

Impact of Surface Functional Groups on The Adsorption of Aliphatic Organic Acids from Aqueous Solutions on Granular Activated Charcoal

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Summary: Adsorption of aliphatic organic acids such as Formic, Acetic, Propionic and n-Butyric acids from aqueous solutions on the surface of granular activated charcoal was studied as a function of stirring time, concentration of adsorbate and evacuation temperature (105°C, 300°C and 800°C). Adsorption equilibrium was found to be established within four hours time in all cases of aliphatic organic acids having concentrations i.e. 0.005M and 0.01 M at temperature of 25°C, which may be due to the uniform distribution of active sites on the surface of adsorbent.

Evacuation temperatures (105°C, 300°C and 800°C) showed a considerable positive effect on the extent of adsorption and it was found that the higher adsorption of the organic acid on the sample evacuated at 800°C may be due to the decomposition of surface oxides and evolution of CO and CO₂ at high evacuation temperature, which make the surface non-polar and thereby increased surface area, which result in greater adsorption of non-polar or weakly polar organic acids, because of high affinity for organic compounds whereas carbon possess surface functional groups having high affinity for water molecules, and thereby decreasing the effective diameter of the pore opening which result in lower adsorption of organic compounds at 105°C. The amount of adsorption of organic acids constantly increases as the homologous series is ascending. Linear form of Freundlich's and Langmuir equations were applied to the adsorption isotherms data and it was found that both the equations obeyed them well.

Introduction

Aliphatic monocarboxylic acids, the adsorbate selected, have found many applications in different industries, like in textile, leather, rubber, pharmaceutical food and other chemical industries [1] because of their reducing properties and action of reactivity. Many elemental determinations such as cobalt, copper, gold, indium, iron, manganese etc can be also carried out by using these organic acids [1].

These aliphatic monocarboxylic acids on one side have provided some suitable products for daily consumption but on the other hand have raised threats to human health, for example in gaseous form they may cause irritation of eye, nose, respiratory tract [2] and in liquid form they cause the acidification of drinking water reservoirs and their greater concentration i.e. (above the permissible limit) may cause many chronic effects like corrosion of mouth, gastro intestinal tract, vomiting, hematemesis.[2] They also disturb the aquatic life and agricultural soil conditions, therefore the removal of these acids from aqueous medium is essential.

Granular activated carbon (GAC) adsorption is one of the most effective techniques for the removal of various pollutants (both organic and inorganic) from polar and non-polar media, through adsorption [3-5]

Activation temperature play an efficient role in controlling the pore size distribution and specific surface area of GAC, because during evacuation, the decomposition of surface oxides and evolution of CO₂ & CO [6] takes place make the surface non-polar and thereby increases the surface area which shows great potential for the adsorption of non-polar or weakly polar organic acids. Whereas carbon possess surface functional groups having high affinity for water molecule and thereby reducing the effective diameter of the pore opening which results in lower adsorption of organic compounds. Earlier investigators have reported the adsorption of aliphatic monocarboxylic acids and other aliphatic organic compounds on GAC and surface modified GAC [7-37]

The purpose of this study is to elucidate batch experimental data on the effect of evacuation

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temperature, concentration of adsorbates and surface functional groups on the adsorption of aliphatic organic acids on GAC.

Results and Discussion

Effect of surface area:

The surface area for three samples (i.e. evacuated at 105°C, 300°C and 800°C) was determined by Snow's iodine adsorption method. The results are given in table 1. The results show that the surface area of 105°C evacuated sample is low and high of the 800°C evacuated sample, which are less than the recommended surface area range, 400 – 1800 m²/gm [1] depending upon their pore size. This lower surface area may be due to the large size of iodine molecules which enter with difficulty into the smaller diameter of micropores and thus reduce the amount of adsorption of iodine. Moreover the low surface area of 105°C evacuated sample may

be due to the presence of surface complexes on the surface of charcoal, such as lactones, phenolic hydroxyl group, carboxylic acid anhydride, cyclic peroxide and chromine [39-41]. These complexes, if present reduce the active sites and thus reduce the amount of adsorption. On the other hand in the sample evacuated at 300°C and 800°C, the surface complexes start to decompose [38] and leave a porous surface, which would adsorb the iodine molecule to a greater extent. The surface area of samples under study are lower than the above mentioned range, therefore more investigation by BET method [38] is required which will give actual surface area of the samples.

