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Adsorption Equilibria of L-(+)-Tartaric Acid onto Alumina

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The adsorption equilibria of L-(+)-tartaric acid onto alumina from wastewaters of wineries were studied, and it has been found that the equilibrium adsorption fits the Langmuir and Freundlich isotherms. Adsorption experiments were carried out at three different temperatures (298, 310, and 325) K. The adsorption of L-(+)-tartaric acid is dependent on the acid concentration and the amount of alumina. The maximum percentage removal of L-(+)-tartaric acid was 22 % by alumina at 298 K. The Langmuir and Freundlich constants have been found to be 0.023 $g \cdot g^{-1}$ and 0.014 $(g \cdot g^{-1})/(L \cdot g^{-1})^{-1/n}$, respectively, at 298 K. The thermodynamic parameters ΔH^0_{ads} and ΔS^0_{ads} for the adsorption of tartaric acid on alumina have been calculated to be −5.62 $kJ \cdot mol^{-1}$ and 50.65 $J \cdot mol^{-1} \cdot K^{-1}$, respectively.

Introduction

Wastewaters from wineries contain tartaric acid. This acid is used in food processing and the pharmaceutical industry. The wastewaters from the winemaking process are the only industrial source for tartaric acid production.[1] Many methods have been investigated to separate organic acids from aqueous solution. Solvent extraction has been used for purification of carboxylic acids,[2,3] but the toxicity of the solvents used is always a problem. Electrodialysis has been used as a technique for the isolation and purification of carboxylic acids from fermentation media. Because other anions also go with the acid and other broth components end up in the product stream by diffusion, further processing is necessary to remove these impurities. The sorption of carboxylic acids on ion exchange resins has also been studied. This latter method requires additional chemicals to recover the acid from the resin. An alternative method of recovery of carboxylic acids from fermentation broth is based on adsorption.[2]

The adsorption of carboxylic acids by a number of substrates has been examined. For example, Aljundi examined the silicalite molecular sieve for adsorption of lactic acid.[3] Inci investigated the adsorption of two carboxylic acids with activated carbon.[4,5] In this study, the adsorption of L-(+)-tartaric acid on alumina is investigated.

Adsorption processes are operative in most natural physical, biological, and chemical systems, and adsorption operations that employ solids such as alumina and synthetic resins are widely used in industrial applications and for purification and separation.[6,7]

The adsorption of carboxylic acids on alumina is very strong with adsorption energies much larger than those of other organic compounds. This is because most carboxylic acids are weak acids, and their degrees of dissociation in 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 has been of considerable interest because their property of forming self-assembled monolayers, the adsorption of water-soluble carboxylic acids on alumina has not been extensively studied.[6]

The nature of the interaction between the carboxylic group and hydroxyls on the surface has been studied by many investigators. In particular, 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 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 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.[8] 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.[5]

L-(+)-Tartaric acid is the dextro form of 2,3-dihydroxysuccinic acid. It has been known since antiquity in the form of its potassium salt, which occurs in grapes. In the fermentation of grape juice, the salt deposits in the fermentation vessels. The free crystallized L-(+)-tartaric acid was first obtained from such fermentation residues by Scheele in 1769. Tartaric acid is employed in the preparation of carbonated drinks, especially those that are grape flavored. It is widely used in effervescent tablets and powders and is frequently mixed with citric acid.[9,10]

There are many studies about the separation of tartaric acid from aqueous solution. In particular, activated carbon,[11] copper,[12] nickel,[13] and oxidized nickel[14] have been used to separate tartaric acid from wastewater streams. Aşci[15] removed some carboxylic acids from aqueous solution by using hydrogels. Ramsier et al.[16] reported adsorption of phosphorus acids on alumina. Chakraborty et al.[17] provided a theoretical insight into physical adsorption for a single-component adsorbent + adsorbate system.

