

Comparison of Solid–Liquid Equilibrium Data for the Adsorption of Propionic Acid and Tartaric Acid from Aqueous Solution onto Amberlite IRA-67

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Investigation of adsorption parameters such as effect of initial acid concentration, effect of amount of adsorbent, effect of temperatures, effect of contact time, fitting data to isotherms, and kinetic models for propionic acid and tartaric acid by using Amberlite IRA-67 adsorbent was studied. The maximum adsorption efficiencies were found to be 97.18% and 84.46% for tartaric acid and propionic acid, respectively. The best fitted isotherm was determined to be Langmuir for tartaric acid. The Langmuir isotherm was better fitted than the Freundlich isotherm for both acids. Elovich model equation was applied for data of each acids. The kinetics of the adsorption for both acids was determined as pseudo-second-order model.

Introduction

Adsorption or ion exchange is a reliable technology. Adsorption on ion-exchange resin has the advantage that it can be coupled with fermentation process. Many fermentations used to produce carboxylic acids operate most effectively at a pH above the pK_a of the acid product.^{1,2} Uslu has extensively worked separation and organic acids from wastewater stream by using an amine extractant.^{3–7}

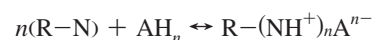
Also the existence of tartaric acid or propionic acid in industrial wastewater streams is an important environmental problem, because of their high affinity to water. Methods of recovery that utilize separating agents, such as solid sorbents, that are selective for carboxylic acids are attractive and have been reported by researchers such as Tung and King.⁸ Important characteristics of solid sorbents are a high capacity for the acid, a high selectivity for the acid as opposed to water, regenerability, and depending upon the process configuration, the biocompatibility with microorganisms.

Propionic acid inhibits the growth of mold and some bacteria at the levels between 0.1 and 1% by weight. As a result, most propionic acid produced is consumed as a preservative for both animal feed and food for human consumption. For animal feed, it is used either directly or as its ammonium salt. This application accounts for approximately half of the world production of propionic acid. Another major application is as a preservative in baked goods, which use the sodium and calcium salts. Propionic acid is also useful as an intermediate in the production of other chemicals, especially polymers. Cellulose–acetate–propionate is a useful thermoplastic. Vinyl propionate is also used. In more specialized applications, it is also used to make pesticides and pharmaceuticals. The esters of propionic acid have fruit-like odors and are sometimes used as solvents or artificial flavorings.⁹ Many researchers have worked to separate propionic acids from aqueous solution and solvents by adsorption. Alexander et al.¹⁰ studied the interaction of propionic acids with

the oxyhydroxide surface of aluminum. Horanyi and rizmayer¹¹ presented a study of the adsorption of propionic acid on a platinized platinum electrode by a tracer method. Robinson and Miles¹² reported adsorption of propionic acid from solvents using Duolite A-Z anion exchange resin.

Tartaric acid is an organic compound of the chemical formula $C_4H_6O_6$, and has the official name 2,3-dihydroxybutanedioic acid. In this name, the 2,3-dihydroxy refers to the two OH groups on the second and third carbon atoms, and the butane portion of the name refers to a four-carbon molecule. The “dioic” acid portion communicates the existence of two organic acid (COOH) groups on the molecule. Tartaric acid is found throughout nature, especially in many fruits and in wine. In addition to existing freely, it is also found as a salt (salts are the products of acids and bases), the most common of which are calcium tartrate, potassium tartrate, and sodium tartrate. Tartaric acid is used making silver mirrors, in the manufacturing of soft drinks, to provide tartness to foods, in tanning leather, and in making blueprints. Tartaric acid is used in cream of tartar (for cooking) and as an emetic (a substance used to induce vomiting). It readily dissolves in water and is used in making blueprints. Tartaric acid is a molecule that demonstrates properties of optical activity, where a molecule can cause the rotation of plane-polarized light. Tartaric acid exists in four forms (isomers are molecular rearrangements of the same atoms), each of which affects plane-polarized light differently.¹³ Yan et al.¹⁴ focused adsorption of tartaric acid enantiomers on Cu(111) in aqueous solution. Uslu and inci investigated adsorption of tartaric acid onto alumina.¹⁵

Using an amine-based adsorbent is an effective separation process for carboxylic acids. The reason of this result can be explained by ion exchange reaction between carboxylic acid and Amberlite IRA-67:



where $n = 1$ for acid and acid–amine complex formed, $R-N$ denotes a tertiary amine, $[AH]$ represents the acid forming the acid–amine complex ($R-(NH^+)_nA^{n-}$).

