich model were applied to experimental data. The adsorption of both acids followed pseudosecond-order kinetics. Diffusion is not the only rate-controlling step.

INTRODUCTION

Carboxylic acids have a wide range of application fields, such as pharmaceuticals, polymers, food, and so forth. So the recovery of carboxylic acids is an important process in chemical engineering. There have been numerous separation techniques developed in recent years for isolating the organic acids from aqueous solutions, such as reactive extraction, electrodialysis, esterification, and reactive distillation. Adsorption is one of these methods. The adsorbents which are commonly used are activated carbon, alumina, and different kinds of ion-exchange resins.

Propionic acid is a colorless, corrosive liquid with a sharp, unpleasant odor. It is produced by fermentation and is widely used in chemical, pharmaceutical, and food industries. It is used primarily for animal feed preservation, including hay, silage, and grains, and in human foods, mainly in baked goods and cheeses. The growing demand of this acid draws attention towards more economical energy-efficient technology.[1] Propionic acid is an important mold inhibitor. Its calcium, sodium, and potassium salts are widely used as food and feed preservatives.[2] Glyoxylic acid (oxoacetic acid) is the smallest α-keto acid. It has a ketone group on the carbon atom next to the acid group. Glyoxylic acid has two functional groups, both carboxylic acid and aldehyde. In industrial fields, it is used as a basic chemical for the synthesis of other chemical products of acids, esters, and cyclic compounds. Application fields include aroma compounds, agrochemicals, pharmaceuticals, and polymers. Glyoxylates, any salt, anion, or ester of glyoxylic acid, are important in biochemical research.[3] Glyoxylic acid is produced by the ozonolysis of maleic acid.

The adsorption of carboxylic acids on alumina has a very strong adsorption energy because most carboxylic acids are weak acids and their degrees of dissociation in an aqueous solutions are affected by the acidity of the medium. For example, the adsorption of aromatic acids on alumina is a strong function of the solution acidity. Although the adsorption of medium- and long-chain aliphatic carboxylic acids on alumina have been of considerable interest due to their property of forming self-assembled monolayers, the adsorption of water-soluble carboxylic acids on alumina has not been studied extensively.[4]

The nature of the interaction between the carboxylic group with hydroxyls on the surface has been studied by many investigators. In particular, the adsorption of carbon dioxide or aromatic acids on alumina were studied. It is generally recognized that both oxygen atoms in the carboxylic group are anchored on the alumina surface, but two models have been proposed for the interaction. The bridging model considers that both oxygen atoms of the carboxylic group are linked to Al—O sites on the surface through 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. 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 strong hydrogen bonding.[4]

Numerous researchers investigated the adsorption of carboxylic acids from aqueous solutions by using polymeric sorbents. Chen and Ju studied the coupled fermentation and adsorption to prevent the product concentration from reaching inhibitory levels for lactic acid.[1−5] Kawabata et al. separated carboxylic acid by using a polymer sorbent of pyridine skeletal structure and a cross-linked structure. The polymer sorbent showed good selectivity and high adsorption capacity for carboxylic acids even in the presence of inorganic salts.[6,7]

The aim of this study is to define the sorption capability of alumina, when used for the adsorption of carboxylic acids from aqueous solutions. Regeneration was not studied in these experiments.

MATERIALS AND METHODS

Materials. Propionic acid, glyoxylic acid monohydrate, and alumina were obtained from Merck Co. The properties of alumina (Merck 101095) are $M = 101.96\ \mathrm{g \cdot mol^{-1}}$ and melting

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point = 2050 °C. Its particle size is between (0.063 and 0.200) mm. It was used without further treatment. Propionic acid stock solution was prepared to 10.63 %, and glyoxylic acid stock solutions were prepared to 10.53 %. For determining the effect of initial acid concentration, approximately (2.71, 5.22, 15.61, and 21.48) % solutions were prepared for propionic acid; (2.65, 5.34, 14.03, and 20.42) % solutions were prepared for glyoxylic acid.