Table 1. Measurement of Surface area of GAC evacuated at 105°C, 300°C and 800°C.

S.No	Evacuated charcoal (°C)	Surface area (m ² /gm)
1	105	283.7
2	300	295.8
3	800	298.7

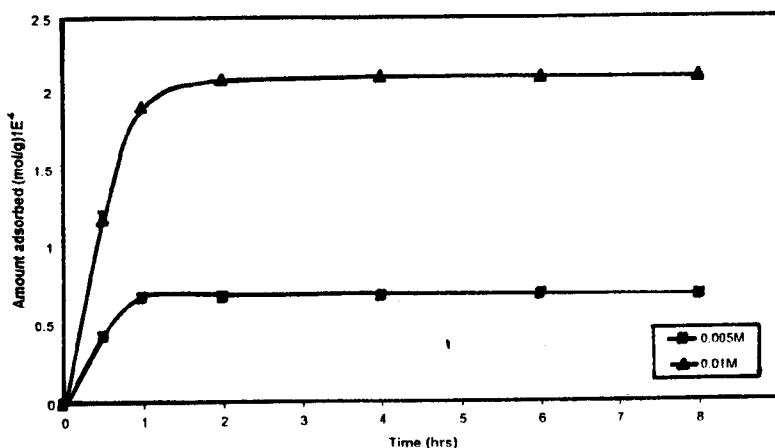


Fig 1.: Adsorption of formic acid (0.005M and 0.01M) on GAC at different durations of time.

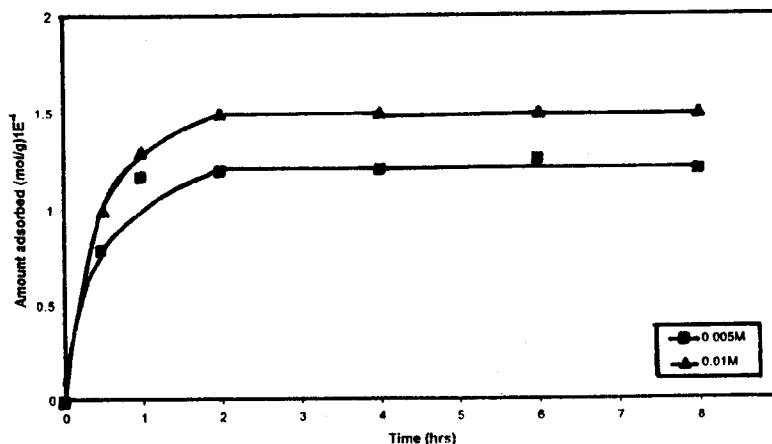


Fig 2.: Adsorption of acetic acid (0.005M and 0.01M) on GAC at different durations of time.

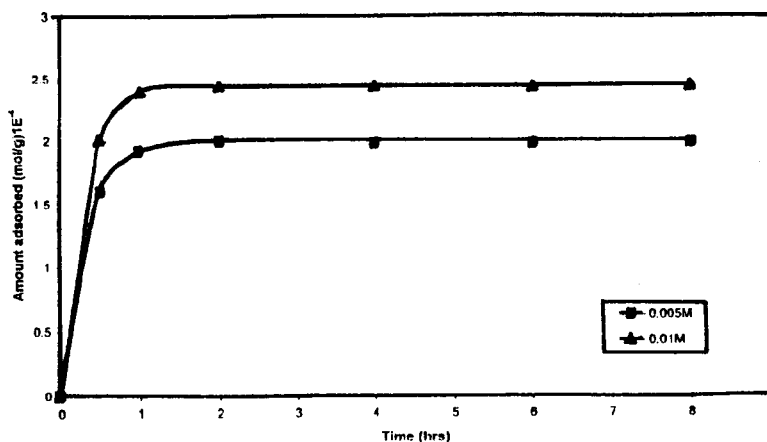


Fig 3.: Adsorption of propionic acid (0.005M and 0.01M) on GAC at different durations of time.