The subject of this study is to separate tartaric acid and propionic acid from aqueous solutions by using weakly basic

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Table 1. Effect of Initial Acid Concentration on the Adsorption of Tartaric Acid and Propionic Acid

initial concn (g·L ⁻¹)	initial concn (mol·L ⁻¹)	initial concn (%w/w)	amount of Amberlite IRA-67 (g)	equilibrium concn C _e (g·L ⁻¹)	adsorbed acid Q _e (g·mg ⁻¹)	removal of acid (%)	temp (K)
Tartaric Acid							
27.02	0.18	2.72	0.5	3.00	0.048	88.89	298
52.53	0.35	5.18	0.5	24.02	0.057	54.29	298
106.56	0.71	10.70	0.5	69.04	0.075	35.21	298
156.09	1.04	15.64	0.5	121.57	0.069	22.12	298
211.63	1.41	21.13	0.5	166.60	0.090	21.27	298
Propionic Acid							
27.80	0.38	2.78	0.5	12.58	0.030	54.75	298
50.50	0.68	5.05	0.5	31.08	0.038	38.45	298
106.80	1.44	10.68	0.5	82.88	0.048	22.40	298
204.50	2.76	20.45	0.5	177.30	0.054	13.30	298

adsorbent Amberlite IRA-67. The Freundlich and Langmuir isotherms have been fitted to experimental data. The Elovich equation has applied for kinetic study of the adsorption. Regeneration was not studied in these experiments.

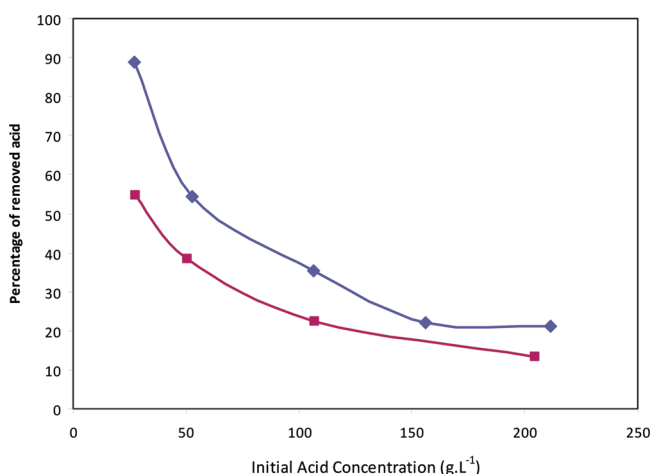


Figure 1. A plot of effect of initial acid concentration on the adsorption of acid: (◆) tartaric acid; (■) propionic acid.

Material and Methods

Material. Propionic acid, tartaric acid, and Amberlite IRA-67 were obtained from Merck Co. with purities > 99.0. Amberlite IRA-67 is a weakly basic gel-type polyacrylic resin with a tertiary amine functional group. It was used without further treatment. The same procedures were applied for samples of known weight of dry resin and acid solutions of known concentrations.

Methods. Different concentrations for both acids were prepared as 2.5%, 5%, 10%, and 20% (w/w). The mixtures of known amount of adsorbent presented in the tables and 5 mL of 10% (w/w) acid solution were prepared and equilibration was carried out in a thermostatted shaker. Every 15 min, a sample was taken and titrated with 0.1 N NaOH. Phenolphthalein was used as an indicator. So, the period of achieving the equilibrium state was determined as 90 min. The samples were shaken for 90 min, and an optimum amount of adsorbent was determined as 0.5 g. The effect of initial acid concentration was investigated at 298 K ± 1 by using this optimum amount of IRA-67. Adsorption isotherms were dependent on initial acid concentration.

