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Adsorption of Lactic Acid from Model Fermentation Broth onto Activated Carbon and Amberlite IRA-67

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ABSTRACT: The aim of this study was to compare the adsorption efficiency of lactic acid onto activated carbon and Amberlite IRA-67, and to define the adsorption isotherms. Activated carbon is a well-known industrial adsorbent and was used in this study; Amberlite IRA-67 is a weakly basic polyacrylic resin with a tertiary amine functional group. Adsorption efficiencies of activated carbon and Amberlite IRA-67 were compared with respect to their percentage of removal acid. The result of this comparison is that Amberlite IRA-67 is more efficient than activated carbon. Each of these adsorbents is in compliance with both the Freundlich and Langmuir isotherms.

INTRODUCTION

One of the most important environmental problems is the recovery of plastic materials. The use of biodegradable polymers is a very promising solution for this problem. Biodegradable polymers can be reduced to carbon dioxide, methane, water, and biomass under biochemical action.[1]

Polylactic acid is a biodegradable polymer. Its main application fields are medical applications, fibers, packaging materials and as solvents. Generally, L-lactic acid polymers are used in medical applications. For the production of polylactic acid, there is a need for high purity lactic acid.

Lactic acid can be produced by both chemical synthesis and fermentation of carbohydrates. If chemical synthesis is used for lactic acid production, only a racemic mixture of lactic acid is obtained. The chemical process is also a more expensive method than fermentation. The fermentation process is widely used for lactic acid production, and this method provides the production of different stereoisomers of lactic acid selectively. The disadvantage of fermentation is that the fermentation broth contains a large number of impurities.[2,3]

Lactic acid can be removed from fermentation broth with several purification methods such as extraction, electrodialysis, reactive distillation, and adsorption. Adsorption or ion exchange is a reliable technology. Adsorption on ion exchange resins has the advantage that it can be coupled with the fermentation process. Fermentation processes to produce carboxylic acids operate most effectively at a pH above the pK_a of the acid product.[4,5]

Several researchers have adsorbed lactic acid using polymeric ion exchange resins. For example, Kulprathipanja and Oroshar adsorbed lactic acid from fermentation broth using strong, moderate, or weak basic anion exchange resins.[6] Cao et al. adsorbed lactic acid using Amberlite IRA-400.[3] However, there is not sufficient information in the literature about lactic acid adsorption on Amberlite IRA-67.

Acid adsorption on Amberlite IRA-67 is a neutralization reaction defined by the following equation,

$$n(\mathrm{R-N}) + \mathrm{AH}_n \leftrightarrow \mathrm{R-(NH^+)}_n\mathrm{A}^{n-}$$

$$(n = 1 \text{ for acid molecule})$$

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

The aim of this study is to investigate the efficiencies of activated carbon and Amberlite IRA-67 on the adsorption of L-lactic acid from fermentation broth or wastewater streams. Regeneration was not studied in these experiments.

MATERIAL AND METHODS

Material. L(+)-Lactic acid, Amberlite IRA-67, and activated carbon were obtained from Merck. 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. Four different concentrations of L(+)-lactic acid were prepared. These concentrations were 2.5%, 5%, 10%, and 20% (w/w).

Mixtures of a known amount of adsorbent and 5 mL of 10% (w/w) lactic acid solution were prepared, and equilibration was carried out in a thermostated shaker. Every 30 min, an aqueous phase sample was titrated to determine the amount of lactic acid using NaOH (0.1 N) with a phenolphthalein indicator. The period for equilibrium was determined to be 180 min. The samples were shaken for 180 min, and the optimum amount of adsorbent was determined to be 0.4 g, and using this optimum amount, the effect of initial acid concentration was investigated at (298 ± 1) K. Adsorption isotherms depend on initial acid concentration.