Methods. Adsorption experiments were carried out as batch type. The aim of these experiments was to determine the effect of important variables on the adsorption, such as the amount of adsorbent, time, initial acid concentration, and temperature. As a result of the pre-experiment, an optimum amount of adsorbent was determined as 0.4 g for propionic acid and 0.8 g for glyoxylic acid. For each experimental run, 5 mL stock acid solution and a known amount of adsorbent were taken in a 50 mL flask. This mixture was shaken at a constant speed and temperature in a thermostatted shaker. A sample was taken out periodically, and the aqueous phase was titrated with 0.1 N NaOH solution, with phenolphtalein used as an indicator. The alumina particles remained suspended and did not settle down easily. Therefore, all of the samples were percolated with filter paper and then analyzed. So, the period of equilibration time was determined as 75 min for propionic acid and 140 min for glyoxylic acid. Preliminary experiments showed these values as sufficient time for equilibration. For determining the effect of amount of adsorbent, 10 solutions (5 mL acid solution-increasing adsorbent doses) were prepared. For determining the temperature effect on adsorption, five different amounts of adsorbent and 5 mL acid stock solution mixture were shaken at (298 and 308) K, and then the aqueous phases were analyzed. Different initial acid concentrations were prepared and mixed with an ptimum sorbent dose. After the equilibration section, the results were used for the calculation of adsorption isotherms. Langmuir, Freundlich, and Temkin isotherms were calculated as depended on initial acid concentration. The Elovich, pseudosecond-order, and Weber-Morris intraparticular diffusion models were applied to the experimental results.

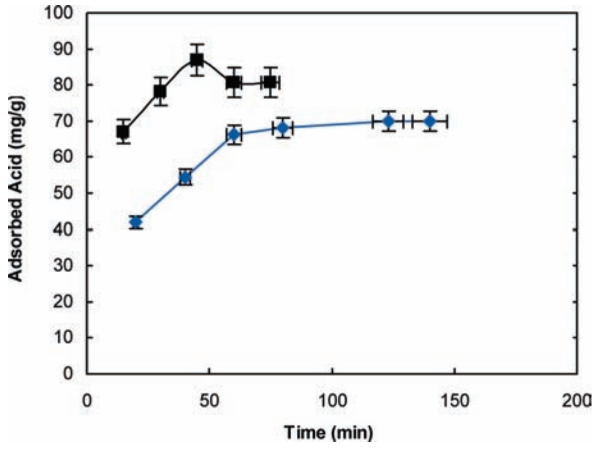

Figure 1. A plot of the effect of contact time on the adsorption. ■, propionic acid; ◆, glyoxylic acid.

■ RESULTS AND DISCUSSION

In this study, the period of the achieving the equilibrium state of the adsorbents and the effect of amount of adsorbent on adsorption, initial acid concentration, and temperature were investigated. Results of this experimental procedure were used for determining the reaction kinetics and equilibrium parameters.

Process Variables. *Effect of Contact Time.* The effects of contact time for the adsorption of propionic acid and glyoxylic acid by alumina were studied for an initial propionic acid concentration of 1.44 mol·L^{-1} and initial glyoxylic acid concentration of 1.07 mol·L^{-1} at 298 K. The alumina dose was an optimum amount. The effect of contact time on the amount of adsorbed acid is shown in Figure 1, and results are shown in Table 1.

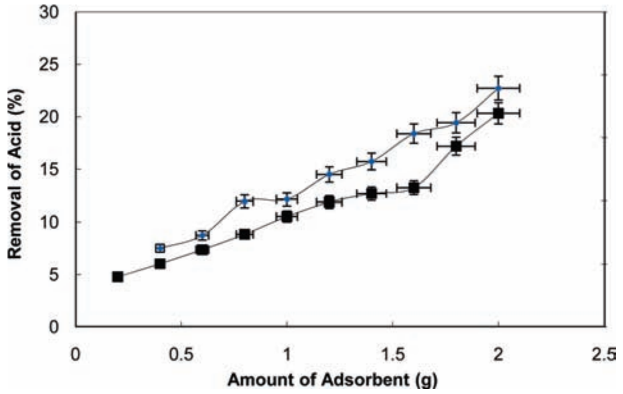

Figure 2. A plot of the effect of amount of adsorbents on the adsorption. ■, propionic acid; ◆, glyoxylic acid.

Table 1. Effect of Contact Time on the Adsorption

acid	initial acid conc. g·L^{-1}	amount of adsorbent g	equilibrium conc. C_e g·L^{-1}	amount of adsorbed acid Q_e mg·g^{-1}	percentage of removal acid %	T K	time min
glyoxylic acid	98.50	0.8	91.8	41.88	6.8	298	20
	98.50	0.8	89.8	54.38	8.83	298	40
	98.50	0.8	87.9	66.25	10.76	298	60
	98.50	0.8	87.6	68.13	11.07	298	80
	98.50	0.8	87.3	70.00	11.37	298	123
	98.50	0.8	87.3	70.00	11.37	298	140
propionic acid	106.56	0.4	101.2	67.00	5.03	298	15
	106.56	0.4	100.3	78.25	5.87	298	30
	106.56	0.4	99.6	87.00	6.53	298	45
	106.56	0.4	100.1	80.75	6.06	298	60
	106.56	0.4	100.1	80.75	6.06	298	75