Results and Discussion

Adsorption experiments were studied at different concentration of initial tartaric acid (0.18, 0.35, 0.71, 1.04, 1.41 mol·L⁻¹)

Table 2. Effect of Amount of Adsorbents on the Adsorption of Tartaric Acid and Propionic Acid

initial concn (g·L ⁻¹)	initial concn (mol·L ⁻¹)	initial concn (%w/w)	amount of Amberlite IRA-67 (g)	equilibrium concn C _e (g·L ⁻¹)	adsorbed acid Q _e (g·mg ⁻¹)	removal of acid (%)	temp (K)
Tartaric Acid							
106.56	0.71	10.7	0.25	87.05	0.078	18.31	298
106.56	0.71	10.7	0.50	69.04	0.075	35.21	298
106.56	0.71	10.7	0.75	54.03	0.070	49.29	298
106.56	0.71	10.7	1.00	40.52	0.066	61.97	298
106.56	0.71	10.7	1.25	27.02	0.064	74.65	298
106.56	0.71	10.7	1.50	19.51	0.058	81.69	298
106.56	0.71	10.7	1.75	13.51	0.053	87.32	298
106.56	0.71	10.7	2.00	9.01	0.048	91.55	298
106.56	0.71	10.7	2.25	4.50	0.045	95.77	298
106.56	0.71	10.7	2.50	3.00	0.042	97.18	298
Propionic Acid							
106.80	1.44	10.68	0.25	94.72	0.048	11.31	298
106.80	1.44	10.68	0.50	82.88	0.048	22.40	298
106.80	1.44	10.68	0.75	71.04	0.047	33.48	298
106.80	1.44	10.68	1.00	63.64	0.043	40.41	298
106.80	1.44	10.68	1.25	55.50	0.041	48.03	298
106.80	1.44	10.68	1.50	42.92	0.043	59.81	298
106.80	1.44	10.68	1.75	39.22	0.038	63.27	298
106.80	1.44	10.68	2.00	28.86	0.039	72.97	298
106.80	1.44	10.68	2.25	19.98	0.039	80.29	298
106.80	1.44	10.68	2.50	16.60	0.036	84.46	298

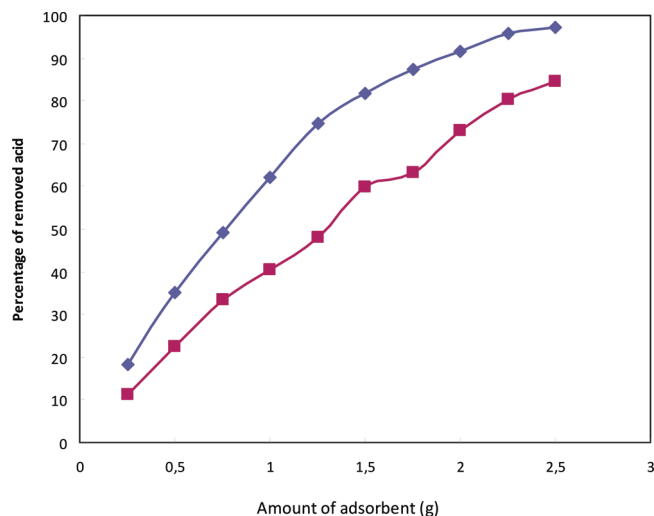


Figure 2. A plot of the effect of amount of adsorbents on the adsorption of acid: (◆) tartaric acid; (■) propionic acid.