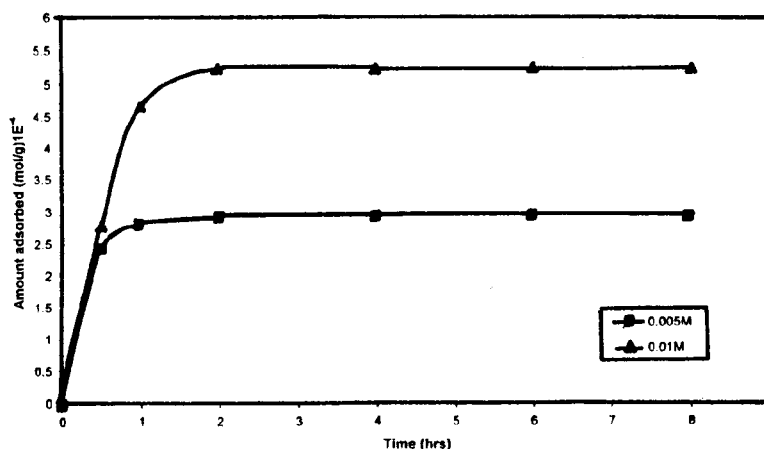


Fig 4.: Adsorption of n-butyric acid (0.005M and 0.01M) on GAC at different durations of time.

Effect of equilibration time:

The effect of equilibrium time for the optimum uptake of aliphatic organic acids i.e. formic, acetic, propionic and n-butyric acid, as can be seen from figures.1-4, shows that equilibrium has been established within 4 hours in all the four cases. This equilibration time indicate that during adsorption process, the adsorbate (carboxylic acids) molecules are removed from the aqueous solution and are diffused into the micropores of charcoal samples while some are adsorbed on the outer surface of the charcoal crystal. So both physical and chemical adsorption mechanism is possible in our case, as has been observed by earlier investigators [43] that is why both solutions (0.005 M and 0.01M)

take longer duration of time for the establishment of equilibrium.

It is evident from figs. 1-4, that the amount of adsorption from 0.01 M carboxylic acids in all cases is more than 0.005 M. This higher removal of adsorbate from concentrated solution may be due to its greater concentration available to the active sites of activated charcoal.

pH of the slurries was noted before and after adsorption. The figures 1-4 show that the pH of all aliphatic organic acids were low before adsorption and after adsorption it was high, therefore it gives an evidence toward the removal of aliphatic organic acids molecules from their respective solutions.

Uptake study at constant temperature (adsorption isotherms):

The uptake study at constant temperature (adsorption isotherms) was conducted for various carboxylic acids such as formic, acetic, propionic and n-butyric acids on activated charcoal, evacuated at three different temperatures i.e., 105°C, 300°C and 800°C. From the figures 5-9 it is quite evident, that the sample evacuated at 105°C shows lower adsorption when compared to 300°C and 800°C evacuated samples in all four cases of the adsorbates studied. The lower adsorption of the adsorbate on charcoal surface in all four cases on 105°C evacuated sample may be due to the presence of surface oxides

on the surface of charcoal [44-46]. These surface complexes (such as lactones, phenolic, hydroxyl group, carboxylic group, quinone type, carboxylic acid anhydride and cyclic peroxides group) [39,40,47,48] reduce the active sites and thus decrease the adsorption of polar compounds⁽⁴⁹⁾ and increase the adsorption of non-polar compounds, as has been observed in all the cases.

The higher adsorption of the organic acids on the sample evacuated at 800°C may be due to the decomposition of the surface oxides and evolution of CO₂ and CO.[6] at high evacuation temperature, which makes the surface non-polar and thereby

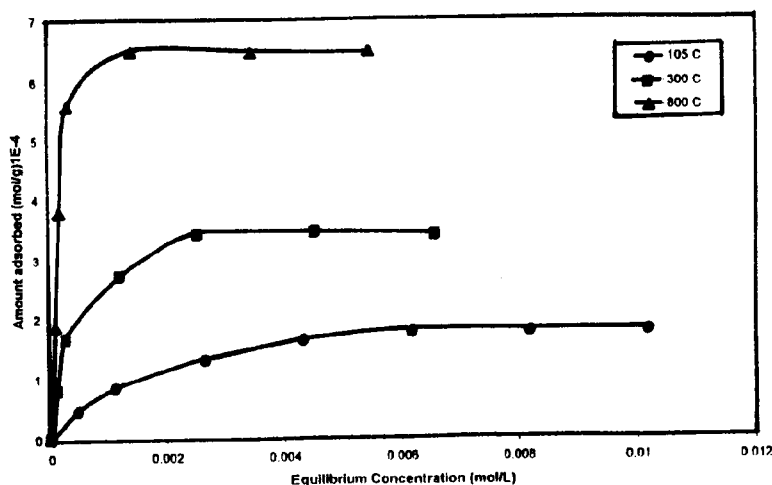


Fig. 5: Uptake study of formic acid on GAC evacuated at different temperature (105°C, 300°C and 800°C).

