Pak J Sci Ind Res 2002 ***45** (2) 82-85*

ADSORPTION BEHAVIOUR OF CITRIC ACID FROM AQUEOUS SOLUTIONS ON ACTIVATED CHARCOAL

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(Received 2 May 2001; accepted 20 July 2001)

Adsorption of citric acid at different concentrations on activated charcoal at 22° has been accomplished. It was found that at low concentrations, langmuir and Freundlich equations are well obeyed. The adsorption of citric acid from aqueous solution on the surface of charcoal is monolayer.

Key words: Adsorption, Citric acid, Langmuir constant, Freundlich constant, Monolayer

Introduction

Since charcoal possesses the property of holding molecules at its surface, the chemists have been using activated charcoal (finely divided) as adsorbent to remove coloring materials or dyestuffs and other organic substances like mono and dibasic acids from aqueous solution. The extent of holding molecules or adsorption of organic acids or dyestuffs depends upon solubility of adsorbate in water, polarity of adsorbate and available surface area of adsorbent. Charcoal is particularly effective in adsorbing compounds having aromatic rings whereas aliphatic compounds like acrylic acid or crotonic acid are usually less adsorbed on the surface of charcoal (Khan *et al* 1989). This is because charcoal has no polar group which participates in hydrogen bonding. Only the polarity of the adsorbate is important. The surface area of adsorbent is another factor which facilitates in holding molecules of adsorbate from aqueous solution. The surface area of the charcoal reported in literature is 3600 square ftg^{-1} (Arthur and Elizabeth 1958).

In our earlier papers the adsorption of acrylic acid, crotonic acid, glycolic acid, lactic acid, trataric acid from aqueous solution on the surface of charcoal have been reported (Khan *et al* 1989; 1991 and 1994). It was observed that the adsorption of the acids on charcoal mainly depends upon nature of acid and functional group attached to the side chain of the acid and concentration of these acids. These parameters significantly influence of the Langmuir and Freudlich isotherms. This paper describes the adsorption of citric acid at the surface of activated charcoal in aqueous solution at 22°C.

Experimental

Materials. All the chemicals, activated charcoal (animal), citric acid, oxalic acid, sodium hydroxide of E. Merck were used without further purification. Redistilled water was used throughout the course of experiments.

Procedure. All experiments were accomplished in nine reagent bottles at 22°C according to the method given elsewhere (Khan *et al* 1989; 1991 and 1994). Known volume of citric acid according to Table 1 were added to each bottle already containing 1 g activated charcoal. The volume of each bottle was then made upto 100 ml by using distilled water. The contents of each bottle were shaken for about half an hour with the help of magnetic stirrer and then allowed to attain an equillibrium. It was then filtered. The amount of acid which could not be adsorbed on the surface of activated charcoal was determined by titrations against standard sodium hydroxide.

Results and Discussion

The results shown in Table-1 indicates that the adsorption of citric acid from aqueous solution on the surface of activated charcoal gets increased with increase in concentration of citric acid. The rate of adsorption of citric acid (Fig 1) from aqueous solution is higher at higher concentration of adsorbate. At the concentration of 0.075 mol. dm^{-3}. the rate of adsorption is higher than at 0.1 mol. dm^{-3}. The reason is not clear, but is very clear that the degree of adsorption of citric acid from aqueous solution on the solid surface is controlled by its functional groups (-COOH,-OH) & the side chain to which they are attached. The same thing was also observed in the adsorption of glycolic acid, lactic acid, and tartaric acid (Khan *et al* 1991 and 1994). The first two acids are monobasic containing functional groups (-COOH,-OH) and tartaric acid

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is dibasic saturated acid whereas citric acid is monohydroxy tribasic saturated acid. The attachement of three -COOH & one -OH groups to the side chain [HOOC-CH_2-C(OH) (COOH) CH_2-(COOH)] makes citric acid monopolar than glycolic acid ($CH_2OH.COOH$), lactic acid ($CH_3.CH.OH.COOH$) and tartaric acid (HOOC. CH(OH)CH(OH).COOH). The adsorption of molecules of citric acid on the surface of charcoal occurs through its hydroxy (one) group, carboxyl (three) groups and the side chain. The polarity of citric acid makes the rate of its adosrption on the surface of adsorbent higher than for glycolic acid, lactic acid and tartaric acid. On comparing the rates of adsorption of citric acid among glycolic, lactic and tartaric acids, the order is as follows (Khan *et al* 1991 and 1994).

Citric acid > tartaric acid > glycolic acid> lactic acid.

