

Adsorption of Some Aliphatic Organic Acids from Aqueous Solutions on Activated Carbons

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Summary: Adsorption of a series of lower aliphatic and different unsaturated organic acids from their aqueous solutions on the surface of activated carbons, prepared from indigenous precursors like wood (*Acacia arabica*), rice husk (low ash) and lignitic coal (Lakhra) have been studied. It has been found that adsorption pattern follows Traube's rule and to a large extent depends upon porosity and chemical nature/surface of the adsorbent. It has further been established that the degree of adsorption of a particular acid depends upon the polarity of carboxylic group, the length of side chain as well as the nature or type of bonding. Freundlich and Langmuir plots were drawn and their constants calculated and elucidated. It has also been inferred that active carbons prepared from cellulosic precursors have proven better towards the acid adsorption as compared to that prepared from lignitic coal.

Introduction

Active carbon has been used for many years in potable water treatment, in the pretreatment of water for its use in industry and in the safe disposal of different industrial effluents. Due to growing awareness of environmental pollution, great emphasis is now-a-days being laid on the use of this commodity as pollution control media specially in the removal of organics from liquid phase [1]. It is extensively used in the adsorption of both aliphatic and aromatic compounds. Due to non-polar nature of this adsorbent, non-polar solutes or adsorbates dissolved in a polar solvent like water will adsorb favourably on its surface than polar adsorbates. The adsorption of lower fatty acids from their solutions on activated carbon was earlier studied by Freundlich and Heller [2]. Kipling [3], observed the behaviour of aqueous solutions of weak and non-electrolytes during their adsorption on activated carbons. They found that the nature of the adsorbed phase is usually determined by the porosity and chemical nature of the adsorbent, the nature of the components of the solution, the concentration of the solution and the mutual solubility of the components [4].

The adsorption of aliphatic organic acids from their aqueous solutions by active carbon was earlier studied by many authors [5-7]. It was thereafter found that the adsorption increases

regularly as we ascend the homologous series. However, adsorption from the solution is a complex phenomenon depending on the adsorbate-solute and adsorbate-solvent interactions and also on the nature of interfacial region. The relationship among the adsorption phenomena, characteristic of adsorbates and physico-chemical nature of the surface of adsorbents has also been studied by Graham [8], Coughlin & Egara [9] and Nandi & Walker [10].

The present authors have been engaged in systematic R&D work on the development of technology for the preparation of active carbons, both powdered and granular, from the raw materials of vegetable and mineral origin and their detailed characterization [11-13]. This study has been undertaken to observe the behaviour of the three activated carbon samples prepared in these laboratories from different precursors, like *Acacia arabica*, low ash rice husk [14], and indigenous lignitic coal of Lakhra (Sindh), towards adsorption of the lower aliphatic and certain unsaturated organic acids from their aqueous solutions all along the homologous series. Langmuir and Freundlich isotherms have been drawn and their constants calculated from the relevant adsorption data. An attempt has been made to correlate these parameters with the other physical and chemical characteristics

of the activated carbon samples determined earlier on. Different factors controlling the isotherms have also been discussed and elucidated.

Results and Discussion

Figs. 1-3 illustrate the 25°C adsorption isotherms of lower aliphatic acids on the activated carbon samples. A, B and C derived from wood (*Acacia arabica*), rice husk (low ash) and coal (Lakhra) respectively. It may be seen from these figures that the adsorption of these acids increases regularly as the homologous series is ascended from formic to valeric acid, which is in conformity with Traube's rule [15]. This behaviour may be explained as such that the solubility of these acids in water decreases with the increase in their molecular weight on ascending the series. Hence the energy required to remove one mole of the solute from the solvent-solid interface is lowered, resulting in higher adsorption of the solute on the surface of charcoal [1]. Another possible explanation of this trend is that, each molecule of the adsorbent has an adsorption potential which is a measure of the free energy of adsorption released when adsorbate molecule moves from solution to the adsorbed state on the surface. Adsorption potential can be linked with molecular weight and the molecular structure. Henceforth higher the molecular weight of a compound, the more strongly it is adsorbed [16]. This adsorption mechanism therefore seems to be the same for each species in the series [17]. This adsorption mechanism is based on the contention that during the adsorption phenomenon, although there is some effect due to film diffusion at the particle-solution boundary, but it is actual diffusion within the pores which is rate limiting for most cases of adsorption from solution on activated carbon [18].