Table 2. Effect of Amount of Adsorbents on the Adsorption

	initial acid conc.		equilibrium conc. C_e	amount of adsorbed acid Q_e	percentage of removal acid	T
acid	$g \cdot L^{-1}$	amount of adsorbent	$g \cdot L^{-1}$	$mg \cdot g^{-1}$	%	K
glyoxylic acid	105.86	0.2	97.5	209.00	7.89	298
	105.86	0.4	97.9	99.50	7.51	298
	105.86	0.6	96.6	77.17	8.74	298
	105.86	0.8	93.2	79.13	11.95	298
	105.86	1.0	93.0	64.30	12.14	298
	105.86	1.2	90.5	64.00	14.50	298
	105.86	1.4	89.2	59.5.	15.73	298
	105.86	1.6	86.4	60.82	18.38	298
	105.86	1.8	85.3	57.11	19.42	298
	105.86	2.0	81.8	60.15	22.72	298
propionic acid	106.56	0.2	102.3	106.50	3.99	298
	106.56	0.4	101.2	67.00	5.03	298
	106.56	0.6	100.0	54.67	6.15	298
	106.56	0.8	98.7	49.13	7.37	298
	106.56	1.0	97.2	46.80	8.78	298
	106.56	1.2	96.0	44.00	9.90	298
	106.56	1.4	95.3	40.21	10.56	298
	106.56	1.6	94.8	36.75	11.03	298
	106.56	1.8	91.3	42.39	14.32	298
	106.56	2.0	88.5	45.15	16.94	298

Table 3. Effect of Initial Acid Concentration on the Adsorption

	initial acid conc.		equilibrium conc. C_e	amount of adsorbed acid Q_e	percentage of removal acid	T
acid	$g \cdot L^{-1}$	amount of adsorbent	$g \cdot L^{-1}$	$mg \cdot g^{-1}$	%	K
glyoxylic acid	26.70	0.8	19.1	47.50	28.46	298
	54.31	0.8	43.7	66.31	19.53	298
	105.86	0.8	93.2	79.13	11.95	298
	140.84	0.8	125.8	94.00	10.67	298
	204.36	0.8	198.2	38.50	3.01	298
propionic acid	27.38	0.4	23.4	49.75	14.53	298
	52.54	0.4	50.6	24.25	3.69	298
	106.56	0.4	101.2	67.00	5.03	298
	156.14	0.4	151.3	60.50	3.09	298
	215.34	0.4	203.4	149.25	5.54	298

For both adsorbents, uptake of adsorbate species is 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 difficult to be occupied due to repulsive forces between the solute molecules on the solid and bulk phases.[8]

Effect of Amount of Adsorbent. The effect of adsorbent dose on the extent of solute adsorption was investigated by varying the dosage from (0.20 to 2.00) g for alumina under the selected initial solute concentration for propionic acid, 1.44 $mol \cdot L^{-1}$, and for glyoxylic acid, 1.15 $mol \cdot L^{-1}$. It can be shown from Figure 2 and Table 2 that the removal of acid increases with an increasing amount of adsorbent, and the percentage of removal acid increased. In the maximum amount for alumina (2.00 g), the maximum adsorption capacity, 16.94 % for propionic acid and 22.72 % for glyoxylic acid, has been obtained.

Effect of Initial Acid Concentration. The adsorption effect was studied at different initial acid concentrations for propionic acid (0.37 $mol \cdot L^{-1}$, 0.71 $mol \cdot L^{-1}$, 1.44 $mol \cdot L^{-1}$, 2.11 $mol \cdot L^{-1}$, and 2.91 $mol \cdot L^{-1}$) and for glyoxylic acid (0.29 $mol \cdot L^{-1}$, 0.59 $mol \cdot L^{-1}$, 1.15 $mol \cdot L^{-1}$, 1.53 $mol \cdot L^{-1}$, and 2.22 $mol \cdot L^{-1}$). It was observed from Table 3 and Figure 3 that, by increasing the initial acid concentration, the adsorbed acid concentration decreased in efficiency. The percentage of removed acid decreased from 14.53 % to 5.54 % for propionic acid and from 28.46 % to 3.01 % for glyoxylic acid with the increased initial acid concentration. This may be explained by the saturation of adsorbent surfaces.

Effect of Temperature. The adsorption effect was studied at two different temperatures for stock acid solution and different dosages of adsorbent mixtures. The temperatures which chosen for this study are (298 and 308) K. As shown in Table 4 and Figure 4, the adsorption efficiency of the adsorbent is decreased with increasing temperature. So, it was understood that the adsorbents have an exothermic nature, like the most of the adsorption reactions.

