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Adsorption Equilibrium Data for Acetic Acid and Glycolic Acid onto Amberlite IRA-67

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The removal of acetic acid and glycolic acid from aqueous solution by the weakly basic adsorbent Amberlite IRA-67 has been studied at three different temperatures. Amberlite IRA-67 removed both acids very well from aqueous solution. The maximum adsorption efficiency has been found to be 86.29 % and 61.36 % for glycolic acid and acetic acid, respectively. Langmuir and Freundlich adsorption isotherms have been applied to the experimental data. The Langmuir isotherm fitted the experimental data better than the Freundlich isotherm for both acids. Thermodynamic parameters ΔG, ΔH, and ΔS were calculated.

Introduction

One common problem is the separation of carboxylic acids from wastewater streams because carboxylic acids have a high affinity for water. Tung and King[1] reported that carboxylic acids can be separated from water by solid sorbents. Solid sorbents have a good selectivity for carboxylic acids. After adsorption they can be easily regenerated.

Acetic acid is one of the simplest carboxylic acids. It is used in the production of polyethylene terephthalate (PET) which is used in soft drink bottles. Other areas of use are for cellulose acetate in photographic film and polyvinyl acetate for wood glue. In households diluted acetic acid is often used in descaling agents. Acetic acid is used as a food additive for acidity (pH controller) regulation. The global demand of acetic acid is around 6.5 million tonnes per year (Mt/a).[2]

Glycolic acid (hydroxyacetic acid) is one of the smallest organic molecules with both acidic and alcoholic functionality. It is used in dermatology for skin care products because of its excellent capability to penetrate skin. It is also used to improve the skin's appearance and texture. Wrinkles, acne scarring, and hyperpigmentation on skin are reduced by glycolic acid. When glycolic acid is applied to the skin it reacts with the upper layer of the epidermis, weakening the binding properties of the lipids that hold the dead skin cells together. This makes it possible for the external skin to dissolve, revealing the underlying skin.[2]

Because of above-mentioned reasons, the separation of these acids is important, requiring consideration of some separation techniques. Adsorption or ion exchange is a possible technique to separate the acids from aqueous or wastewater streams when they can be coupled with fermentation processes. Many fermentation processes that produce carboxylic acids operate most effectively at pHs above the pK_a of the acid product.[3,4] Separation of organic acids from wastewater streams and aqueous solutions using amine extractants have been studied by Uslu.[5–9]

The aim of this study is to define the efficiencies of Amberlite IRA-67 on the adsorption of acetic acid and glycolic acid from fermentation broth or wastewater streams. Regeneration was not studied in these experiments.

Materials and Methods

Materials. Glycolic acid (purity > 99 %), acetic acid (purity > 99 %), and Amberlite IRA-67 were obtained from the Merck Co. 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 a known amount of adsorbent are presented in the tables, and 5 mL of 10 % (w/w) acid solution was prepared; equilibration was carried out in a thermostatted shaker. At every 15 min interval, a sample was taken out and titrated with 0.1 N NaOH, and phenolphthalein was used as the indicator. This period of achieving equilibrium state was determined as 90 min. 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 ±

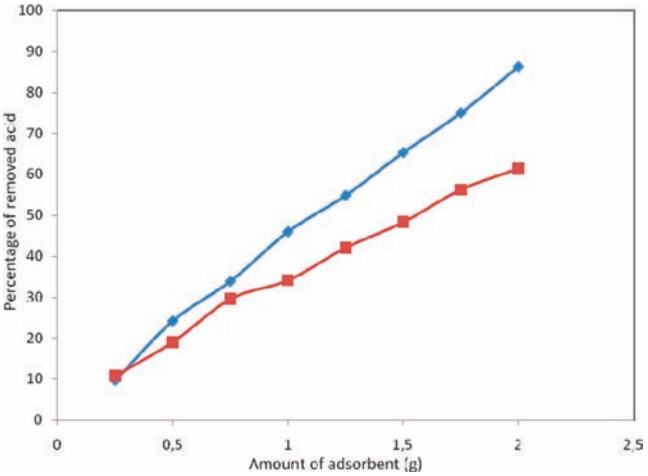

Figure 1. Plot of the effect of contact time on the adsorption of acid. ◆, glycolic acid; ■, acetic acid.