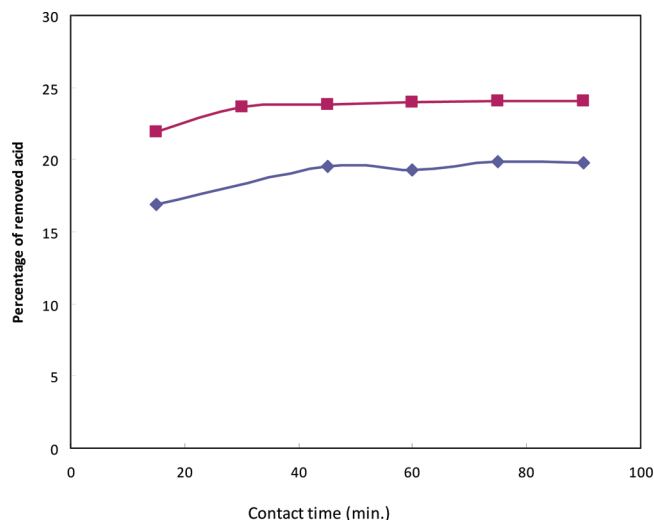


Figure 3. A plot of effect of contact time on the adsorption of acid: (◆) tartaric acid; (■) propionic acid.

and propionic acid concentrations (0.38, 0.68, 1.44, 2.76 mol·L⁻¹) by Amberlite IRA-67 to see the effect of initial acid concentration on adsorption. It was observed from Table 1 and shown in Figure 1 that increasing initial acid concentration from 0.18 mol·L⁻¹ to 2.76 mol·L⁻¹ adsorbed acid concentration decreased in the efficiency for both acids. In this respect, the efficiency of removal decreased from 88.99% to 21.27% for tartaric acid and from 54.75% to 13.30% for propionic acid. This may be explained by the saturation of accessible exchangeable sites of this adsorbent.

Table 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 0.25 to 2.50 g for Amberlite IRA-67 under the selected 0.71 and 1.44 mol·L⁻¹ of initial tartaric acid and propionic acid concentration, respectively, at temperature 298 K. It was observed that as the dose increases the amount of adsorbed solute increases. At the maximum Amberlite IRA-67 dose of 2.50 g, the maximum adsorption capacities 97.18% and 84.46% for tartaric acid and propionic acid, respectively, were reached.

Table 3 and Figure 3 show that the results of effect of contact time on the removal of tartaric acid and propionic acid, respectively. The effect of contact time for the adsorption of tartaric acid and propionic acid by Amberlite IRA-67 was studied for a period of 90 min for initial tartaric acid and propionic acid concentrations of 0.71 mol·L⁻¹ and 1.44 mol·L⁻¹ at 298 K, respectively. Amberlite IRA-67 dosage was 0.5 g.

The adsorbent uptakes 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.¹⁶

The effect of temperature on the adsorption of acids onto the Amberlite IRA-67 was studied at 298, 308, and 318 K. Table 4 shows results of adsorption efficiency in different temperatures. It can be seen from the experimental results in Table 4 that the adsorption capacity of the IRA 67 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.

In the Langmuir equation,^{17,18}

$$Q_e = \frac{K_A Q_0 C_e}{1 + K_A C_e} \quad (1)$$

Q_e and Q_0 denote the adsorbent-phase concentrations of acid and saturation capacity.

Table 3. Effect of Contact Time on the Adsorption of Tartaric Acid and Propionic Acid

initial concn (g·L ⁻¹)	initial concn (mol·L ⁻¹)	initial concn (%w/w)	amount of Amberlite IRA-67 (g)	equilibrium concn C_e (g·L ⁻¹)	adsorbed acid Q_e (g·mg ⁻¹)	removal of acid (%)	time (min)	temp (K)
Tartaric Acid								
106.56	0.71	10.7	0.5	88.55	0.0360	16.9	15	298
106.56	0.71	10.7	0.5	86.15	0.0408	19.5	45	298
106.56	0.71	10.7	0.5	86.00	0.0411	19.29	60	298
106.56	0.71	10.7	0.5	85.40	0.0420	19.86	75	298
106.56	0.71	10.7	0.5	85.50	0.0420	19.76	90	298
Propionic Acid								
106.80	1.44	10.68	0.5	83.40	0.0468	21.91	15	298
106.80	1.44	10.68	0.5	81.50	0.0506	23.69	30	298
106.80	1.44	10.68	0.5	81.40	0.0508	23.78	45	298
106.80	1.44	10.68	0.5	81.20	0.0512	23.97	60	298
106.80	1.44	10.68	0.5	81.10	0.0514	24.06	75	298
106.80	1.44	10.68	0.5	81.10	0.0514	24.06	90	298