As for the pattern of adsorption (Figs. 1-5), on the three different carbon samples under study is concerned, it may be seen, that carbon derived from low ash rice husk (B) has the highest adsorption whereas that of the coal (C) has the lowest. This behaviour may be explained in the light of different characteristics of these samples depicted in Table-1. It may be observed that sample B has the highest carbon and lowest ash contents of the three. Moreover, iodine no and porosity of this sample are also quite higher as compared to the samples A and C. All these factors may have contributed towards its

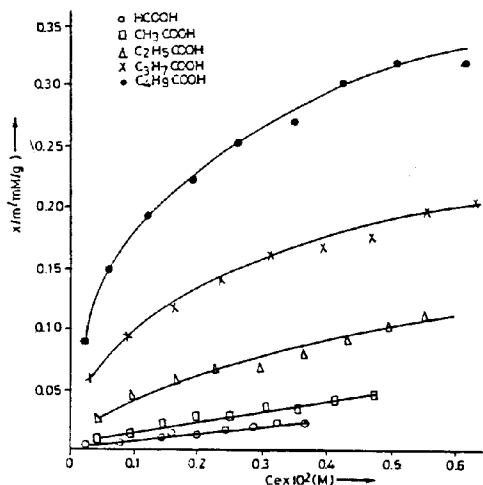


Fig. 1: Adsorption isotherms of lower aliphatic acids on carbon #A.

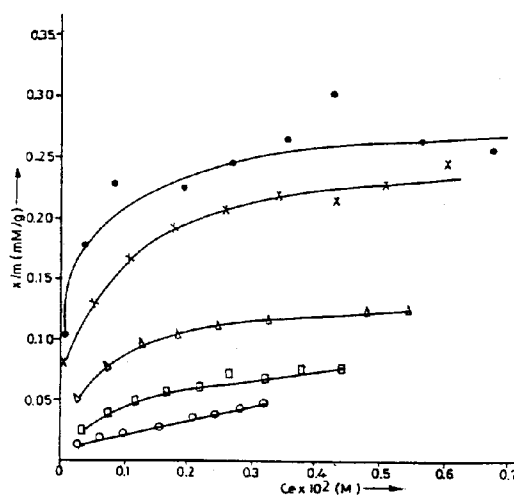


Fig. 2: Adsorption isotherms of lower aliphatic acids on carbon #B.

higher adsorptive capacity [19]. Contrary to that, carbon content, iodine no and porosity of the sample C are quite low. Higher ash content of 6.3% with quite an acidic pH of 3.4 may also be imparting their role in lower adsorption of these acids on sample C. Furthermore, another factor which might be contributing towards comparatively higher acid

Table-1: Composition and Different Characteristics of Activated Carbons

Sample Code	Origin	C%	Composition			Ash%	Iodine No. (mg/g)	Characteristics		pH
			H%	N%	O*%			Surface area of pores > 10 Å (m ² /g)	Porosity (cc/100g)	
A	WOOD	86.21	1.62	0.37	6.50	5.30	975	895	172	4.55
B	RICE HUSK	90.89	.043	Nil.	4.75	3.90	1340	1236	297	5.92
C	COAL	83.20	1.67	1.31	7.52	6.30	869	796	165	3.44

*Determined by difference and includes sulfur.