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Table 1. Effect of Contact Time on the Adsorption of Glycolic Acid

initial conc.	initial conc.	initial conc.	amount of Amberlite IRA-67	equilibrium conc. C	adsorbed acid Q	removal of acid	time	temp.
$g \cdot L^{-1}$	$mol \cdot L^{-1}$	(% w/w)	g	$g \cdot L^{-1}$	$g \cdot mg^{-1}$	%	min	K
				Glycolic Acid				
94.3	1.24	9.4	1.0	84.42	$9.88 \cdot 10^{-3}$	10.47	15	298
94.3	1.24	9.4	1.0	81.91	0.0124	13.15	45	298
94.3	1.24	9.4	1.0	81.67	0.0126	13.36	75	298
94.3	1.24	9.4	1.0	81.15	0.0132	13.99	90	298
94.3	1.24	9.4	1.0	81.07	0.0132	13.99	105	298
				Acetic Acid				
105.60	1.76	10.56	0.5	96.60	0.018	8.52	30	298
105.60	1.76	10.56	0.5	95.40	0.0204	9.66	45	298
105.60	1.76	10.56	0.5	94.80	0.0216	10.23	60	298
105.60	1.76	10.56	0.5	94.20	0.0223	10.79	75	298
105.60	1.76	10.56	0.5	93.60	0.024	11.36	90	298
105.60	1.76	10.56	0.5	93.60	0.024	11.36	105	298

Table 2. Effect of the Amount of Adsorbent on the Adsorption of Glycolic Acid and Acetic Acid

initial conc.	initial conc.	initial conc.	amount of Amberlite IRA-67	equilibrium conc. C	adsorbed acid Q	removal of acid	time	temp.
$g \cdot L^{-1}$	$mol \cdot L^{-1}$	(% w/w)	g	$g \cdot L^{-1}$	$g \cdot mg^{-1}$	%	min	K
				Glycolic Acid				
94.3	1.24	9.4	0.25	85.17	0.037	9.67		298
94.3	1.24	9.4	0.50	71.48	0.046	24.19		298
94.3	1.24	9.4	0.75	62.36	0.043	33.87		298
94.3	1.24	9.4	1.00	50.95	0.043	45.97		298
94.3	1.24	9.4	1.25	42.58	0.041	54.84		298
94.3	1.24	9.4	1.50	32.70	0.041	65.32		298
94.3	1.24	9.4	1.75	23.58	0.0404	75.00		298
94.3	1.24	9.4	2.00	12.93	0.0407	86.29		298
				Acetic Acid				
105.60	1.76	10.56	0.25	94.2	0.0456	10.80		298
105.60	1.76	10.56	0.50	85.50	0.0402	19.03		298
105.60	1.76	10.56	0.75	74.40	0.0416	29.55		298
105.60	1.76	10.56	1.00	69.60	0.0360	34.10		298
105.60	1.76	10.56	1.25	61.20	0.0350	42.05		298
105.60	1.76	10.56	1.50	54.60	0.0340	48.30		298
105.60	1.76	10.56	1.75	46.20	0.0340	56.25		298
105.60	1.76	10.56	2.00	40.80	0.0330	61.36		298

1) K by using this optimum amount of IRA-67. Adsorption isotherms were dependent on the initial acid concentration.

Results and Discussion

Table 1 and Figure 1 show the results of the effect of contact time on the removal of glycolic acid and acetic acid. The effect of contact time for the adsorption of glycolic acid and acetic acid by Amberlite IRA-67 was studied for a period of 90 min for initial acid concentrations of 1.24 $mol \cdot L^{-1}$ and 1.76 $mol \cdot L^{-1}$ at 298 K. The 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 occupy because of the repulsive forces between the solute molecules on the solid and bulk phases.[10]

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 2.00) g for IRA-67 under the selected 1.24 $mol \cdot L^{-1}$ and 1.76 $mol \cdot L^{-1}$ of initial solute concentration at a temperature of 298 K. It was observed that as the dose increases the amount of adsorbed solute increases. In the maximum Amerlite IRA-67 dose (2.00 g) the maximum adsorption capacities are 86.29 % and 61.36 % for glycolic acid and acetic acid, respectively.