In this work, systematic studies of the adsorption of L-(+)-tartaric acid from aqueous solutions have been investigated using alumina. Experimental results for the adsorption of L-(+)-tartaric

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Table 1. Experimental Results of the Adsorption of L-(+)-Tartaric Acid onto Alumina

initial acid concn ($g \cdot L^{-1}$)	amount of alumina (g)	298 K		310 K		325 K	
		C ($g \cdot L^{-1}$)	Q ($g \cdot L^{-1}$)	C ($g \cdot L^{-1}$)	Q ($g \cdot L^{-1}$)	C ($g \cdot L^{-1}$)	Q ($g \cdot L^{-1}$)
58.79	0.05	57.37	1.42	57.62	1.17	58.01	0.78
	0.10	55.75	3.04	55.72	3.07	56.27	2.52
	0.15	51.41	7.38	52.53	6.26	53.62	5.17
	0.20	48.38	10.41	49.77	9.02	50.96	7.83
	0.25	45.66	13.13	47.21	11.58	48.42	10.37
103.53	0.05	100.81	2.72	101.11	2.42	101.76	1.77
	0.10	97.78	5.75	98.98	4.55	99.84	3.69
	0.15	96.06	7.47	97.68	5.85	98.52	5.01
	0.20	94.44	9.09	95.64	7.89	97.04	6.49
	0.25	87.47	16.06	88.96	14.57	90.16	13.37
164.00	0.05	160.17	3.83	160.51	3.49	161.05	2.95
	0.10	155.76	8.24	156.14	7.86	157.03	6.97
	0.15	150.61	13.39	151.93	12.07	152.90	11.1
	0.20	147.27	16.73	148.52	15.48	149.77	14.23
	0.25	143.23	20.77	144.84	19.16	145.76	18.24
210.10	0.05	203.54	6.56	205.20	4.9	206.31	3.79
	0.10	198.79	11.31	199.84	10.26	201.07	9.03
	0.15	186.57	23.53	188.18	21.92	189.73	20.37
	0.20	180.61	29.49	182.36	27.74	184.55	25.55
	0.25	168.38	41.72	169.94	40.16	171.24	38.86
328.59	0.05	318.69	9.90	320.13	8.46	322.21	6.38
	0.10	298.59	30.00	300.45	28.14	302.62	25.97
	0.15	283.43	45.16	285.28	43.31	287.34	41.25
	0.20	273.53	55.06	275.68	52.91	278.19	50.4
	0.25	264.34	64.25	266.57	62.02	268.87	59.72

acid by alumina at (298, 310, and 325) K are presented. All experimental data were then fitted using the Freundlich and Langmuir isotherm equations to obtain the parameters of each isotherm.[18]

Experimental Section

L-(+)-Tartaric acid (purity > 99.5 %) and neutral (purity > 99.0 %) alumina were obtained from Merck. They were used without further treatment. We prepared L-(+)-tartaric acid stock solution by dissolving the appropriate amount of L-(+)-tartaric acid with distilled water in a flask. We prepared five different concentrations of L-(+)-tartaric acid solutions by diluting appropriate amounts of the stock acid solution. These concentrations were 5.82 %, 10.25 %, 16.25 %, 20.80 %, and 32.53 % (*w*/*w*). For the equilibrium studies, experiments were performed using 100 mL Erlenmeyer flasks at constant temperatures (298, 310, and 325) K in an electrical shaker. The prepared solutions (25 mL each) were placed in 100 mL Erlenmeyer flasks, which were previously cleaned and dried. To show the effect of the initial L-(+)-tartaric acid concentrations on the adsorption, 0.05 g, 0.10 g, 0.15 g, 0.20 g, and 0.25 g of alumina was agitated with 25 mL of the L-(+)-tartaric acid solutions at five different concentrations, 5.82 %, 10.25 %, 16.25 %, 20.80 %, and 32.53 % (*w*/*w*). All solutions were left in a temperature-controlled shaking bath at (298, 310, and 325) K for 2 h and were then kept for 24 h to reach equilibrium. Preliminary experiments were used to validate the time for the experiments to reach equilibrium. After the adsorption experiments, a known quantity of the adsorbate solutions was withdrawn from each bottle for analysis. Concentrations of the L-(+)-tartaric acid after filtration were determined by titration with 0.1 N aqueous sodium hydroxide. In most cases, the deviation between the amount of acid analyzed and the first prepared acid solutions did not exceed ± 1 %.