Equilibrium. A dynamic phase equilibrium is established in adsorption for the distribution of the adsorbate between the fluid and the adsorbent surface. This equilibrium is generally expressed in terms of the concentration of the adsorbate in the fluid and the adsorbate loading on the adsorbent. The adsorption isotherms obtained from the experimental studies will provide an upper limit on the adsorption of adsorbate from a given fluid mixture on a specific adsorbent for a designated set of conditions.[9] Langmuir, Freundlich, and Temkin isotherms were applied to the experimental data in this study.

Langmuir Isotherm. The Langmuir equation[10−14]

$$Q_e = \frac{K_A \cdot Q_{max} \cdot C_e}{1 + K_A \cdot C_e} \qquad (1)$$

Q_{max} denotes the maximum adsorbent uptake. Q_e denotes the experimental adsorbent uptake. K_A is a coefficient. It is related to the affinity between the adsorbent and the adsorbate. The values of K_A and Q_{max} are determined by the following equation to which eq 2 is transformed.

$$\frac{C_e}{Q_e} = \frac{1}{Q_{max}K_L} + \frac{C_e}{Q_{max}} \qquad (2)$$

$$K_L = \frac{1}{K_A} \qquad (3)$$

The values of K_L and Q_{max} are determined from the intercept and slope of the straight line in Figure 5. Calculated parameters of the Langmuir equation are presented in Table 5.

Freundlich Isotherm. The second isotherm was used in this study is Freundlich isotherm.[11,15]

$$Q_e = K_f . C_e^{1/n} \qquad (4)$$

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

$$\log Q_e = \log K_f + (1/n)\log C_e \qquad (5)$$

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 6 shows the plots of Freundlich equilibrium isotherms for propionic acid and glyoxylic acid adsorption. Results of the Freundlich equation were presented in Table 5.

Temkin Isotherm. The Temkin isotherm contains a factor that explicitly takes into the account adsorptive−adsorbent interac-

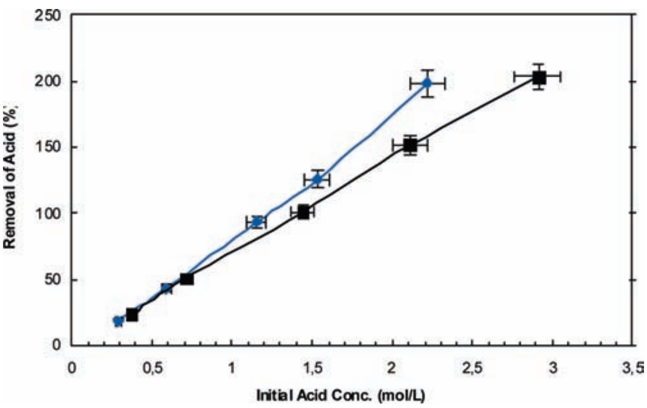

Figure 3. A plot of the effect of initial acid concentration on the adsorption. ■, propionic acid; ◆, glyoxylic acid.

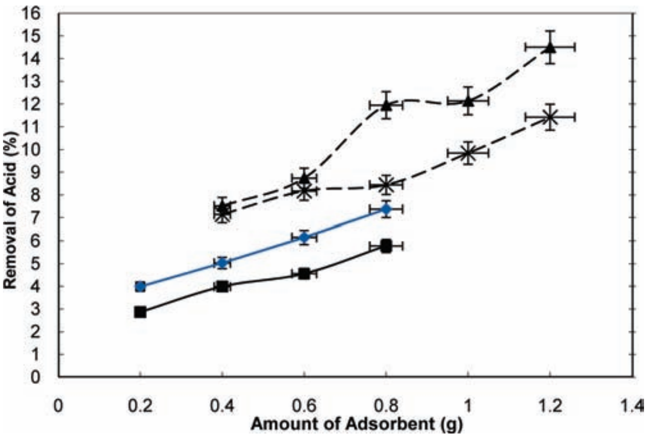

Figure 4. A plot of the effect of temperature on the adsorption. ▲, 25 °C, glyoxylic acid; ×, 35 °C, glyoxylic acid; ◆, 25 °C, propionic acid; ■, 35 °C, propionic acid.