Adsorption was studied at different concentrations of initial glycolic acid (0.33 $mol \cdot L^{-1}$, 0.55 $mol \cdot L^{-1}$, 1.24 $mol \cdot L^{-1}$, 1.87 $mol \cdot L^{-1}$, 2.43 $mol \cdot L^{-1}$) and acetic acid concentrations (0.41 $mol \cdot L^{-1}$, 0.87 $mol \cdot L^{-1}$, 1.76 $mol \cdot L^{-1}$, 2.65 $mol \cdot L^{-1}$, 3.50 $mol \cdot L^{-1}$) by Amberlite IRA-67. It can be observed from Table 3 and Figure 3 that increasing the initial acid concentration from 0.33 $mol \cdot L^{-1}$ to 2.43 $mol \cdot L^{-1}$ adsorbed acid concentration decreased the efficiency for both acids. In this respect, the efficiency of removal decreased from 80.91 % to 15.23 % for

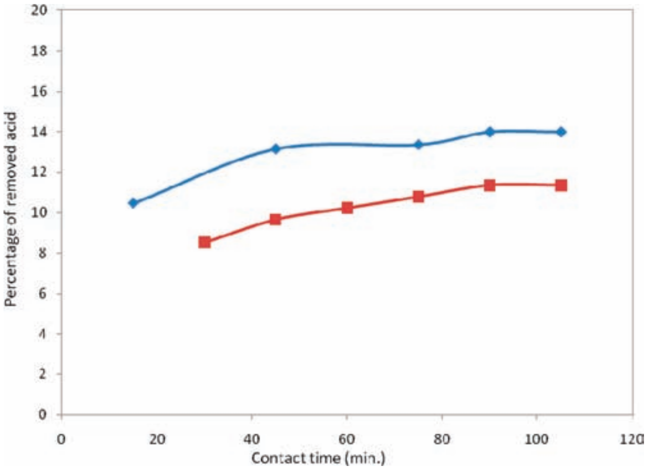

Figure 2. Plot of the effect of the amount of adsorbent on the adsorption of acid. ◆, glycolic acid; ■, acetic acid.

Table 3. Effect of the Initial Acid Concentration on the Adsorption of Glycolic Acid and Acetic Acid

initial conc. $g \cdot L^{-1}$	initial conc. $mol \cdot L^{-1}$	initial conc. (% w/w)	amount of Amberlite IRA-67 g	equilibrium conc. *C* $g \cdot L^{-1}$	adsorbed acid *Q* $g \cdot mg^{-1}$	removal of acid %	time min	temp. K
				Glycolic Acid				
25.09	0.33	2.5	0.5	4.79	0.0406	80.91		298
41.83	0.55	4.2	0.5	20.53	0.0426	50.91		298
94.30	1.24	9.4	0.5	71.48	0.0456	24.19		298
142.2	1.87	14.2	0.5	117.12	0.0502	17.65		298
184.8	2.43	18.5	0.5	156.66	0.0563	15.23		298
				Acetic Acid				
24.60	0.41	2.42	0.5	10.80	0.0276	56.09		298
50.40	0.87	5.21	0.5	36.60	0.0276	27.38		298
105.60	1.76	10.56	0.5	85.80	0.0396	18.75		298
159	2.65	15.88	0.5	133.80	0.0504	15.85		298
210	3.50	21	0.5	184.20	0.0516	12.29		298

Table 4. Results of Langmuir Isotherms for the Adsorption of Acids by Amberlite IRA-67

glycolic acid					acetic acid				
$1/Q_0$	K_L/Q_0	Q_0	K_L $(g \cdot g^{-1})/(L \cdot g^{-1})^{-1/n}$	R^2	$1/Q_0$	K_L/Q_0	Q_0	K_L $(g \cdot g^{-1})/(L \cdot g^{-1})^{-1/n}$	R^2
0.0384	$4.89 \cdot 10^{-4}$	26.042	0.0127	0.978	0.0513	−0.00011	19.4931	−0.0021	0.986

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

glycolic acid					acetic acid				
log K_f $mg \cdot g^{-1}$	$1/n$	K_f $g \cdot g^{-1}$	*n*	R^2	log K_f $mg \cdot g^{-1}$	$1/n$	K_f $g \cdot g^{-1}$	*n*	R^2
−1.568	0.124	0.0271	8.0775	0.963	−2.0058	0.3174	0.0099	3.1506	0.931

Table 6. Effect of the Temperature on the Adsorption of Glycolic Acid and Acetic Acid

initial conc. $g \cdot L^{-1}$	initial conc. $mol \cdot L^{-1}$	initial conc. (% w/w)	amount of Amberlite IRA-67 g	equilibrium conc. *C* $g \cdot L^{-1}$	adsorbed acid *Q* $g \cdot mg^{-1}$	removal of acid %	time min	temp. K
				Glycolic Acid				
94.3	1.24	9.4	0.5	71.48	0.046	24.19		298
94.3	1.24	9.4	0.5	73.01	0.043	22.58		308
94.3	1.24	9.4	0.5	76.81	0.035	18.55		318
				Acetic Acid				
105.60	1.76	10.56	0.5	85.50	0.0402	19.03		298
105.60	1.76	10.56	0.5	86.0	0.0392	18.56		308
105.60	1.76	10.56	0.5	86.30	0.0386	18.27		318

glycolic acid and from 56.09 % to 12.29 % for acetic acid. This may be explained by the saturation of accessible exchangeable sites of the adsorbent.