Table 4. Effect of Temperature on the Adsorption of Tartaric Acid and Propionic Acid

initial concn (g·L ⁻¹)	initial concn (mol·L ⁻¹)	initial concn (%w/w)	amount of Amberlite IRA-67 (g)	equilibrium concn C _e (g·L ⁻¹)	adsorbed acid Q _e (g·mg ⁻¹)	removal of acid (%)	temp (K)
Tartaric Acid							
106.56	0.71	10.7	0.5	67.54	0.078	36.62	288
106.56	0.71	10.7	0.5	69.04	0.075	35.21	298
106.56	0.71	10.7	0.5	70.54	0.072	33.80	308
106.56	0.71	10.7	0.5	75.05	0.063	29.57	318
Propionic Acid							
106.80	1.44	10.68	0.5	82.90	0.048	22.38	298
106.80	1.44	10.68	0.5	84.00	0.046	21.35	308
106.80	1.44	10.68	0.5	85.60	0.042	19.85	318

The values of K_A and Q_e are determined by the following equations:

$$C_e = -K_L + C_e \frac{Q_0}{Q_e} K_L = \frac{1}{K_A} \quad (2)$$

The values of K_L and Q_0 are determined from the intercept and slope of the straight line in Figure 4, and calculated parameters of the Langmuir equation were presented in Table 5.

The second isotherm used in this study is the Freundlich isotherm.^{19,20}

$$Q_e = K_f C_e^{1/n} \quad (3)$$

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

$$\log Q_e = \log K_f + (1/n) \log C_e \quad (4)$$

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 $\log C_e$. Figure 5 shows the plot of the Freundlich equation isotherm for acid adsorption for IRA-67 adsorbent. Results of the Freundlich equation were presented in Table 6.

The results shows that the Langmuir isotherm obeys to experimental data for IRA 67 adsorbent R square value of 0.999 and 0.959 for tartaric acid and propionic acid, respectively. Freundlich isotherms show some deviations from good result.

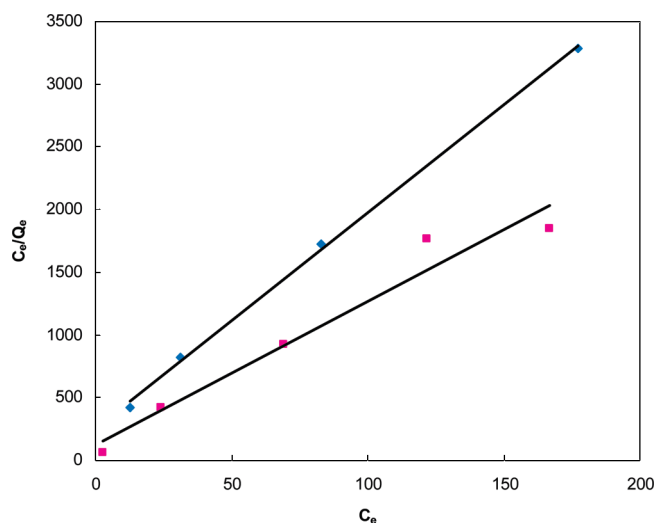


Figure 4. A plot of the Langmuir isotherm equation for the adsorption of acid: (◆) tartaric acid; (■) propionic acid.

Table 5. Results of Langmuir Isotherms for the Adsorption of Acids by Amberlite IRA-67

	$1/Q_0$	K_L/Q_0	Q_0	K_L	R^2
tartaric acid	17.212	1.164	0.058	0.068	0.999
propionic acid	11.485	1.091	0.087	0.095	0.959

The Pseudo-first-order Equation. Pseudo-first-order rate equation is

$$\frac{dQ}{dt} = k_1(Q_e - Q) \quad (5)$$

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

$$\ln \frac{(Q_e - Q)}{Q_e} = -k_1 t \quad (6)$$

where q and q_A are the grams of solute absorbed per gram of sorbent at any time and at equilibrium, respectively, and k_1 is the rate constant of first-order sorption. The pseudo-first-order equation was used extensively to describe the sorption kinetics.^{21,22}