Results and Discussion

Equilibria and Isotherms. Results for the adsorption of L-(+)-tartaric acid on alumina are given in Table 1 and are illustrated in Figure 1. Figure 1 demonstrates the plot of C versus Q on the adsorption of L-(+)-tartaric acid at 298 K. (Only data of 298 K were demonstrated in the Figures so as to prevent confusion.) Other results at different temperatures (310 and 325) K show the same trends as the result of 298 K.

The adsorption of gas molecules or solutes in a solution onto the surface of a solid is an important phenomenon in physical chemistry, surface science, and industry. The plotting of isotherms is important to obtain an equation that represents the results and that could be used for the design of adsorption equipment. Adsorption isotherms depend on the specific surface area and the surface chemistry of solid adsorbents, the nature of adsorbates, and the acidity of the medium. The Langmuir isotherm is valid for monolayer adsorption onto a surface containing a finite number of identical sites. The model assumes uniform energies of adsorption onto the surface and no transmigration of adsorbate in the plane of the surface. When a physisorption process is carried out at a constant temperature, the amount adsorbed, Q, can be quantitatively described by the Langmuir equation. The Langmuir isotherm is represented by the following equation

$$\frac{C}{Q} = \frac{1}{K_L \cdot Q_0} + \frac{C}{Q_0} \tag{1}$$

where C is the equilibrium concentration (milligrams per liter), Q is the mass adsorbed at equilibrium (milligrams per gram), K_L is the Langmuir equilibrium parameter, and Q_0 is the sorption maxima. A plot of C/Q versus C gives a straight line showing the applicability of the isotherm. Values of Q_0 and K_L at different concentrations have been determined from the slope and intercept of the plot. The Langmuir adsorption parameters are very useful in predicting adsorption capacities and for incorporating a mass transfer relationship. This shows a system that exists with a monolayer coverage of the adsorbent on the surface of the adsorbate. The isotherms are shown in Figure 2. The values of the isotherm parameters are given in Table 2.

The Freundlich equation is used for heterogeneous surface energies in which the energy term in the Langmuir equation varies as a function of the surface coverage strictly because of

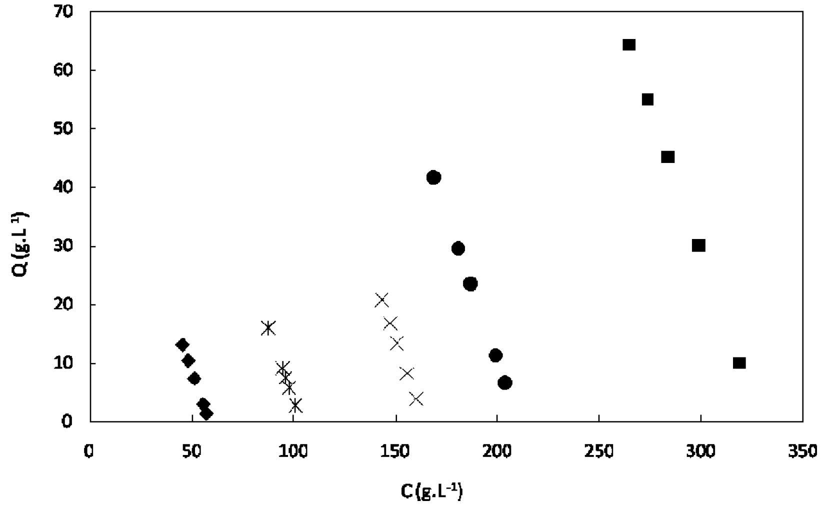

Figure 1. Plot of Q versus C for adsorption L-(+)-tartaric acid at 298 K: ▲, 58.79 (g·L^{-1}); *, 103.53 (g·L^{-1}); ×, 164.00 (g·L^{-1}); ●, 210.10 (g·L^{-1}); ■, 328.59 (g·L^{-1}).