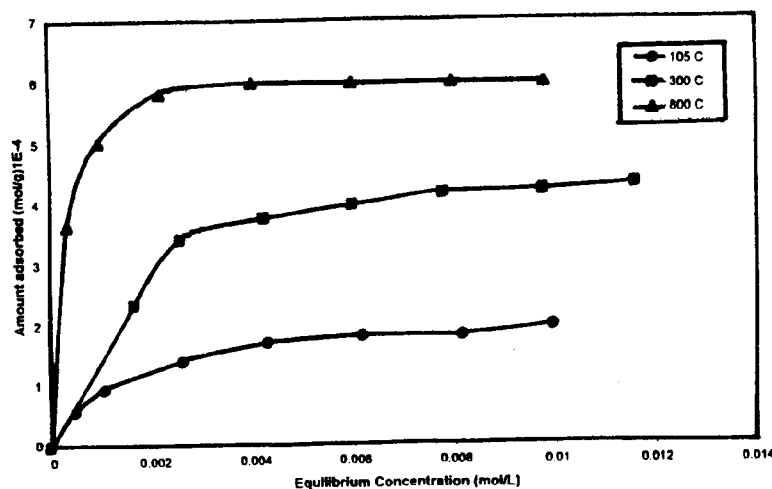


Fig. 6: Uptake study of acetic acid on GAC evacuated at different temperature (105°C, 300°C and 800°C).

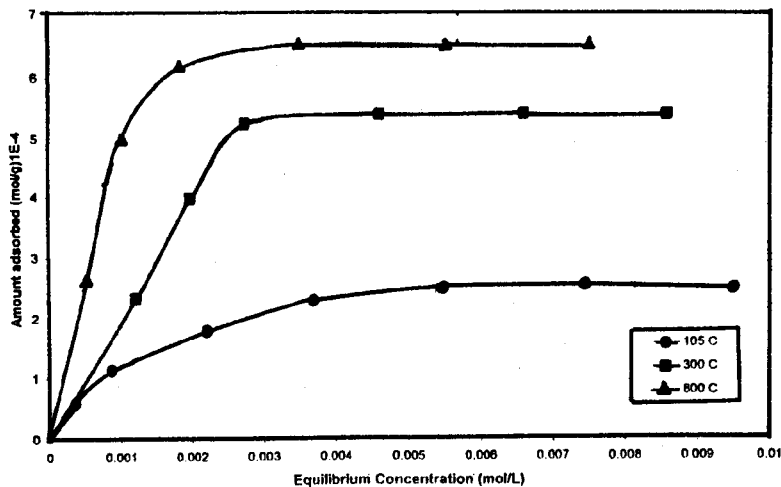


Fig. 7: Uptake study of propionic acid on GAC evacuated at different temperature (105°C, 300°C and 800°C).

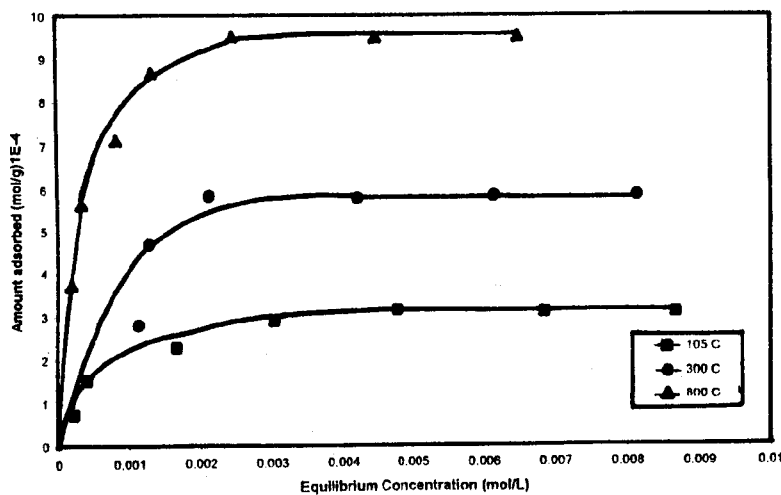


Fig. 8: Uptake study of n-butyric acid on GAC evacuated at different temperature (105°C, 300°C and 800°C).