If the adsorption kinetics obeys the pseudo-first-order model, then the plot of $\ln(Q_e - Q)$ vs t should be linear. Figure 6 shows the plot for adsorption of formic acid on Amberlite IRA-67. The constants of eq 6 were obtained from Figure 6 at different

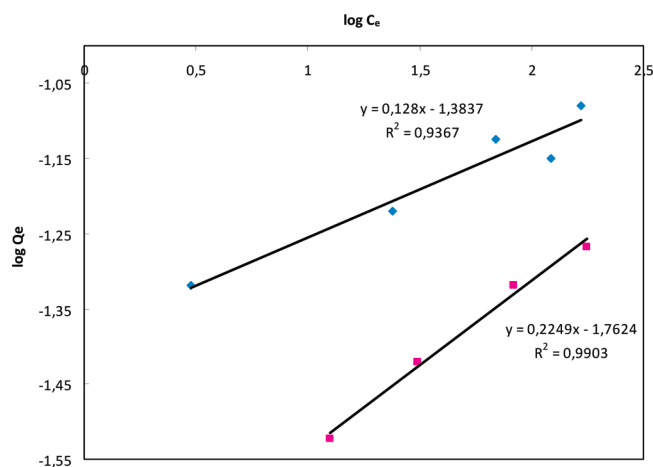


Figure 5. A plot of the Freundlich isotherm equation for the adsorption of acid: (◆) tartaric acid; (■) propionic acid.

Table 6. Results of Freundlich Isotherms for the Adsorption of Acids by Amberlite IRA-67

	$\log K_f$ (mg/g)	$1/n$	K_f	n	R^2
tartaric acid	-1.384	0.128	0.041	7.812	0.937
propionic acid	-1.762	0.225	0.017	4.446	0.990

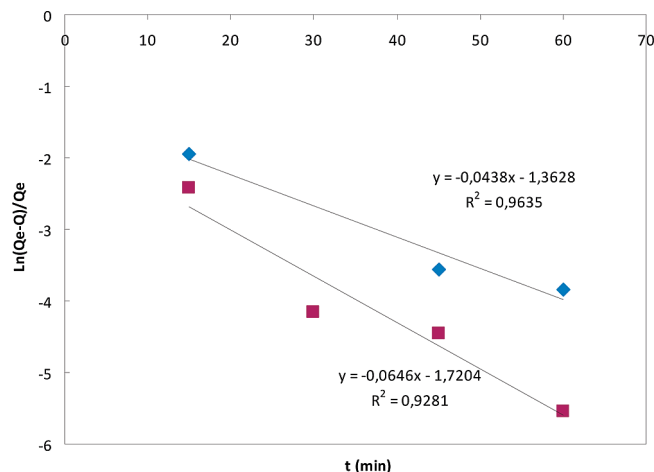


Figure 6. The linear plot of pseudo-first-order kinetic model: (◆) tartaric acid; (■) propionic acid.

concentrations and were listed in Table 7 including the correlation coefficients, R^2 . As it is clear from Figure 6 and Table 7, the fitting of experimental data to the pseudo-first-order model is not so good. Although the correlation coefficients are good, it can be seen in Figure 6 that there is some deviation from the pseudo-first-order model.

The Pseudo-second-order Equation. Another model for the analysis of sorption kinetics is pseudo-second-order. The rate law for this system is expressed as

$$\frac{dQ}{dt} = k_2(Q_e - Q)^2 \quad (7)$$

Integrating eq 7, for the boundary conditions $t = 0$ to $t = t$ and $Q = 0$ to $Q = Q$, gives

$$\frac{1}{(Q_e - Q)} = \frac{1}{Q_e} + k_2 t \quad (8)$$

Where k_2 is the pseudo-second-order rate constant of sorption. Equation 8 can be rearranged to obtain a linear form

$$\frac{t}{Q} = \frac{1}{k_2 Q_e^2} + \frac{1}{Q_e} t \quad (9)$$

The plot of t/Q versus t gives a straight line with intercept of $1/(k_2 Q_e^2)$ 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 pseudo-second-order model was recently applied for analysis of sorption kinetics from liquid solutions by Ho et al.^{23–25}

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 were listed in Table 7. As it can be seen in Figure 7 this model was fitted to these experimental results very well.