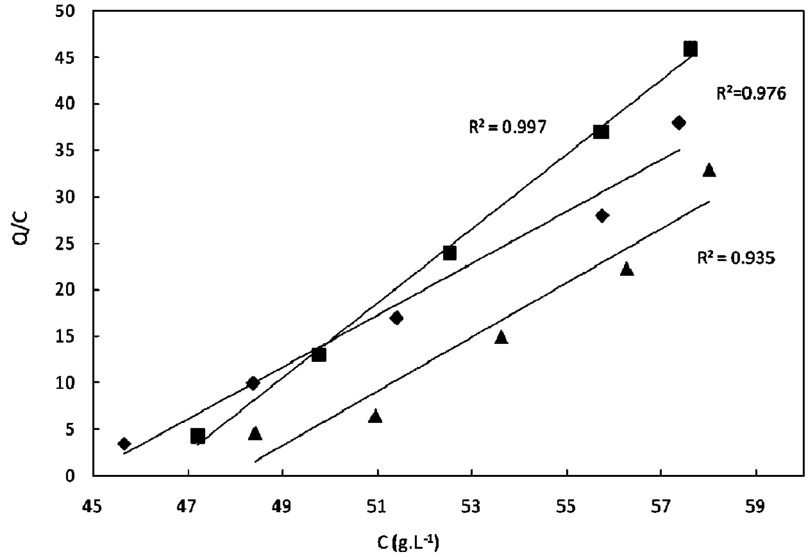

Figure 2. Langmuir isotherm for amount of 0.05 g L-(+)-tartaric acid at different temperatures: ◆, 298 K; ■, 310 K; ▲, 325 K.

Table 2. Freundlich and Langmuir Isotherm Parameters of L-(+)-Tartaric Acid onto Alumina

	Freundlich parameters				Langmuir parameters		
temperature (K)	Log K_f	K_f (g·g^{-1})/(L·g^{-1})$^{-1/n}$	n	R^2	$1/Q_0$	K_L (g·g^{-1})	R^2
298	−1.85	0.014	0.88	0.96	4.01	0.023	0.99
310	−1.90	0.012	0.88	0.99	2.79	0.022	0.98
325	−2.21	0.006	0.83	0.99	2.91	0.021	0.94

the variation in the heat of adsorption. The Freundlich equation has the general form

$$Q = K_f \cdot C^{1/n} \tag{2}$$

A logarithmic plot linearizes the equation enabling the exponent n and the constant K_f to be determined.[18−21]

$$\log Q = \log K_f + (1/n) \log C \tag{3}$$

The constants are listed in Table 2 for the batch system. 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 versus log C.[21−24] Data are shown in Figure 3. (Only data with the optimum amount of alumina, 0.5 g, are demonstrated in the Figures so as to prevent confusion.) The values of the isotherm parameters are given in Table 2. The obtained fits show that adsorption of tartaric acid from wastewater onto alumina obeys both isotherms.

Effect of Temperature. The effect of temperature on the adsorption of tartaric acid onto the alumina was studied at (298, 310 and 325) K. Table 1 shows results of adsorption efficiency at the different temperatures. It can be seen from Table 1 that the adsorption capacity of the alumina decreases with increasing temperature.

As related to the temperature effect, the thermodynamic parameters have been calculated for this adsorption system. The first parameter is Gibbs energy change of adsorption, ΔG^0_{ads}, which was calculated by using equation

$$\Delta G^0_{\text{ads}} = -R \cdot T \cdot \ln K_L \tag{4}$$

where R is the universal gas constant and T is the temperature in kelvins. K_L is the thermodynamic equilibrium constant for

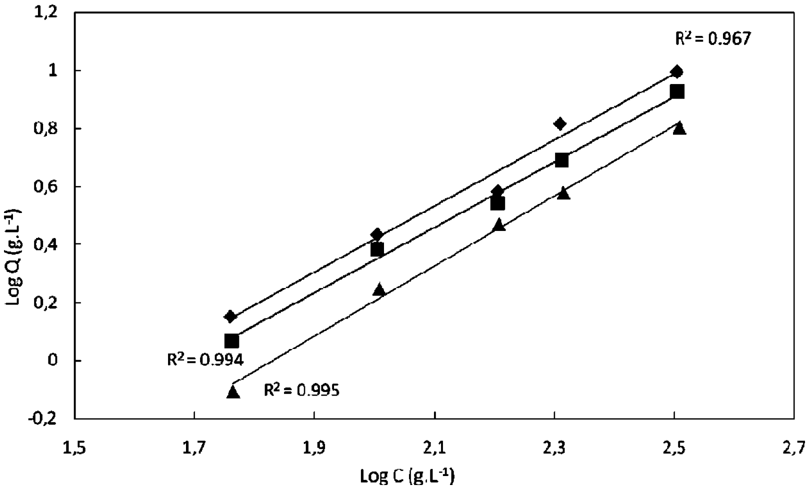

Figure 3. Freundlich isotherm for 0.05 g L-(+)-tartaric acid at different temperature: ◆, 298 K; ■, 310 K; ▲, 325 K.