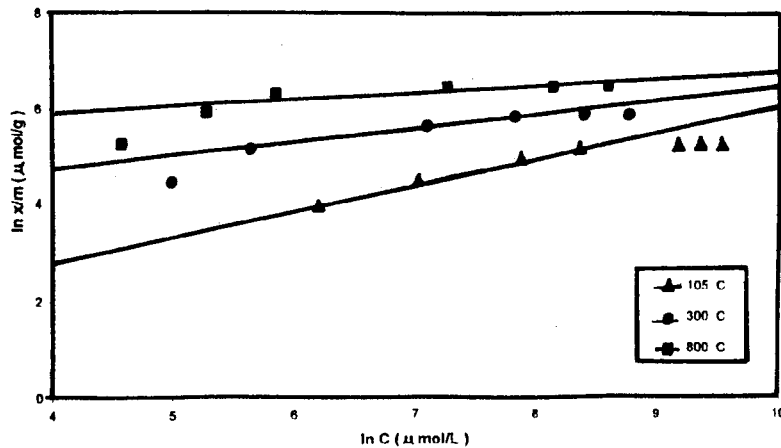


Fig. 9: Freundlich's plots for the adsorption of formic acid on activated charcoal evacuated at different temperature (105°C, 300°C, and 800°C).

increase the surface area, which results in greater adsorption of the non-polar or weakly polar organic acids, because of high affinity for organic compounds, whereas carbon possess surface functional groups having high affinity for water molecule (non-polar) which reduce the effective diameter of the pore opening after adsorption on charcoal, resulting in lower adsorption of organic compounds at 105°C.

The 300°C evacuated sample show intermediate adsorption of organic compounds, which indicates that sample degassed at 300°C carries appreciable amount of surface functional groups which has affinity for water than organic compounds, which results in lower adsorption of organic compounds on this sample as compared to 800°C evacuated sample, but still they show higher adsorption than 105°C evacuated sample, due to the removal of some of the surface functional groups.

In this study it is clearly evident from the figures that the amount of adsorption of organic acid constantly increases as the homologous series is ascended, from formic acid to n-butyric acids which is in conformity with Traube's rule [50]. This trend of increased adsorption of organic acid, with ascending order of homologous series may be explained on the basis of solubility. As we are ascending from formic acid to n-butyric acid, the molecular weight increases and solubility of these acids in water decreases, therefore low energy is needed for the removal of one mole of adsorbate from solvent- solid interface, which results in higher adsorption of carboxylic acid on the surface of charcoal [51] as has been observed in our case. Another point which affects the adsorption of organic acid is the attachment of side chain of carboxylic group to the solid surface of charcoal. Therefore the polarity of carboxylic group increases as the homologous series is descending. As the side chain of carboxylic acid increases the polar effect of the carboxylic group decreases and thus attachment of the less polar molecule to the non-polar surface is easy [52]. So the amount of adsorption increases from formic acid to n-butyric acid. Another possible explanation for high adsorption is that, each molecule of the adsorbate has an adsorption potential which is a measure of the free energy of adsorption released when adsorbate molecules move from solution to the adsorbed state on the surface.

Adsorption can be linked with molecular weight and the molecular structure. Thus higher the molecular weight of a compound, the more strongly it is adsorbed. [53] Similar results have been reported by earlier investigators [35,54]

The equilibrium data for all carboxylic acids of the three different evacuated samples i.e., 105°C, 300°C, and 800°C, have been correlated with the linearized form of Freundlich isotherm. $\ln x/m = \ln k + 1/n \ln c$, and plotted in figures 10-13. The data obey a straight line relationship. The value "n" which is the inverse of the slope was determined and given in table 2-5, shows the variations in adsorption with concentration. These tables also show high adsorption from concentrated solution and low adsorption from dilute solution. This increase is more at higher temperature evacuated sample compared to low temperature evacuated sample (Tables 2-5). The value of adsorption capacity (K) increases regularly from formic acid to n-butyric acid for all evacuated samples i.e., 105°C, 300°C, and 800°C, which is in good agreement with adsorption data.