Table 4. Effect of Temperature on the Adsorption

	initial acid conc.		equilibrium conc. C_e	amount of adsorbed acid Q_e	percentage of removal acid	T
acid	$g \cdot L^{-1}$	amount of adsorbent	$g \cdot L^{-1}$	$mg \cdot g^{-1}$	%	K
glyoxylic acid	107.7	0.4	100	96.25	7.14	308
	107.7	0.6	98.9	73.33	8.17	308
	107.7	0.8	98.6	56.88	8.44	308
	107.7	1	97.1	53.00	9.84	308
	107.7	1.2	95.4	51.25	11.42	308
propionic acid	1.44	0.2	103.5	76.50	2.87	308
	1.44	0.4	102.3	53.25	3.99	308
	1.44	0.6	101.7	40.50	4.56	308
	1.44	0.8	100.4	38.50	5.78	308

tions. This isotherm assumes that the heat of adsorption of all of 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.[8]

$$q_e = \frac{RT}{b}\ln(K_T C_e) \tag{6}$$

Equation 6 can be linearized as,

$$q_e = B_1 \ln K_T + B_1 \ln C_e \tag{7}$$

In eq 7,

$$B_1 = \frac{RT}{b} \tag{8}$$

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.[8−15] Figure 7 shows the Temkin isotherm plots for both of acids, and isotherm parameters are shown in Table 5.

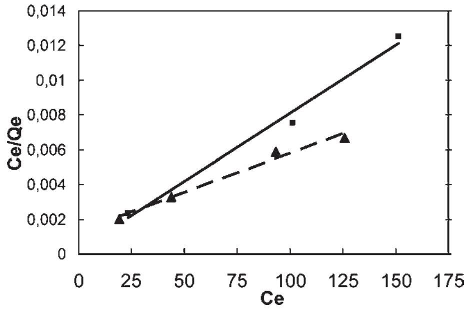

Figure 5. A plot of the Langmuir isotherm equation for the acid adsorption onto alumina. ■, propionic acid; ▲, glyoxylic acid.

The Langmuir isotherm gives good results with experimental results for both acids, with R^2 values of 0.983 for glyoxylic acid and 0.988 for propionic acid. For this reason, Langmuir was found to best represent the data for propionic and glyoxylic acid adsorption onto alumina.

Kinetics. Surface diffusion has an extremely important role for intraparticle diffusion in many cases of liquid-phase adsorption systems. A number of studies on surface diffusion have been carried out to elucidate the mechanism of surface diffusion and to develop an estimation procedure of surface-diffusion coefficient. The estimation of diffusion coefficient, however, is extremely difficult because it varies to a high degree according to the combination of adsorbates, adsorbents, and solvents. A strict understanding of the surface-diffusion mechanism is essential for the establishment of the estimation procedure of diffusion coefficients. The dependence of this coefficient, on both temperature and the amount adsorbed, q, can be investigated as

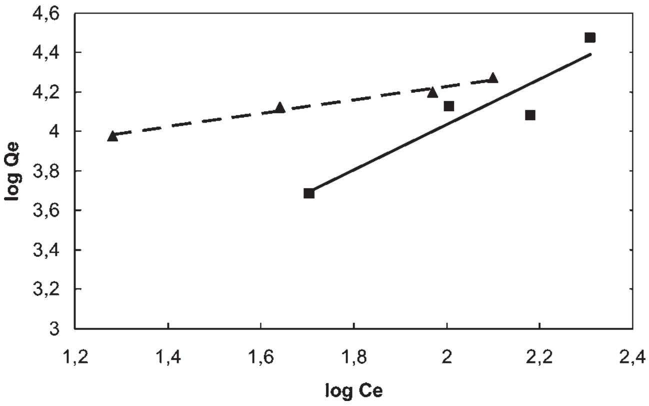

Figure 6. A plot of the Freundlich isotherm equation for the acid adsorption onto alumina: ■, propionic acid; ▲, glyoxylic acid.

Table 5. Isotherm Parameters for the Adsorption of Propionic and Glyoxylic Acid onto Alumina

Langmuir Isotherm					
glyoxylic acid			propionic acid		
Q_{max}	K_L		Q_{max}	K_L	
mg·g^{-1}	L·g^{-1}	R^2	mg·g^{-1}	L·g^{-1}	R^2
20000	0.0385	0.983	12500	0.2666	0.988

Freundlich Isotherm									
glyoxylic acid					propionic acid				
		K_f					K_f		
log K_f	1/n	mg$^{1-(1/n)}$·g^{-1}·L$^{-1/n}$	n	R^2	log K_f	1/n	mg$^{1-(1/n)}$·g^{-1}·L$^{-1/n}$	n	R^2
3.5441	0.3429	3500.26	2.916	0.984	1.7292	1.1532	53.60	0.867	0.872

Temkin Isotherm							
glyoxylic acid				propionic acid			
B_1		K_T		B_1		K_T	
J·mol^{-1}	ln K_T	L·g^{-1}	R^2	J·mol^{-1}	ln K_T	L·g^{-1}	R^2
4612.9	−0.914	0.401	0.972	8151.3	−2.186	0.112	0.716

characteristic features of surface diffusion.[14−16] For the estimation of the surface-diffusion coefficient, numerous diffusion models are developed. The Weber−Morris intraparticle diffusion model is one of them.