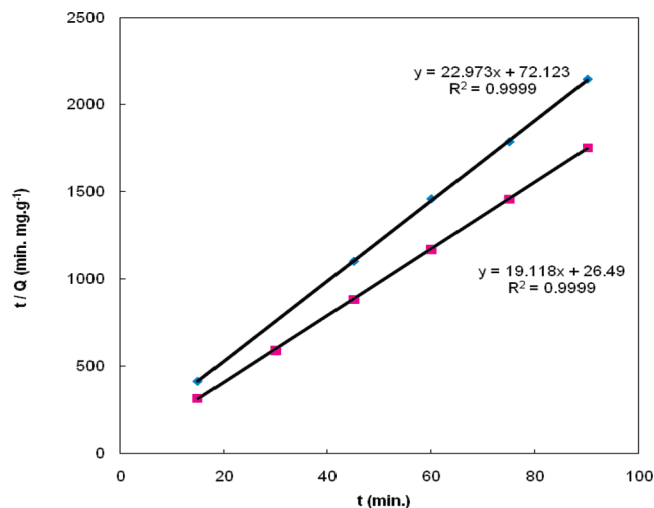


Figure 7. The linear plot of pseudo-second-order kinetic model: (◆) tartaric acid; (■) propionic acid.

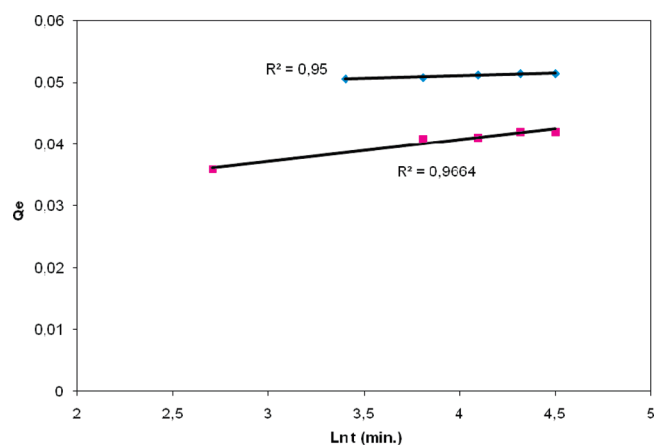


Figure 8. The linear plot of Elovich model equation: (◆) tartaric acid; (■) propionic acid.

The Elovich Equation. The Elovich model equation²⁶ is generally expressed as

$$\frac{dQ}{dt} = \alpha \exp(-\beta Q) \quad (10)$$

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

$$Q = \frac{1}{\beta} \ln(\alpha\beta) + \frac{1}{\beta} \ln(t) \quad (11)$$

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 7.

Table 7. Obtained Constant for Elovich Equation and Pseudo-second-order Kinetic Models

	Elovich equation			pseudo-first-order kinetic model		pseudo-second-order kinetic model		
	α	β	R^2	k_1 (min^{-1})	R^2	Q_e (mg/g)	k_2 (mg/g min)	R^2
tartaric acid	311.286	303.030	0.9500	0.0438	0.9635	0.043	7.317	0.9999
propionic acid	7.405	285.714	0.9664	0.0646	0.9281	0.052	13.797	0.9999

Conclusions

The adsorption of propionic acid and tartaric acid in terms of effect of initial acid concentration, effect of amount of adsorbent, effect of contact time, fitting isotherms, and kinetic models was investigated. The results show that the weakly basic adsorbent Amberlite IRA-67 is effective adsorbent for the removal of carboxylic acids from wastewater streams or fermentation broth.

Pseudo-second-order reaction was fitted for adsorption mechanism of both acids. Freundlich and Langmuir isotherms fitted to adsorption data.

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