Adsorption of Malic Acid on Activated Charcoal

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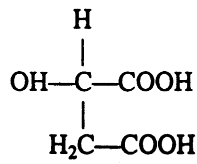
Attempts were made to adsorb malic acid from aqueous solutions by activated charcoal. Adsorption experiments were carried out in the system of aqueous malic acid solutions in four different concentrations [3, 5, 10 and 15 (w/w)] and in seven different amounts of activated charcoal (0.005, 0.010, 0.015, 0.020, 0.025, 0.030 and 0.040 g) as adsorbent. Adsorption experiments were carried out at 298 K. The adsorption of malic acid was found to be appreciable in activated charcoal. The percentage removal of malic acid was 94.14% by activated charcoal. The equilibrium data fit well within Langmuir and Freundlich isotherms.

Key Words: Adsorption, Malic acid, Activated charcoal, Langmuir isotherm, Freundlich isotherm

INTRODUCTION

The traditional use of activated charcoal in both water and wastewater treatment is well known. These materials are very versatile adsorbents due to their high surface area, a well developed pore structure and surface properties. In spite of their huge application in removing of organic substances, however, the mechanism of the adsorption process is not yet fully understood and no clear studies exist in the literature regarding these mechanisms. The significance of the carbon surface chemistry in the adsorption process was first raised by Hassler[1] and Gusler *et al.*[2]. A decade later, other authors shed significant light on the effects of surface carbon-oxygen groups and the sorbate-sorbent-interactions on the adsorption mechanism of organic compounds. Since then, theoretical and experimental approaches have come a long way, as demonstrated by various reviews in the last twenty years.

As an acidulant, malic acid (**1**) is especially suitable for jelly and foodstuff containing fruit ingredients. It can maintain the natural colour of juice in health drinks, it can resist fatigue and protect liver, kidney and heart. Malic acid can enhance pharmaceutical stability and improve pharmaceutical absorption. It can be added into composite amino acid injections, directly participating in the metabolic cycle of organisms—Krebs cycle. It can reduce the metabolic loss of amino acids and can compensate hypohepatia, cure uremia and hypertension and weaken the damage of anticancer drugs to normoblasts. It is also used as skin disinfector, air depurative and deodorizer.



(1)

For separation of organic acids from aqueous solutions several methods have been investigated. Inci[3-5] has used organic solutions of tertiary amines for separation of citric acid and obtained high distribution coefficients for malic acid such as for other many organic acids. However, in this study the possibilities of seprating malic acid from aqueous solutions have been investigated using activated charcoal. Keeping in view the low cost, ease of operation, physico-chemical treatment, an adsorption process has been developed. In this work, experimental results for adsorption of malic acid by activated charcoal at 298 K are presented. All experimental data were then fitted into the Freundlich isotherm equation to obtain the corresponding factors[6, 7].

Theoretical

The analysis of the isotherm data is important in developing an equation which accurately represents the results and which could be used for design purposes. Out of the several isotherm equations available, Freundlich isotherm equations were found most suitable for the present equilibria. 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. Langmuir equation is represented in the following equation:

$$(C_e/Q_e) = (K_1/Q^0) + (C_e/Q^0) \qquad (1)$$

where C_e is the equilibrium concentration (mg/L), Q_e is the adsorbed at equilibrium (mg/g) and K, Q^0 can be related to the equilibrium constant and sorption maxima respectively. The plot of C_e/Q_e *vs.* C_e gives a straight line showing the applicability of Langmiur isotherm. The values of K and Q^0 at different concentrations have been determined from the slope and intercept of the plot.

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

$$Q_e = K_f C_e^{1/n} \qquad (2)$$

A logarithmic plot linearizes the equation enabling the exponent n and the constant K_f to be determined[8–11].

$$\log Q_e = \log K_f + (1/n) \log C_e \qquad (3)$$

The constants are listed in Table-3 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[12–15] of Q_e *vs.* log $C_{..}$