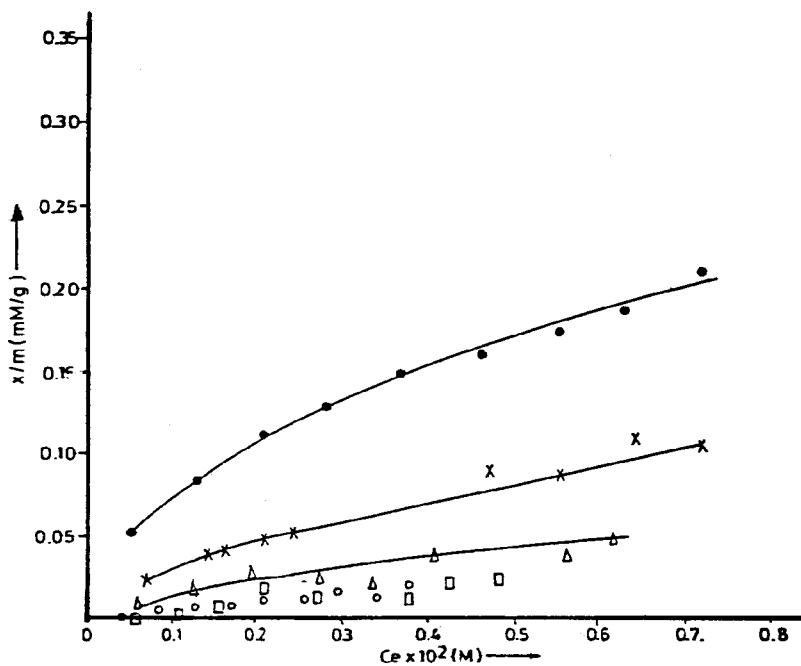


Fig. 3: Adsorption isotherms of lower aliphatic acids on carbon #C

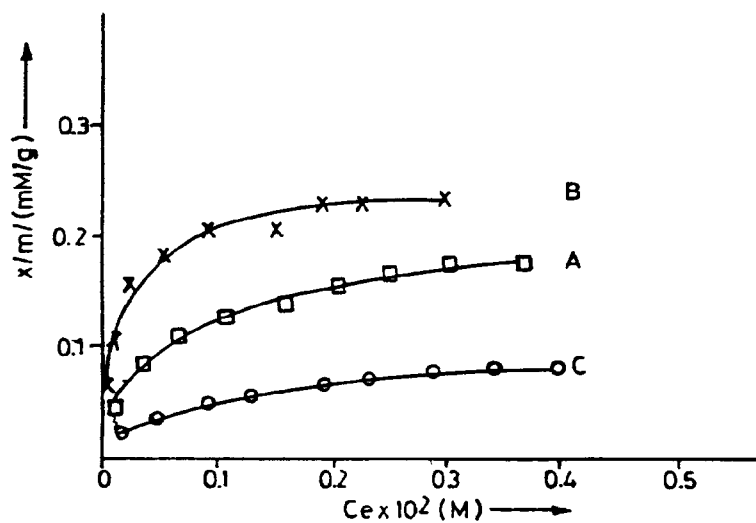


Fig. 4: Adsorption isotherms of fumaric acid on carbons # A,B and C.

adsorption in sample B is the chemical structure of its surface (Table-1), where residual gases are on the lower side and plenty of adsorption sites are available.

It may also be seen in Figs 1-3 that lower aliphatic acids like formic and acetic do not yield conventional Langmuir type of isotherms, whereas long chain higher aliphatic acids tend to obey Freundlich as well as Langmuir isotherms. This behaviour may be explained in terms of polarity of carboxylic groups. In higher acids, the side chain is long and the polarity of carboxylic group is not transmitted through the side chain, resulting in attachment of these molecules to the solid surface of carbon. This phenomenon results in a monolayer packing and higher adsorption [7]. In lower acids, the side chain is small and is effected by the polarity of -COOH group, resulting in a non-uniform packing and lower adsorption. It is therefore not possible to compute standard isotherms of formic and acetic acids and henceforth to calculate surface area of the carbon samples by adsorption of these lower acids.

This adsorption study has also been extended to the unsaturated organic acids like fumaric and crotonic to observe the effect of unsaturation and chain length on the phenomenon of adsorption on the solid surface of carbon samples A, B and C. It may be observed in Figs. 4 and 5 that the adsorption in case of crotonic acid is comparatively higher than fumaric acid in all the carbon samples under study. This behaviour may also be due to the small chain length in crotonic acid ($\text{CH}_3\text{CH}=\text{CH}.\text{COOH}$) as compared to fumaric acid ($\text{HOOC}.\text{CH}=\text{CH}.\text{COOH}$), due to which the polarity of carboxylic group in the former is higher than the later resulting in enhanced adsorption of crotonic acid as it is adsorbed both through side chain as well as carboxylic group. Lower adsorption of fumaric acid may be due to the lesser polarity of its -COOH group and comparatively longer chain length. It may also be seen in Figs 4 and 5 that adsorption of these unsaturated organic acids on the three activated carbon samples is far less than that of lower aliphatic acids of formic-valeric series. It rather supports the observation [20], that the nature of bonding (π or α) also affect the trend of adsorption on the solid surface of activated carbon samples. Moreover, the pattern of adsorption in case of these unsaturated acids is $B>A>C$, which is same as obtained in case

of the series of lower aliphatic acids described earlier. It has therefore been inferred from these studies that the degree of adsorption of a particular acid depends upon the polarity of carboxylic group, the length of side chain to which it is attached as well as the nature or type of bonding. Using the experimental equilibrium results, from the adsorption data of these aliphatic organic acids, on the three carbon samples.