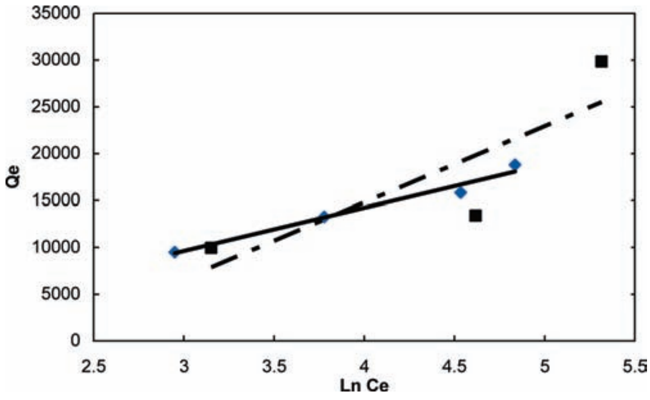

Figure 7. A plot of the Temkin isotherm equation for the acid adsorption onto alumina. ■, propionic acid; ◆, glyoxylic acid.

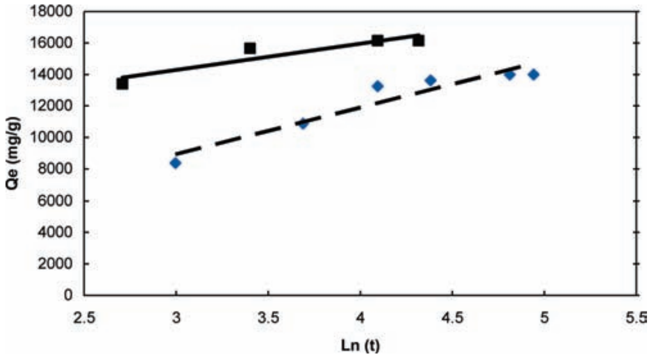

Figure 8. A plot of the Elovich model equation for the acid adsorption onto alumina. ■, propionic acid; ◆, glyoxylic acid.

To determine the kinetics of adsorption of propionic and glyoxylic acid onto alumina, pseudosecond-order, Weber−Morris intraparticle diffusion model, and Elovich model were applied.

The Elovich Equation. The Elovich model equation[15−17] is generally expressed as:

$$\frac{\mathrm{d}Q}{\mathrm{d}t} = \alpha \exp(-\beta \cdot Q) \tag{9}$$

where α is the initial adsorption rate $(\mathrm{mg \cdot g^{-1} \cdot min^{-1}})$ and β is the desorption constant $(\mathrm{g \cdot mg^{-1}})$ during any one experiment. To simplify the Elovich equation, $\alpha\beta t \gg t$ is assumed, and by applying the boundary conditions $Q = 0$ at $t = 0$ and $Q = Q$ at $t = t$ the equation becomes:

$$Q = \frac{1}{\beta}\ln(\alpha\beta) + \frac{1}{\beta}\ln(t) \tag{10}$$

A plot of q_t versus $\ln(t)$ should yield a linear relationship with a slope of $(1/\beta)$ and an intercept of $(1/\beta)\ \ln(\alpha\beta)$ (Figure 8). The constants are listed in Table 6.

Pseudosecond-Order Model.[8−13] The equation for the pseudosecond-order model is shown below.

$$\frac{\mathrm{d}q_t}{\mathrm{d}t} = k_s(q_e - q_t)^2 \tag{11}$$

In this equation, k_s is the pseudosecond-order rate coefficient $(\mathrm{g \cdot mg^{-1} \cdot min^{-1}})$. If eq 11 is integrated, a linear equation is obtained. This equation is shown as follows;

$$\frac{t}{q_t} = \frac{1}{k_s {q_e}^2} + \frac{1}{q_e}t \tag{12}$$

The initial sorption rate, Γ $(\mathrm{mg \cdot g^{-1} \cdot min^{-1}})$, at $t \to 0$ is defined as;

$$\Gamma = k_s {q_e}^2 \tag{13}$$

The values of k_s and calculated q_e are obtained from the slope of the plot t/q_t versus t. Γ and k_s are obtained from the intercept. The

Table 6. Kinetic Parameters for the Removal of Carboxylic Acids by Alumina

Elovich Model					
propionic acid			glyoxylic acid		
α	β	R^2	α	β	R^2
438726.6	$6 \cdot 10^{-4}$	0.854	3000	$3.37 \cdot 10^{-4}$	0.908