EXPERIMENTAL

The activated charcoal and malic acid were supplied as pure by Merck Co. For equilbrium studies experiments were performed using 100 mL glass bottles at room temperature on electrial shaker. In 100 mL glass bottles which were cleaned and dried previously 5 ml each of the prepared solutions were taken. To show the effect of initial malic acid concentrations on adsorption, 0.005, 0.010, 0.015, 0.020 and 0.025 g charcoal activated were agitated with 5 mL of malic acid solutions at five different concentrations 3, 5, 10 and 15% (w/w). At the second stage, to show the effect of shaking times on the adsorption, aqueous solutions of malic acid (3 and 15% w/w) and 0.010, 0.020, 0.030 and 0.040 g charcoal activated were agitated in a shaking bath for 4 h. All the solutions were left in a temperature controlled shaking bath (298 K) for 5 h. After adsorption experiments, a known quantity of the adsorbate solutions was withdrawn from the bottle for analysis. Concentrations of malic acid after filtration were determined by titration with 0.1 N aqueous sodium hydroxide.

RESULTS AND DISCUSSION

The adsorption of malic acid on the charcoal activated was investigated (Fig. 1 and Table-1). The isotherms in Figs. 2 and 3 are plotted using a mass based acid concentration Q_e (in mg of the solute adsorbed per g of charcoal) *vs.* the liquid concentration C_e at equilibrium conditions.

Fig. 1 demonstrates the influence of the amount of activated charcoal on the adsorption of malic acid. It can be seen that the adsorption of malic acid increases with increasing amount of activated charcoal. With increase in amount of activated charcoal from 0.005 to 0.0025 g sorption of malic acid increases from 0.33 to 11.60% for initial concentration of 3% of malic acid.