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

The Langmuir equation is as follows[11,12]

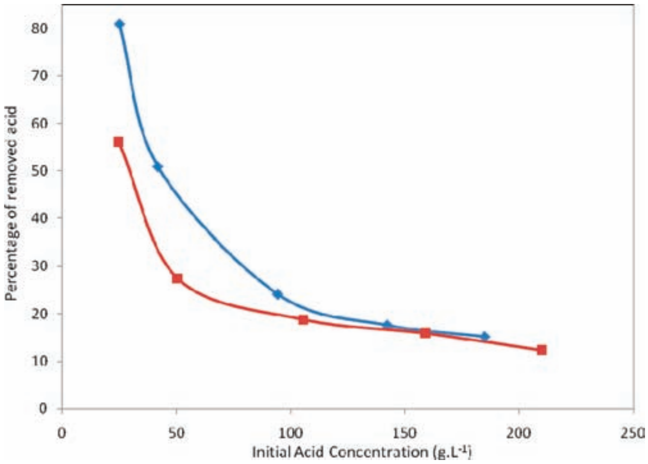

Figure 3. Plot of the effect of the initial acid concentration on the adsorption of acid. ◆, glycolic acid; ■, acetic acid.

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

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

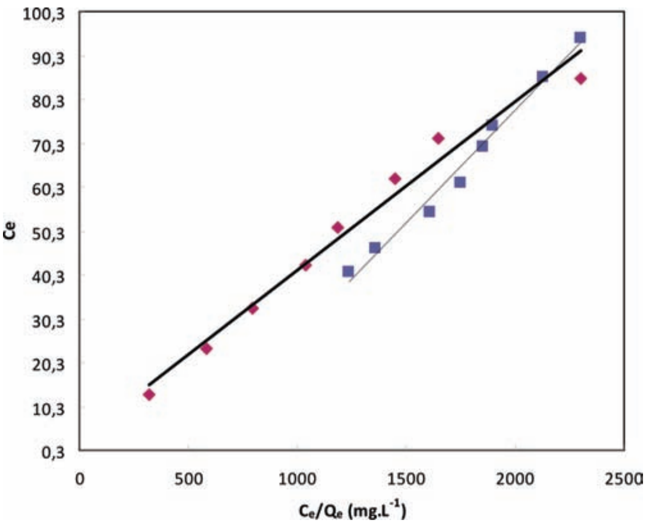

Figure 4. Plot of the Langmuir isotherm equation for the adsorption of acid. ◆, glycolic acid; ■, acetic acid.

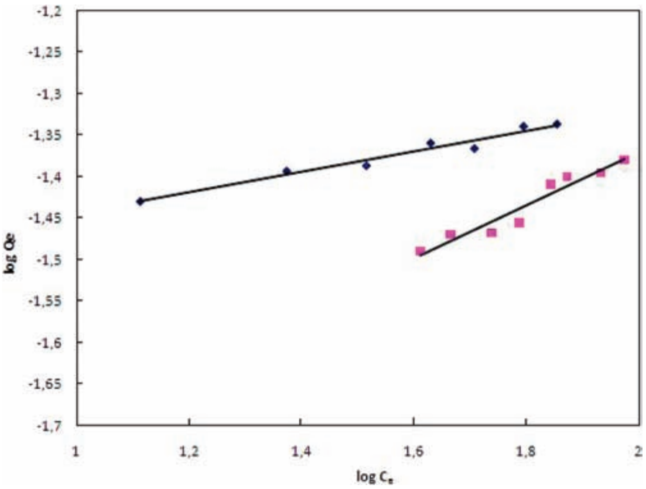

Figure 5. Plot of the Freundlich isotherm equation for the adsorption of acid. ◆, glycolic acid; ■, acetic acid.