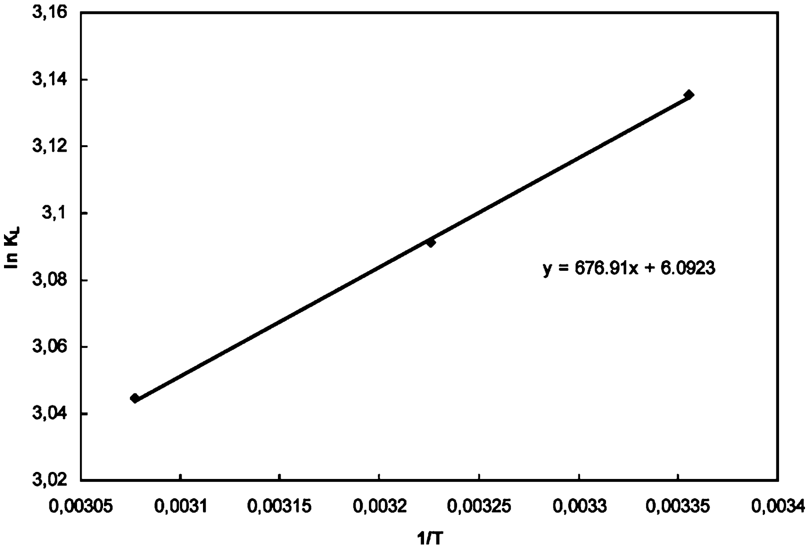

Figure 4. van't Hoff plot of ln K_L against $1/T$.

Table 3. Thermodynamic Parameters for Adsorption of Tartaric Acid onto Alumina at Different Temperatures

temperature K	ΔG^0_{ads} kJ·mol⁻¹	ΔS^0_{ads} J·mol⁻¹·K⁻¹	ΔH^0_{ads} kJ·mol⁻¹
298	−7.76	50.65	−5.62
310	−7.96		
325	−8.22		

the adsorption process that was determined by plotting ln(C/Q) versus C and extrapolating to zero C, as suggested by Khan and Singh.[25]

The other thermodynamic parameters, the enthalpy change, ΔH^0_{ads}, and the entropy change, ΔS^0_{ads}, were calculated from the slope and intercept of the plot of ln K_0 against $1/T$ according to the van't Hoff equation

$$\ln K_L = \frac{\Delta S^0_{\text{ads}}}{R} - \frac{\Delta H^0_{\text{ads}}}{R \cdot T} \qquad (5)$$

ΔH^0_{ads} was obtained from the slope of the straight line, and ΔS^0_{ads} was determined from the intercept of the graph[26,27] (Figure 4). To evaluate the thermodynamic equilibrium constant, K_L, we plotted the C/Q values versus the C values at (298, 310, and 325) K, as seen in Figure 2. Linear graphs were obtained for all temperatures. The K_L parameters obtained were used to calculate the ΔG^0_{ads} function.[28] The calculated thermodynamic parameters (ΔH^0_{ads}, ΔS^0_{ads}, and ΔG^0_{ads}) at the temperatures above are given in Table 3.

Conclusions

In this study, the adsorption of L-(+)-tartaric acid onto alumina has been investigated, and it has been found that the adsorption fits the Langmuir and Freundlich isotherms at different temperatures. The maximum percentage removal of L-(+)-tartaric acid was 22 % by alumina at 298 K. Thermodynamic parameters of tartaric acid adsorption such as ΔH^0_{ads}, ΔS^0_{ads}, and ΔG^0_{ads} have been calculated.

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