RESULTS AND DISCUSSION

In this study, first the period of the equilibrium state of the adsorbents was determined; the effect of the amount of adsorbent on adsorption was also investigated. Second, the effect of

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

adsorbent	initial acid concentration g L^{-1}	amount of adsorbent g	time min	equilibrium conc C_e g L^{-1}	amount of adsorbed acid Q_e mg g^{-1}	percentage of removal acid %	pH
activated carbon	99.08	0.25	30	93.68	108.00	5.45	2.35
	99.08	0.25	150	93.05	120.60	6.09	2.25
	99.08	0.25	180	92.78	126.00	6.36	2.33
Amberlite IRA 67	99.08	1.00	40	53.59	227.45	45.90	2.36
	99.08	1.00	80	52.97	230.55	46.54	2.35
	99.08	1.00	120	53.06	230.10	46.45	2.34
	99.08	1.00	240	53.15	229.65	46.45	2.35
	99.08	1.00	280	53.06	230.10	46.45	2.34

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

adsorbent	initial acid concentration g L^{-1}	amount of adsorbent g	equilibrium concentration C_e g L^{-1}	amount of adsorbed acid Q_e mg g^{-1}	percentage of removal acid %	pH
activated carbon	99.08	0.2	93.68	135.20	5.45	2.27
	99.08	0.4	84.68	180.10	14.53	2.45
	99.08	0.6	80.17	157.65	19.09	2.64
	99.08	0.8	71.16	174.55	28.18	2.79
	99.08	1.0	67.56	157.64	31.81	2.89
Amberlite IRA-67	99.08	0.25	85.57	270.36	13.64	2.07
	99.08	0.50	76.57	225.18	22.72	2.15
	99.08	0.75	63.95	234.25	35.46	2.23
	99.08	1.00	53.15	229.69	46.36	2.35
	99.08	1.25	43.24	223.39	56.36	2.48
	99.08	1.50	31.78	224.36	67.93	2.66
	99.08	1.75	22.52	218.77	77.27	2.87
	99.08	2.00	10.81	220.69	89.09	3.27

initial acid concentration on adsorption was determined. Last, the Langmuir, Freundlich, and Temkin isotherms were applied.

Effect of Contact Time. The effect of contact time for the adsorption of lactic acid by activated carbon and Amberlite IRA-67 was studied for a period of 280 min for an initial lactic acid concentration of 99.08 g L^{-1} at 298 K. The activated carbon dosage was 0.25 g and IRA-67 was 1 g. The effect of contact time on the removal of lactic acid is shown in Table 1. For both adsorbents, uptake of adsorbate species is fast in the initial stages of the contact period, and thereafter, it becomes slower near the equilibrium. Between these two stages of 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.[7]

Effect of Amount of Adsorbent. The effect of adsorbent dose on the extent of solute adsorption was investigated by varying the dose from (0.2 to 1.0) g for activated carbon and (0.25 to 2.00) g for IRA-67 under the selected initial solute concentration of 99.08 g L^{-1} at 298 K. It is observed from Table 2 and Figure 1 that as the dose increases the amount of solute adsorbed increases. At the maximum dose of 1.0 g for activated carbon and 2.00 g for IRA-67, the maximum adsorption capacity was (31.81 and 89.09)%, respectively for a 99.08 g L^{-1} initial solute concentration.

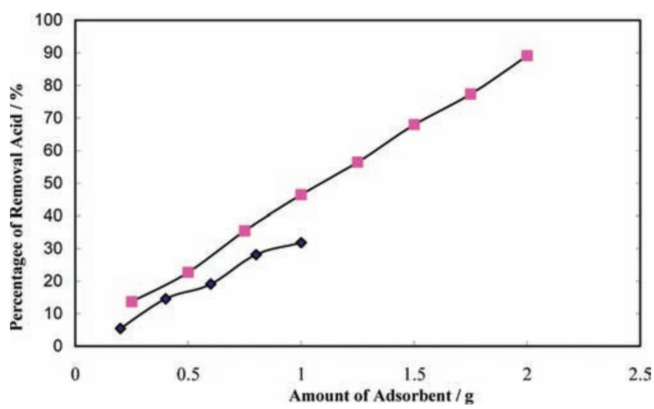

Figure 1. Effect of the amount of adsorbents on the adsorption of lactic acid: ■, IRA-67; ◆, activated carbon.

Effect of Initial Acid Concentration. Different initial lactic acid concentrations (25.22, 51.35, 99.08, and 208.98 g L^{-1}) were studied for both adsorbents. It can be observed from Table 3 that increasing the initial acid concentration from (25.22 to 208.98) g L^{-1} the adsorbed acid concentration decreased in the efficiency for both adsorbents. The efficiency of removal decreased from (32.14 to 8.18)% for activated carbon and from (64.63 to 28.45)% for IRA-67 with increasing initial acid concentration of lactic acid. This may be explained by saturation of the accessible exchangeable sites of these adsorbents.