Pseudosecond-Order Model							
propionic acid				glyoxylic acid			
$Q_{e,calc}$	Γ	K_s		$Q_{e,calc}$	Γ	K_s	
$\mathrm{mg \cdot g^{-1}}$	$\mathrm{mg \cdot g^{-1} \cdot min^{-1}}$	$\mathrm{g \cdot mg^{-1} \cdot min^{-1}}$	R^2	$\mathrm{mg \cdot g^{-1}}$	$\mathrm{mg \cdot g^{-1} \cdot min^{-1}}$	$\mathrm{g \cdot mg^{-1} \cdot min^{-1}}$	R^2
16949.15	7038.21	$2.45 \cdot 10^{-5}$	0.99	15797.78	1012.14	$4.05 \cdot 10^{-6}$	0.99

W-M Intraparticle Diffusion Model					
propionic acid			glyoxylic acid		
k_{id}	I		k_{id}	I	
$\mathrm{mg \cdot g^{-1} \cdot min^{-1/2}}$	$\mathrm{mg \cdot g^{-1}}$	R^2	$\mathrm{mg \cdot g^{-1} \cdot min^{-1/2}}$	$\mathrm{mg \cdot g^{-1}}$	R^2
614.3	11083	0.967	755.41	5654.3	0.929

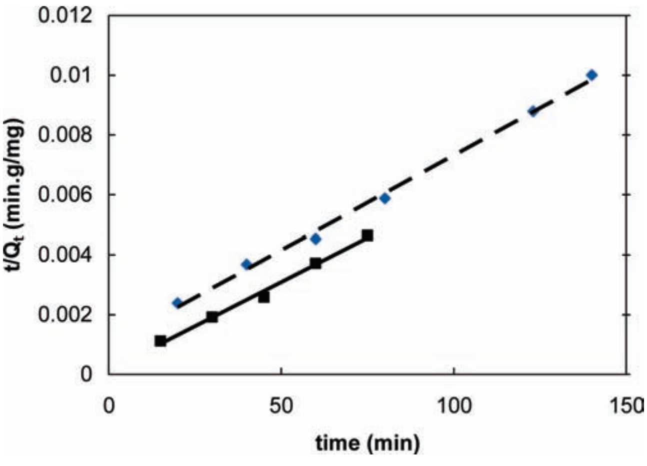

Figure 9. Pseudosecond-order plot for the removal of carboxylic acids by alumina. ■, propionic acid; ◆, glyoxylic acid.

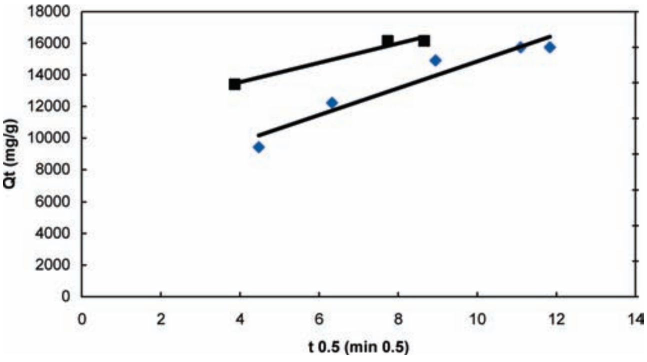

Figure 10. Weber and Morris intraparticle diffusion plot for the removal of carboxylic acids by alumina. ■, propionic acid; ◆, glyoxylic acid.

pseudosecond-order model parameters are shown in Table 6, and plots of both acids can be seen from Figure 9.

Pseudosecond-order models were investigated for both of the acids, calculated from linear regression. The correlation coefficients of pseudosecond-order model are approximate to unity. The correlation coefficients are 0.99 for both. Therefore, the adsorption of propionic acid and glyoxylic acid on alumina is fitted to the pseudosecond-order kinetic model.

Weber and Morris Intraparticle Diffusion Model.[8,16,17] Intraparticle diffusion can be estimated by using the Weber−Morris intraparticle diffusion model.

$$q_t = k_{id} t^{1/2} + I \qquad (14)$$

In eq 14, k_{id} is the intraparticle diffusion rate coefficient, and I gives an idea about the thickness of the boundary layer. These values can be found by a plot, q_t versus $t^{1/2}$. The slope is k_{id}, and the intercept is I. As seen in Figure 10, the straight lines deviate from the origin. The difference between final mass transfer rate and initial mass transfer rate may cause the deviations of straight lines. Also, this deviation can show that the pore diffusion is not the only rate-controlling step.[8] I and k_{id} values are shown in Table 6.