Freundlich

$$\chi/m = KC^{1/n}$$

and Langmuir

$$\frac{C}{\chi/m} = \frac{1}{ab} + \frac{1}{a}C$$

isotherms were drawn and a representative of each for fumaric acid is given(Figs. 6 & 7). The constants of the isotherms have also been calculated from the slope and the intercept of the plots [21]. It may be seen in Table-2, that Freundlich constant of $1/n$, determined from the slope of the plot, decreases as the length of the side chain increases from formic to valeric acid in all of three carbon samples. Moreover, in all of the cases $1/n < 1$, so adsorption increases less rapidly than concentration. Similarly, the value of $\log K$ for valeric acid is greater than for formic acid in case of samples A and B, whereas in case of sample C, it tends to become less negative with the increase in the length of side chain.

Table-3 presents Langmuir constants of "a", and "b" for the three carbon samples A,B, and C, where "a" is the measure of the surface area of solid and "b" is the intensity or strength of adsorption. These results indicate that at higher concentration of adsorbent (Acid), more surface area (a) of adsorbate (carbon) is utilized. Moreover, the intensity of adsorption of acid molecules on the solid surface of activated carbon increase with decrease in concentration of the acid. Therefore, these acid molecules will tend to lie erect on the carbon surface [7]. The value of both of the constants $1/a$ and $1/b$ (Table-3), decreases from propionic to valeric acid. This difference may be due to the length of side chain attached to the carboxylic group of the acid which makes the acid more or less polar. Freundlich

Table-2: Freundlich parameters for the adsorption of different aliphatic and unsaturated organic acids on the surface of activated carbon samples obtained from different sources.

S.No.	Acids	Wood based carbon (A)			Low ash rice husk based carbon (B)			Coal based carbon (C)		
		Slope (1/n)	Intercept (log K)	Correlation Coefficient (r)	Slope (1/n)	Intercept (log K)	Correlation Coefficient (r)	Slope (1/n)	Intercept (log K)	Correlation Coefficient (r)
1.	Formic acid	0.76	0.24	0.9695	0.53	0.46	0.9725	0.73	-1.80	0.9735
2.	Acetic acid	0.75	0.40	0.9742	0.40	0.62	0.8525	0.70	-1.02	0.9846
3.	Propionic acid	0.56	0.46	0.9643	0.30	0.86	0.9249	0.62	-0.50	0.8725
4.	Butyric acid	0.47	0.49	0.9713	0.27	0.90	0.9130	0.53	-0.22	0.8855
5.	Valeric acid	0.40	0.56	0.8753	0.20	1.22	0.9245	0.50	-0.16	0.8196
6.	Crotonic Acid	0.40	0.38	0.9928	0.28	0.77	0.8685	0.52	0.11	0.9222
7.	Fumaric acid	0.32	0.59	0.9613	0.14	1.14	0.8493	0.36	0.25	0.8561

Table-3: Langmuir parameters for the adsorption of different aliphatic and unsaturated organic acids on the surface of activated carbon samples obtained from different sources.