Table 3. Effect of Initial Acid Concentration on the Adsorption of Lactic Acid

adsorbent	initial acid concentration g L^{-1}	amount of adsorbent g	equilibrium concentration C_e g L^{-1}	amount of adsorbed acid Q_e mg g^{-1}	percentage of removal acid %	pH
activated carbon	25.22	0.4	17.12	101.28	32.12	3.28
	51.35	0.4	42.34	112.57	17.55	2.77
	99.08	0.4	84.67	180.23	14.54	2.45
	208.98	0.4	191.87	213.95	8.18	2.09
Amberlite IRA-67	25.22	1.0	8.92	203.78	64.63	5.30
	51.35	1.0	13.51	472.95	73.68	
	99.08	1.0	53.15	574.23	46.36	2.35
	208.98	1.0	149.53	743.20	28.45	1.93

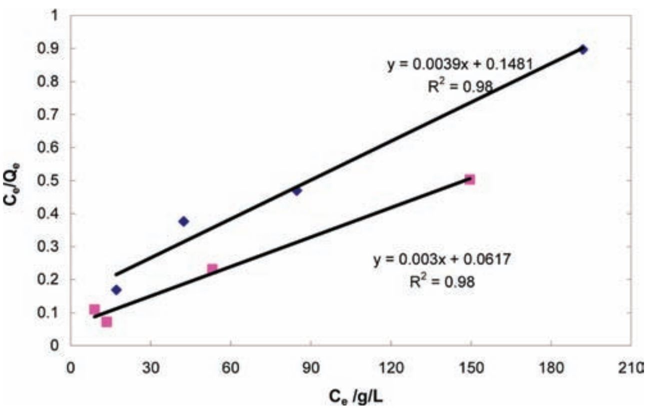

Figure 2. Langmuir isotherm model for lactic acid adsorption: ■, IRA-67; ◆, activated carbon.

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

The Langmuir equation[8,9] is

$$Q_e = \frac{K_L \cdot q_m \cdot C_e}{1 + K_L \cdot C_e} \quad (1)$$

where K_L and q_m denote the adsorbent-phase concentrations of lactic acid and saturation capacity.

C_e is the acid concentration of the solution phase at the equilibrium and Q_e is the acid concentration of the solid phase at the equilibrium.

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

$$\frac{C_e}{Q_e} = \frac{C_e}{q_m} + \frac{1}{K_L q_m} \quad (2)$$

The values of K_L and q_m were determined from the intercept and slope of the straight line in Figure 2. The calculated parameters of the Langmuir equation are presented in Table 4.

The Freundlich isotherm was used in this study as a second isotherm[10,11] and is given by

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

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

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

Table 4. Results of Langmuir Isotherms for the Lactic Acid Adsorption by Different Adsorbent

Langmuir Isotherm Data					
activated carbon			Amberlite IRA-67		
R^2	q_m mg g^{-1}	K_L	R^2	q_m mg g^{-1}	K_L
0.98	256.41	0.026	0.98	333.33	0.048
Freundlich Isotherm Data					
activated carbon			Amberlite IRA-67		
R^2	K_f	n	R^2	K_f	n
0.92	36.75	2.97	0.74	124.79	2.68
Temkin Isotherm					
activated carbon			Amberlite IRA-67		
R^2	A L g^{-1}	B	R^2	A L g^{-1}	B
0.91	0.35	50.31	0.87	0.68	65.04

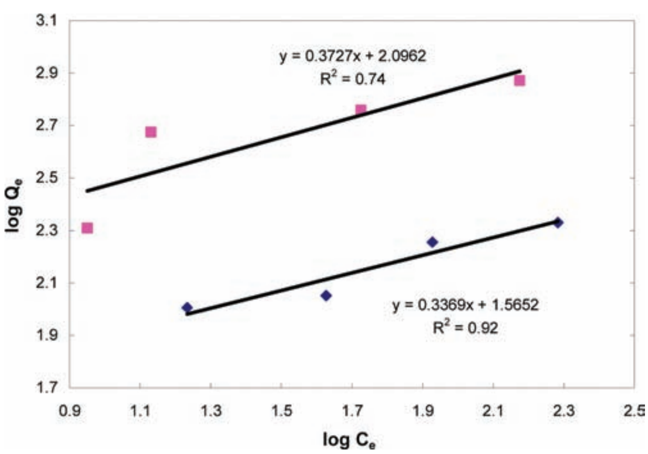

Figure 3. Freundlich isotherm model for lactic acid adsorption: ■, IRA-67; ◆, activated carbon.