Table 2: Freundlich's constants for the adsorption of Formic acid on GAC evacuated at 105°C, 300°C and 800°C.

Evacuated Adsorbent (°C)	Slope (1/n)	K (μmol/g)	n
105	0.48	14.15	2.08
300	0.33	81.45	3.03
800	0.1	330	10

Table 3: Freundlich's constants for the adsorption of acetic acid on GAC evacuated at 105°C, 300°C and 800°C.

Evacuated adsorbent (°C)	Slope (1/n)	k (μmol/g)	n
105	0.49	24.53	2.04
300	0.40	148.4	2.50
800	0.16	403.4	6.25

Table 4: Freundlich's constants for the adsorption of Propionic acid on GAC evacuated at 105°C, 300°C and 800°C.

Evacuated adsorbent (°C)	Slope (1/n)	k (μmol/g)	n
105	0.63	29.9	1.59
300	0.36	181.2	2.77
800	0.035	445.8	

Table 5: Freundlich's constants for the adsorption of n-Butyric acid on GAC evacuated at 105°C, 300°C and 800°C.

Evacuated adsorbent (°C)	Slope (1/n)	K (μmol/g)	n
105	0.26	99.48	3.84
300	0.17	221.4	5.88
800	0.25	492.7	4.0

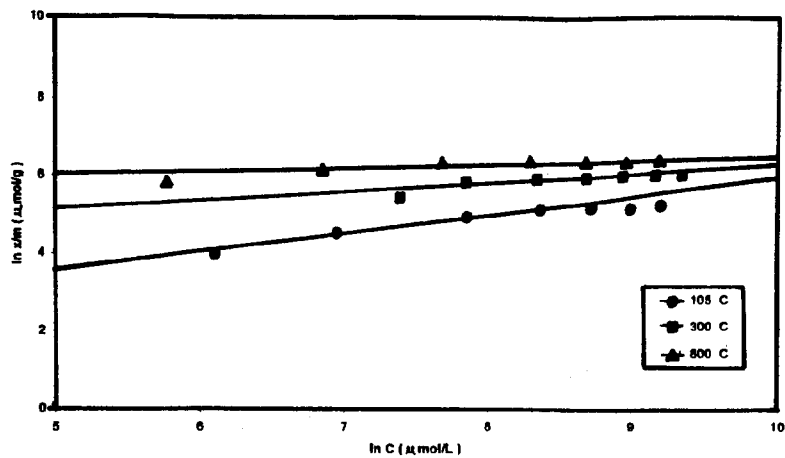


Fig. 10: Freundlich's plots for the adsorption of acetic acid on activated charcoal evacuated at different temperature (105°C, 300°C, and 800°C).

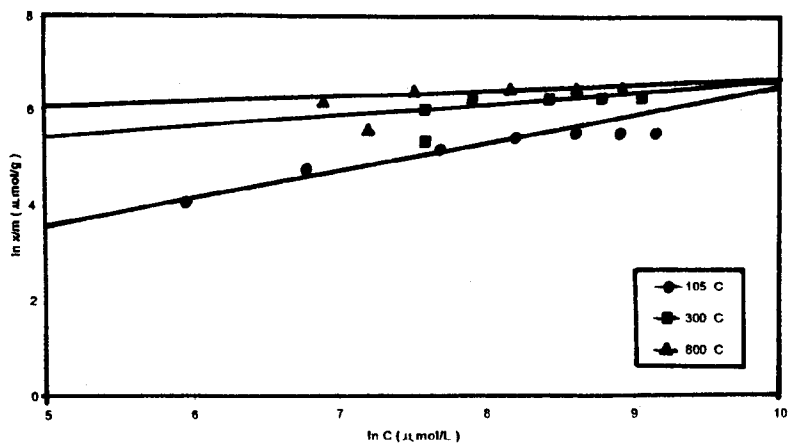


Fig. 11: Freundlich's plots for the adsorption of Propionic acid on activated charcoal evacuated at different temperature (105°C, 300°C, and 800°C).