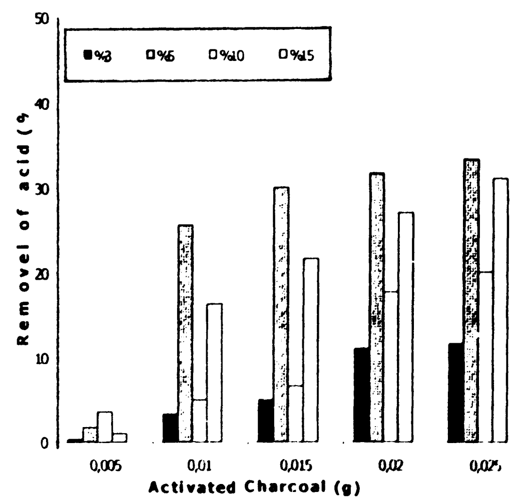


Fig. 1. Adsorption of malic acid

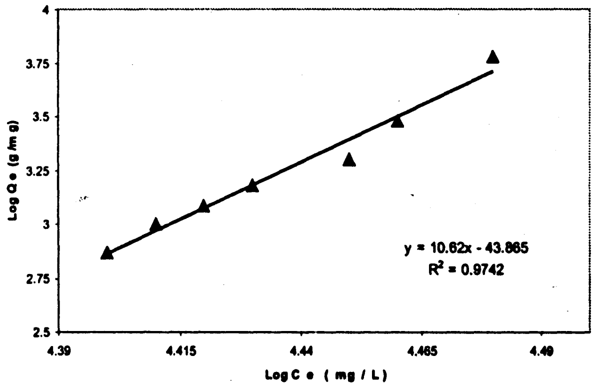


Fig. 2. Freundlich isotherm of malic acid

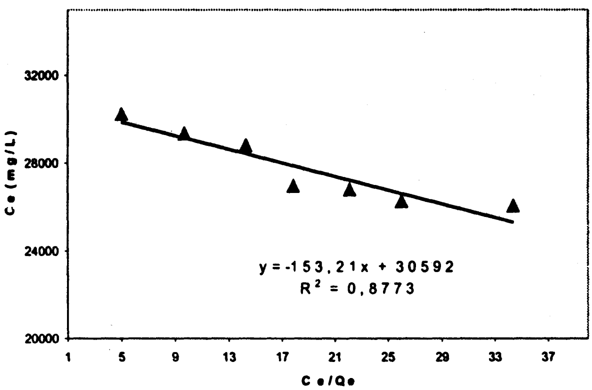


Fig. 3. Langmuir isotherm of malic acid

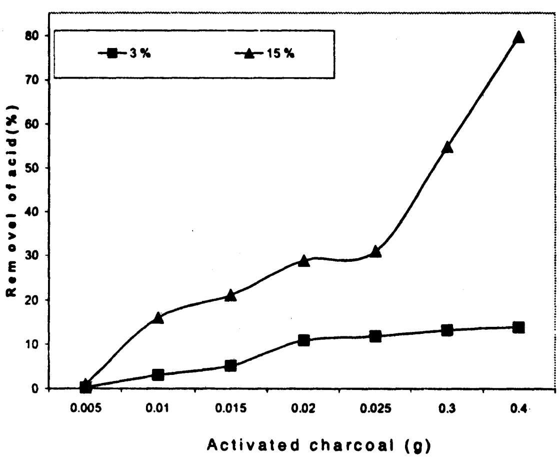


Fig. 4. Effect of activated charcoal amount on malic acid adsorption

TABLE-1
ADSORPTION OF MALIC ACID INTO ACTIVATED CHARCOAL

Initial concentration (g/L)	Initial concentration (% w/w)	Amount of charoal activated (mg)	Equilibrium conc., C_e (g/L)	Adsorbed acid, Q_e (g/mg)	Removal of acid (%)
30.30	3.00	0.005	30.20	0.020	0.33
30.30	3.00	0.010	29.29	0.010	3.33
30.30	3.00	0.015	28.79	0.010	4.99
30.30	3.00	0.020	26.97	0.166	10.90
30.30	3.00	0.025	26.77	0.141	11.66
50.50	5.00	0.005	50.00	0.101	1.66
50.50	5.00	0.010	42.72	0.777	25.66
50.50	5.00	0.015	41.41	0.606	29.99
50.50	5.00	0.020	40.90	0.479	31.66
50.50	5.00	0.025	40.40	0.404	33.33
101.01	10.00	0.005	99.89	0.222	3.66
101.01	10.00	0.010	99.49	0.151	4.99
101.01	10.00	0.015	98.98	0.134	6.66
101.01	10.00	0.020	95.65	0.267	17.66
101.01	10.00	0.025	94.94	0.242	19.99
151.51	15.00	0.005	151.21	0.059	0.98
151.51	15.00	0.010	146.56	0.494	16.31
151.51	15.00	0.015	144.94	0.437	21.64
151.51	15.00	0.020	142.72	0.439	28.98
151.51	15.00	0.025	142.12	0.375	30.98

TABLE-2
EFFECT OF ACTIVATED CHARCOAL AMOUNT ON THE ADSORPTION OF MALIC ACID

Initial concentration (g/L)	Initial concentration (% w/w)	Amount of charoal activated (mg)	Equilibrium conc., C_e (g/L)	Adsorbed acid, Q_e (g/mg)	Removal of acid (%)
30.30	3.00	0.010	29.29	0.010	3.33
30.30	3.00	0.020	26.97	0.166	10.99
30.30	3.00	0.030	26.26	0.134	13.33
30.30	3.00	0.040	26.06	0.106	13.99
151.51	15.00	0.010	146.56	0.494	16.31
151.51	15.00	0.020	142.72	0.439	28.98
151.51	15.00	0.030	134.84	0.555	54.98
151.51	15.00	0.040	127.37	0.603	79.64

TABLE-3
FREUNDLICH ISOTHERM PARAMETERS OF MALIC ACID BY ACTIVATED CHARCOAL

Freundlich parameters	
log $K_{f\ (mg/g)}$	1/n
10.62	9.73

TABLE-4
LANGMUIR ISOTHERM PARAMETERS OF MALIC ACID BY ACTIVATED CHARCOAL

Langmuir parameters	
$1/Q^0$	K_L/Q^0
30592	–153.21

where C_e = equilibrium concentration, mg/L, K_l = equilibrium constant, Q_e = adsorbed at equilibrium, mg/g, Q_0 = sorption maxima, K_f = constant, n = constant

It can be seen that from Fig. 4 adsorbed amount of malic acid increases with increasing amount of activated charcoal. The increase in amount of activated charcoal from 0.010 to 0.040 g sorption of malic acid increases from 3.33 to 13.99% for 3% initial concentration of malic acid and from 16.31 to 79.64% for 15% initial concentration of malic acid. Adsorption isotherms were fitted into Langmuir and Freundlich isotherm equations to calculate the isotherm parameters. The values of isotherm parameters are given in Tables 3 and 4.

Conclusion

It was found that the adsorption capacity of activated charcoal was dependent on the amount of activated charcoal and the initial concentration of malic acid. On the basis of isotherm constants analysis it was confirmed that activated charcoal exhibits promising adsorption characteristics for malic acid.

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