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

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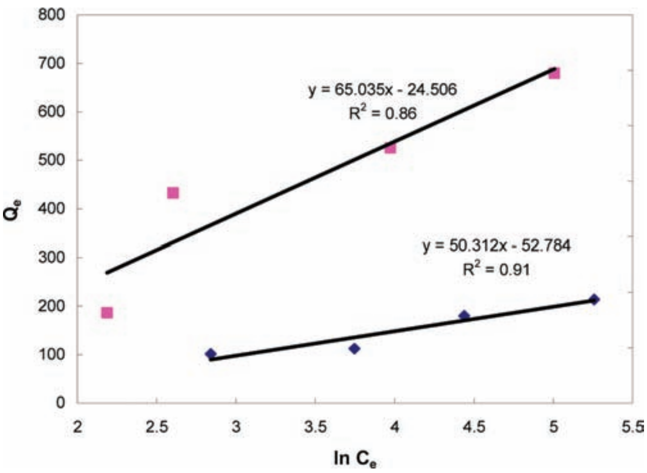

Figure 4. Temkin isotherm equation for the lactic acid adsorption: ■, IRA-67; ◆, activated carbon.

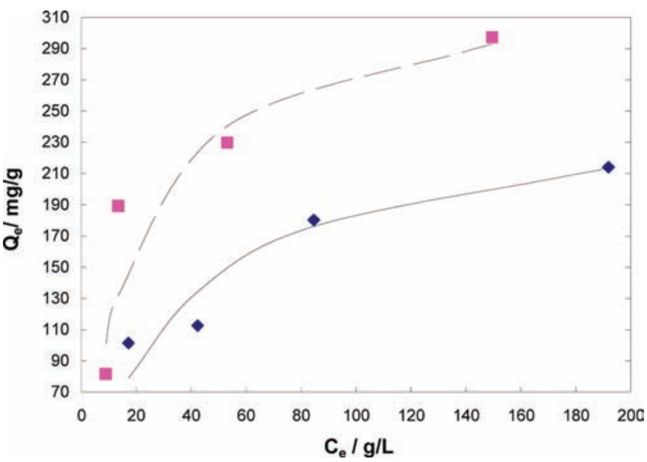

Figure 5. Comparison of the theoretical and experimental values of lactic acid adsorption using the Langmuir isotherm equation: ■, IRA-67 exp plot; ◆, AC exp plot; —, AC Langmuir plot; ---, IRA-67 Langmuir plot.

Q_e and log C_e. Figure 3 shows a plot of the Freundlich isotherm for lactic acid adsorption for both adsorbents. The results of the Freundlich model are presented in Table 4.

The Temkin isotherm supposes that the heat of adsorption of all molecules in a layer decreases linearly with coverage due to adsorbent−adsorbate interactions and that the adsorption is characterized by a uniform distribution of the bonding energies, up to some maximum binding energy. The Temkin isotherm (Figure 4) is given as

$$Q_e = B \ln A + B \ln C_e \qquad (5)$$

The value of A is the equilibrium binding constant, corresponding to the maximum binding energy, and constant B is related to the heat of adsorption.[12] The isotherm constants are shown in Table 4.

The results show that the Langmuir isotherm fits the experimental data for both adsorbents with an R^2 value of 0.98. The consistency of the experimental and the Langmuir isotherm results is shown in Figure 5. The Freundlich isotherm and Temkin isotherm show some deviation from the experimental results.

CONCLUSIONS

The following conclusions can be presented related to this work:

1. The results of present study, especially when using the same amount of adsorbents shows that the weakly basic absorbent Amberlite IRA-67 is a more effective adsorbent than activated carbon for the removal of lactic acid from aqueous solution.
2. The study shows that for both adsorbents, if the maximum adsorbent dose is used, the maximum efficiency is achieved. Equilibrium data for adsorption of lactic acid on activated carbon and IRA-67 were best represented by the Langmuir isotherm with R^2 values of 0.98.

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