CONCLUSIONS

In this study, the adsorption of propionic and glyoxylic acid on alumina was investigated. The parameters which affect the adsorption reaction were determined. The increase of the amount of adsorbent is a positive effect (for propionic acid, sorbent dose was increased from (0.2 to 2.0) g and the percentage of removal of acid increased from (3.99 to 16.94) %); the increase of the initial acid concentration is a negative effect, and the increase of temperature is a negative effect. So, it is understood that the adsorption reaction is an exothermic reaction. Langmuir, Freundlich, and Temkin isotherms were applied to the experimental data, and equilibrium data for the adsorption of both of acid were represented by the Langmuir isotherm. This result shows that, as the adsorption processes progress, monolayers form. Adsorption kinetics was found to follow a second-order rate expression for propionic acid and glyoxylic acid. The diffusion is not the only rate-controlling step.

AUTHOR INFORMATION

Corresponding Author

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

REFERENCES

(1) Kumar, S.; Babu, B. V. *A brief review on propionic acid: a renewal energy source*; National Conference on Environmental Conservation (NCEC-2006); Birla Institute of Technology and Science (BITS): Pilani, September 1−3, 2006; pp 459−464.

(2) Lewis, P. V.; Shang, T. Y. Continous propionic acid fermentation by immobilized Propionibacterium acidipropionici in a novel packed-bed bioreactor. *Biotechnol. Prog.* **1992**, *8*, 104–110.

(3) http://chemicalland21.com/industrialchem/organic/GLYOXYLIC%20ACID.htm (accessed Jan 5, 2011).

(4) Mao, Y.; Fung, B. M. A study of the adsorption of acrylic acid and maleic acid from aqueous solutions onto alumina. *J. Colloid Interface Sci.* **1997**, *191*, 216–221.

(5) Chen, C. C.; Ju, L. K. Coupled lactic acid fermentation and adsorption. *Appl. Microbiol. Biotechnol.* **2002**, *59*, 170.

(6) Joglekar, H. G.; Rahman, I.; Babu, S.; Kulkarni, B. D.; Joshi, A. Comparative assessment of downstream processing options for lactic acid. *Sep.Purif. Technol.* **2006**, *52*, 1–17.

(7) Kawabata, N.; Yasuda, S.; Yamazaki, T. Process for recovering a carboxylic acid. U.S. Patent 4,323,702, 1982.

(8) Rajoriya, R. K.; Prasad, B.; Mishra, I. M.; Wasewar, K. L. Adsorption of benzaldehyde on granular activated carbon: kinetics, Equilibrium, and Thermodynamic. *Chem. Biochem. Eng. Q.* **2007**, *21*, 219–226.

(9) Peters, M. S.; Timmerhaus, K. D.; West, R. E. *Plant design and economics for chemical engineers*, 5th ed.; McGraw-Hill Company, Inc.: New York, 2003.

(10) Azizian, S. Kinetic models of sorption: a theoretical analysis. *J. Colloid Interface Sci.* **2004**, *276*, 47–52.

(11) Azizian, S.; Haerifar, M.; Bashiri, H. Adsorption of methyl violet onto granular activated carbon: Equilibrium, kinetics and modeling. *Chem. Eng. J.* **2009**, *146*, 36–41.

(12) Takatsuji, W.; Yoshida, H. Adsorption of organic acids on weakly basic ion exchanger: Equilibria. *J. Chem. Eng. Jpn.* **1997**, *30*, 396–405.

(13) Costa, C.; Rodrigues, A. Intraparticle diffusion of phenol in macroreticular adsorbents: Modeling and experimental study of batch and CSTR adsorbers. *Chem. Eng. Sci.* **1985**, *40*, 983–993.

(14) Li, P.; Xiu, G. H.; Rodrigues, A. E. Modeling separation of proteins by binding ligand shell-inert core sorbent in a batch adsorber. *Chem. Eng. Sci.* **2003**, *58*, 3361–3371.

(15) Iftikhar, A. R.; Bhatti, H. N.; Hanif, M. A.; Nadeem, R. Kinetic and thermodynamic aspects of Cu(II) and Cr(III) removal from aqueous solutions using rose waste biomass. *J. Hazard. Mater.* **2009**, *161*, 941–947.

(16) Miyabe, K.; Takeuchi, S. Model for Surface Diffusion in Liquid-Phase Adsorption. *AIChE J.* **1997**, *43*, 2997–3006.

(17) Urano, K.; Tachikawa, H. Process development for removal and recovery of phosphorus from wastewater by a new adsorbent. II. Adsorption rates and breakthrough curves. *Ind. Eng. Chem. Res.* **1991**, *30*, 1897–1899.