When the activated charcoal is shaken with the aqueous solution of citric acid, the molecules of adsorbate strikes the uncovered area of the surface of adsorbent. The striking of molecules of adsorbate on the surface of charcoal will remain affecting till whole surface gets covered by acid molecules resulting a monolayer on the surface. The covered surface will remain unaffected and charcoal will not hold any molecule of acid on its surface. Actually the action of partial forces at the boundary of the activated charcoal results the adsorption. Since the functional groups (three-COOH & one-OH) are attached to the ends of adsorbate, citric acid will get adsorbed on the solid surface more preferably through-COOH and -OH

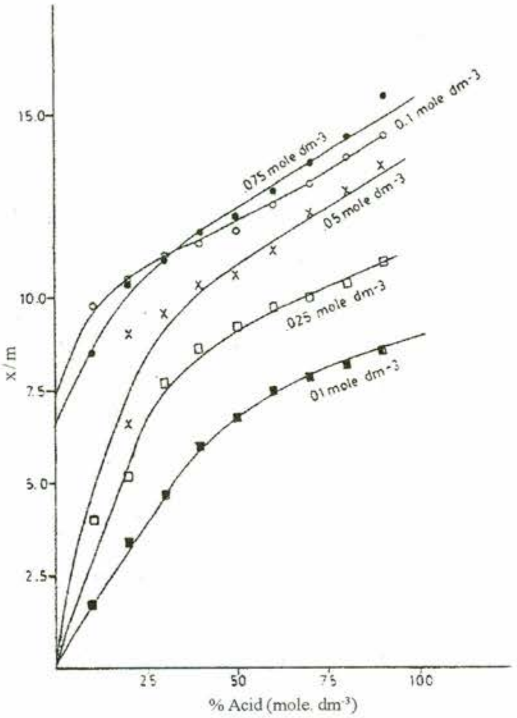

Fig 1. Effect of concentration on the rate of adsorption of citric acid on activated charcoal at 22°C.

Table 1

Adsorption of citric acid on the surface of 1 g activated charcoal at 22°C

Acid composition (%)	Amount of acid adsorbed x (g dm^{-3})	Equilibrium conc. of 10^2C (mol.dm^{-3})	$\frac{10^2 C}{(x/m)}$
	Acid concentration 0.100 mol dm^{-3}		
90	14.41	73.01	5.06
80	13.76	63.90	4.64
70	13.11	55.50	4.23
60	12.46	46.80	3.75
50	11.81	38.60	3.26
40	1147	29.60	2.58
30	11.15	21.20	1.90
20	10.48	12.80	1.22
10	09.83	04.40	0.45
	Acid concentration 0.075 mol dm^{-3}		
90	15.51	56.60	3.65
80	14.39	48.87	3.39
70	13.65	41.84	3.06
60	12.92	34.98	2.70
50	12.19	28.47	2.33
40	11.81	21.80	1.84
30	11.07	15.11	1.36
20	10.34	08.79	0.85
10	08.49	02.98	0.35
	Acid concentration 0.05 mol dm^{-3}		
90	13.57	33.13	2.44
80	12.92	29.35	2.27
70	12.25	24.61	2.01
60	11.26	20.82	1.85
50	10.61	16.72	1.57
40	10.27	12.62	1.22
30	09.60	08.52	0.88
20	08.95	04.57	0.51
10	06.62	01.42	0.21
	Acid concentration 0.25 mol dm^{-3}		
90	11.05	14.76	1.34
80	10.38	12.61	1.21
70	10.04	10.61	1.06
60	09.70	08.62	0.89
50	09.20	06.62	0.72
40	08.55	04.71	0.55
30	07.71	02.95	0.38
20	06.20	01.43	0.23
10	04.02	00.32	0.08
	Acid concentration 0.01 mol dm^{-3}		
90	8.59	3.98	0.46
80	8.21	3.22	0.39
70	7.90	2.52	0.32
60	7.52	1.90	0.25
50	6.76	1.32	0.19
40	5.98	0.84	0.14
30	4.68	0.44	0.09
20	3.44	0.18	0.05
10	1.69	0.07	0.04

groups. The polar ends of the molecules will attach themselves to the active sites of the solid surface (Lemieux and Morrison 1947). In the adsorption of formic, acetic, propionic, butyric acids (Langmuir 1981), tartaric acid (Khan *et al* 1994) lactic and glycolic acids (Khan *et al* 1991) and crotonic and acrylic acids, (Khan *et al* 1989), similar results were obtained.

In the adsorption of citric acid from aqueous solution on the surface of charcoal, Langmuir and Freundlich isotherms may be used for the determination of intensity of adsorption, surface area utilized during the process of adsorption and amount of adsorbate adsorbed on the surface of charcoal. In terms of concentration, the adsorption equation (Langmuir 1918) can be written as:

$$\frac{C}{(x/m)} = \frac{1}{K\,K_1} + \frac{1}{K}\,C \;\ldots\ldots (1)$$

where x is the amount of adsorbate on 'm' g of adsorbent, C is the concentration in mol. dm^{-3} in solution at equillibrium, K is the measure of the surface area of solid surface, K_1 is the measure of strength of adsorption, and $(1/K)$ & $(1/KK_1)$ are Langmuir constants. A plot of $C/(x/m)$ versus C gives straight line of intercept $(1/KK_1)$ and slope $(1/K)$. The values obtained for different concentration of citric acid (Fig.2) are summarized in Table 2. From these results, it is obvious that $(1/K)$ is increasing with decrease in the concentration of acid. It means that at the higher concentration more surface area will be utilized by acid molecules. On the other hand the value of $(1/KK_1)$ gets decreased with decrease in the concentration of acid. It shows that the strength of adsorption of K_1 of citric acid on the surface of adsorbent increases with decrease in the concentration of acid.