Table 7. Thermodynamic Parameters for the Adsorption of Acids onto Amberlite IRA-67 at Different Temperatures (298 K, 308 K, and 318 K)

	temperature	ΔG^0_{ads}	K_0	ΔS^0_{ads}	ΔH^0_{ads}
	K	J·mol^{-1}	kg^{-1}	J·mol^{-1}·K^{-1}	J·mol^{-1}
acetic acid	298	−20192.7	3464	47.467	−6034.8
	308	−20627.8	3151		
	318	−21143.7	2973		
glycolic acid	298	−21112	5021	46.430	−7290.8
	308	−21622	4647		
	318	−22038	4171		

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

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

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

The second isotherm used in this study was the Freundlich isotherm.[13,14]

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

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 linear plots of log Q_e against log C_e. Figure 5 shows a plot of the Freundlich equation isotherm for adsorption of both acids onto IRA-67. Results of the Freundlich equation are presented in Table 5.

The results show that the Langmuir isotherm fits the experimental data for both adsorbents with R^2 values of 0.978 and 0.986 for glycolic acid and acetic acid, respectively. Freundlich isotherms show some deviation from good results.

Thermodynamic Parameters. The effect of temperature on the adsorption of acids onto Amberlite IRA-67 was studied at 298 K, 308 K, and 318 K. Table 6 shows the results of the adsorption efficiency at different temperatures. It can be seen from the experimental results in Table 6 that the adsorption capacity of the IRA-67 decreases with increasing temperature.

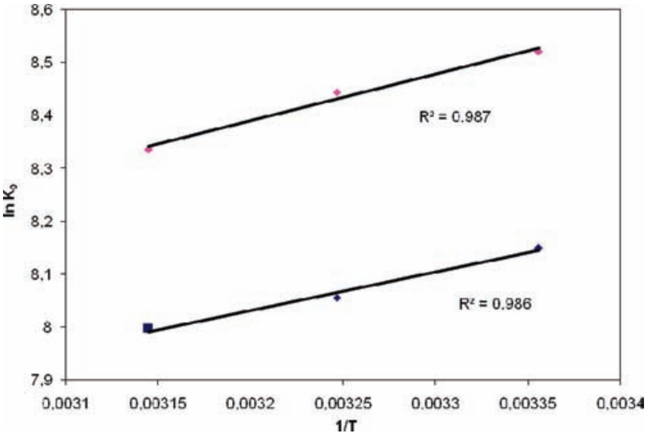

Figure 6. Plot of ln K_0 against $1/T$. ◆, glycolic acid; ■, acetic acid.

Related to the temperature effect, the thermodynamic parameters have been calculated for these adsorption systems. The free energy change of adsorption ΔG^0_{ads} was calculated by using the equation:

$$\Delta G^0_{\text{ads}} = -RT \ln K_0 \tag{5}$$

where R is the universal gas constant and T is the Kelvin temperature.

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 equation:

$$\ln K_0 = \frac{\Delta S^0_{\text{ads}}}{R} - \frac{\Delta H^0_{\text{ads}}}{RT} \tag{6}$$

ΔH^0_{ads} was obtained from the slope of the straight line, and ΔS^0_{ads} was determined from the intercept of the graph.[15,16]

K_0 is the thermodynamic equilibrium constant for the adsorption process. It was determined by plotting ln(C_e/q_A) versus C_e and extrapolating to zero C_e as suggested by Khan and Singh.[17]

Linear graphs were obtained for all temperatures. The obtained K_0 parameters were used to calculate the ΔG^0_{ads} function.[18] The calculated thermodynamic parameters (ΔH^0_{ads}, ΔS^0_{ads}, and ΔG^0_{ads}) at different temperatures are given in Table 6. ΔH^0_{ads} and ΔS^0_{ads} were obtained plotting ln K_0 against $1/T$ as shown in Figure 6.

Conclusions

The present study shows that the weakly basic adsorbent Amberlite IRA-67 is an effective adsorbent for the removal of monocarboxylic acids from wastewater streams. The reason for this result of the adsorption of carboxylic acids on Amberlite IRA-67 is a neutralization reaction shown by following equation

$$n(\text{R-N}) + \text{AH}_n \leftrightarrow \text{R-(NH}^+)_n\text{A}^{n-} (n = 1 \text{ for acid})$$

where R-N denotes a tertiary amine, [AH] represents an acid, and the acid−amine complex (R-(NH$^+$)$_n$A^{n-}) is formed.

Thermodynamic parameters show that this reaction is exothermic. The Langmuir isotherm fits the results of both acids.

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