S.No.	Acids	Wood based carbon (A)			Low ash ric husk based carbon (B)			Coal based carbon (C)		
		a (m ² /g)	b (g/g)	Correlation Coefficient (r)	a (m ² /g)	b (g/g)	Correlation Coefficient (r)	a (m ² /g)	b (g/g)	Correlation Coefficient (r)
1.	Formic acid	--	--	0.8740	--	--	0.9642	--	--	0.9989
2.	Acetic acid	--	--	0.9630	--	--	0.9945	--	--	0.9805
3.	Propionic acid	0.1143	0.2857	0.9996	0.1333	1.2500	0.9968	0.0555	0.1923	0.9920
4.	Butyric acid	0.2222	1.6129	0.9888	0.2000	5.0000	0.9958	0.1428	0.3773	0.9798
5.	Valeric acid	0.4000	3.3330	0.9895	0.2500	14.2857	0.9913	0.2000	1.0000	0.9968
6.	Crotonic acid	0.4717	4.545	0.9978	0.2666	4.5454	0.9986	0.1600	2.5000	0.9840
7.	Fumaric acid	0.2000	4.0000	0.9965	0.2584	2.9412	0.9964	0.1250	0.5714	0.9955

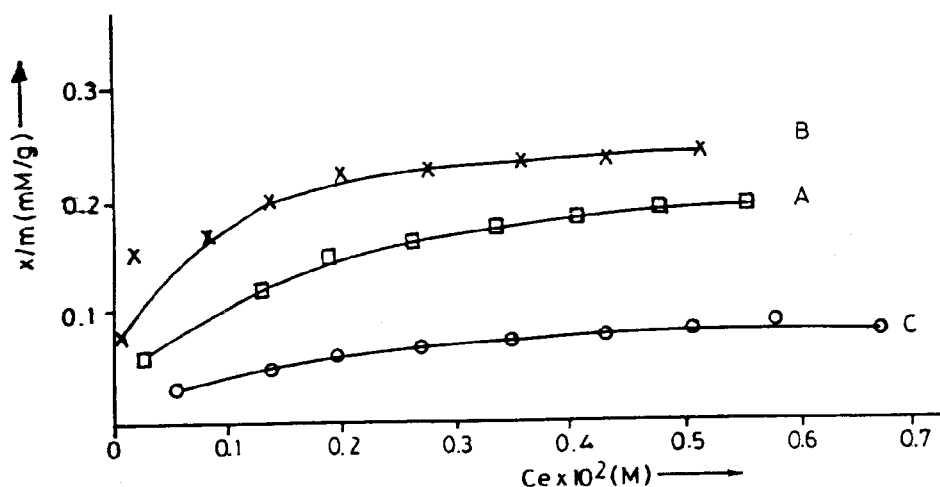


Fig. 5: Adsorption isotherms of crotonic acid on carbons # A,B and C.

and Langmuir constants calculated for the unsaturated acids have also been given in Tables-2 and 3, and show the same pattern as of lower aliphatic acids with the increase in chain length from crotonic to fumaric acid. It therefore shows that the polarity of an adsorbate plays an important role in the process of adsorption on the surface of an adsorbent like activated carbon [20].

Correlation coefficient (r) of the entire data in connection with Freundlich and Langmuir plots fitting respective data points for the three carbon samples under study have been calculated and incorporated in Tables 2 and 3. It is evident that in most of the cases "r" approaches unity which rather signifies the validity of the data for a straight line.

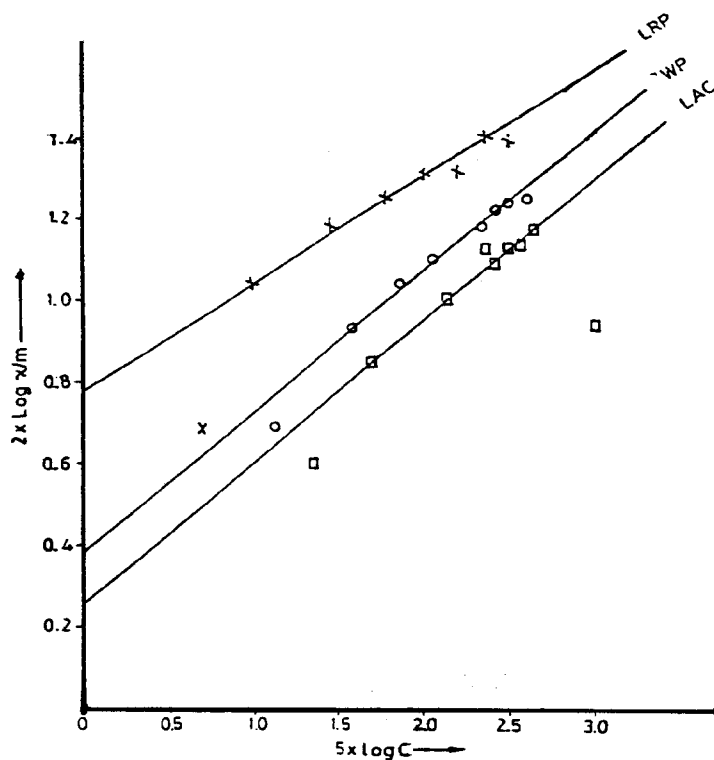


Fig. 6: Freundlich plots for the adsorption of fumaric acid on different activated carbon samples.