The linear form of Freundlich isotherm (Adamson 1960) may be written as:

$$\text{Log}\,(x/m) = (1/n).\log C + \text{Log}\,K \;\ldots\ldots\ldots\ldots (2)$$

where x is the amount of adsorption on 'm' g of adsorbent. C is the concentration of adsorbate in mol. dm^{-3} in solution of equilibrium. Log K and (1/n) are Freundlich constants. A plot of log (x/m) versus log C gives a straight line of intercept log K and slope (1/n). The plot of (1 + log x) versus (3 + log C) are shown in Fig-3 for different concentrations of citric acid.

The values obtained from these plots for Freundlich constants are summarized in Table-2. These results indicate that the values of 10/n increases with decrease in concentration of citric acid whereas the values of log K get decreased with decrease in concentration of adsorbate. But in the adsorption of monobasic aromatic acids (Fahim Uddin *et al* 1988) both the values of (1/n) and log K decrease with decrease in concentration of adsorbate. Furthermore, in the adsorption of tartaric acid, the value of (1/n) decreases with concentration of acid.

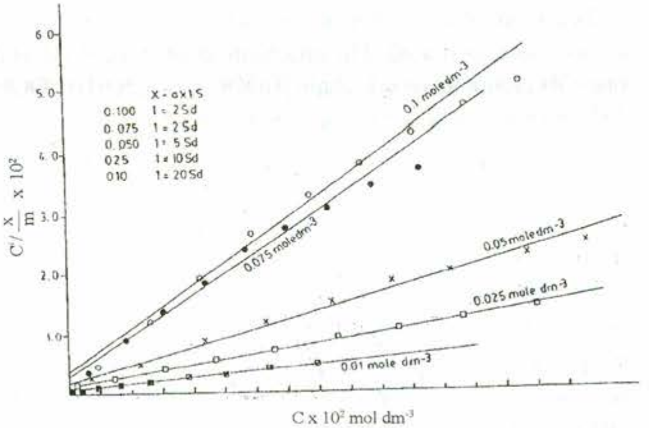

Fig 2. Langmuir plot for the adsorption studies of citric acid for its different concentration from aqueous solution on activated charcoal at 22°C. X-axis is different for different concentration as given here sd means small division.

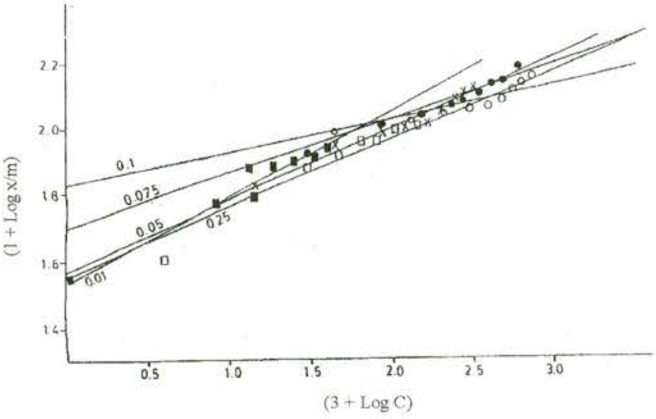

Fig 3. Freundlich plot for the adsorption studies of citric acid for its different concentration from aqueous solution on activated charcoal at 22°C.

The difference may be due to the attachment of the functional groups to the side chain and polarity of the adsorbate (Khan *et al* 1989; 1991 and 1994). Citric acid is more polar than tartaric acid. Our data also show that the value of (1/n) in all cases is in between zero and 1 (0.11-0.26). If (1/n) approaches

Table 2

Langmuir and Freundlich parameters in the adsorption of citric acid from aqueous solution on the surface of activated charcoal at 22°C.

Concentration of acid (mol.dm^{-3})	Langmuir parameters $\frac{10^2}{K}$	$\frac{10^3}{K K_1}$	Freundlich parameters $\frac{10}{n}$	log K
0.100	7.1545	4.00	1.10	1.82
0.075	6.500	3.00	1.65	1.70
0.05	7.222	2.00	2.20	1.57
0.025	8.500	1.50	2.20	1.51
0.010	11.110	0.75	2.60	153

to zero, then (x/m) equals to K, which indicates the formation of monolayer with no further adsorption. At relatively low concentration, the Langmuir & Freundlich equations are well obeyed, It can be concluded that citric acid yields good Langmuir & Freundlich adsorption isotherms at low concentrations. Charcoal may be useful for the separation of such organic acids which contain functional groups attached in either or all ends in aqueous medium.

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