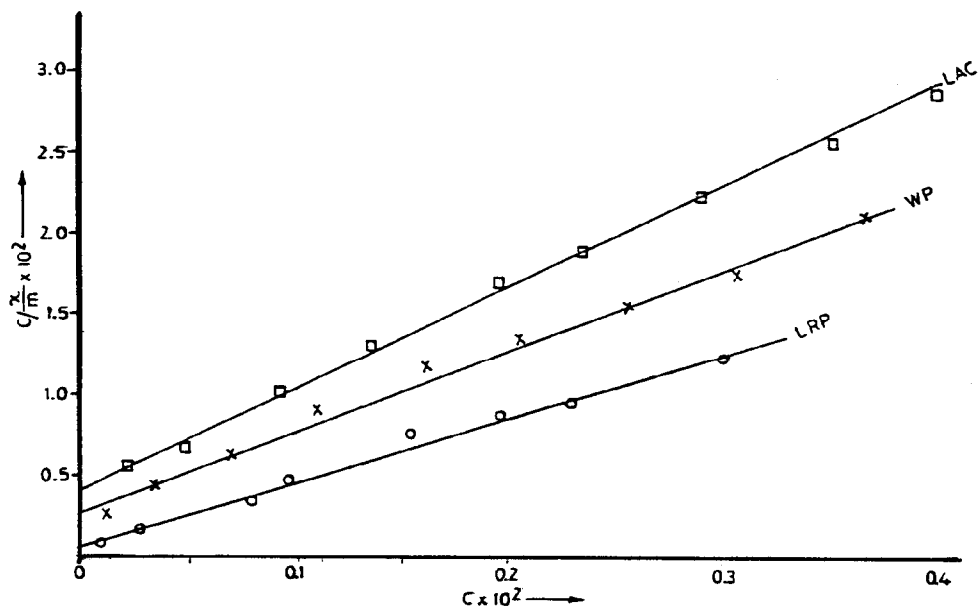


Fig. 7: Langmuir plots for the adsorption of fumaric acid on different activated carbon samples.

It may be concluded from these studies that activated carbons prepared from cellulosic raw materials have been found better towards adsorption of aliphatic organic acids as compared to that prepared from lignitic coal. It has also been inferred that lower ash content, higher iodine no./porosity, surface free of residual gases and lower acidity in a carbon sample are conducive for acid adsorption. Furthermore, the degree of adsorption of a particular acid depends upon the polarity of carboxylic group, length of the side chain and the nature of bonding involved it.

Experimental

The three activated carbon samples used in these studies were prepared from Acacia arabica (A), low ash rice husk (B) and Lakhra coal (C). Their preparation have been described elsewhere [11-13]. The elemental analysis of the sample was carried out on a Perkin Elmer 240 elemental analyzer. The ash content, iodine no. and pH of the samples, A, B and C were determined by standard methods [22]. Prior to use, all of the samples were thoroughly refluxed with boiling distilled water in order to remove water soluble material, dried at 120°C, ground and sieved to yield 200 x 325 mesh size. All of the adsorbates were reagent grade and dissolved in distilled water.

Sorption was studied by adding 0.1 g of the carbon sample in nine clean and well stoppered Erlenmeyer flasks. 90, 80, 70, 60, 50, 40, 30, 20 and 10 ml of 1N acid was pipetted out in each of the flasks and 10, 20 --- 90 ml of distilled water was then added into each of the flasks respectively. The flasks were then shaken on an orbital shaker for one hour. A set of preliminary experiments showed that this time was quite ample for attaining equilibration. The carbons were then filtered out through Whatman No. 42 filter paper. First two ml of filtrate from each flask was rejected. The residual solute/acid concentration in each of the flasks was then determined by titration against standard NaOH solution.

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