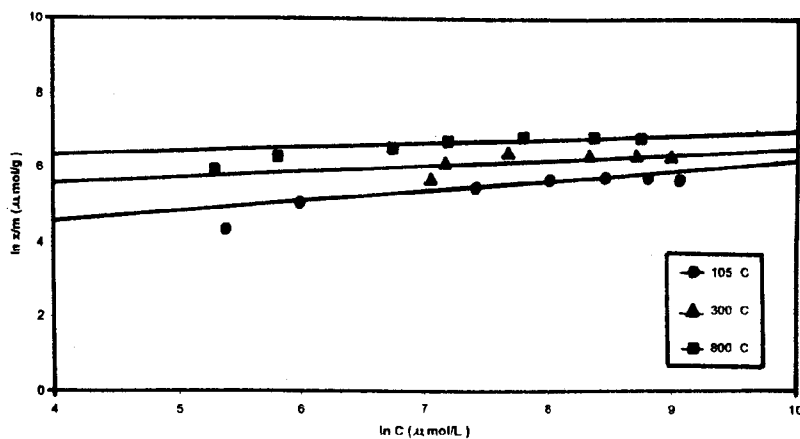


Fig. 12: Freundlich's plots for the adsorption of n-butyric acid on activated charcoal evacuated at different temperature (105°C, 300°C, and 800°C).

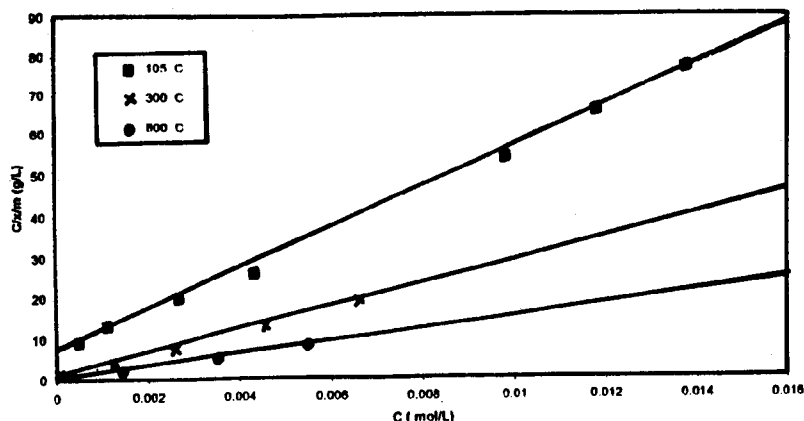


Fig. 13: Langmuir's plots for the adsorption of formic acid on activated charcoal evacuated at different temperature (105°C, 300°C, and 800°C).

The linear form of Langmuir isotherm $c/x = 1/ab + c/b$ was applied to the adsorption isotherms of all adsorbate i.e., Formic, Acetic, Propionic and n-Butyric acids, and plotted as shown in Figs. 14-16. The values of Langmuir constants "b" and "a" were determined from the slope and intercept of the graph and are given in tables 6-9, which shows that "b" is monolayer adsorption capacity and increases from formic acid to n-butyric acid in the homologous series. This increase may be due to the length of the side chain attached to the carboxylic group, which is responsible for the polarity of the acids. From the value of "b" it was concluded that the amount of adsorption increases as temperature of evacuation increases from 105°C, to 800°C, in case of all the acids under study. Therefore this shows a good agreement of Langmuir equation with adsorption isotherm data.

Table 6: Langmuir's constants for the adsorption of formic acid on GAC evacuated at different temperatures (105°C, 300°C and 800°C)

Evacuated adsorbent (°C)	Slope (1/b)	b (μmol/g)	Intercept (1/ab)	a (L/g)
105	5500	180	6.0	925.9
300	2500	400	2.0	1250
800	2000	400	1.0	2500

Table 7: Langmuir's constants for the adsorption of acetic acid on GAC evacuated at different temperatures (105°C, 300°C and 800°C)

Evacuated adsorbent (°C)	Slope (1/b)	b (μmol/g)	Intercept (1/ab)	a (L/g)
105	4250	230	6.5	668.89
300	2000	500	3.8	526.3
800	1500	600	1.0	1666

Table 8: Langmuir's constants for the adsorption of Propionic acid on GAC evacuated at different temperatures (105°C, 300°C and 800°C)

Evacuated adsorbent (°C)	Slope (1/b)	b (μmol/g)	Intercept (1/ab)	a (L/g)
105	3250	300	5.0	666.6
300	1500	660	1.2	1262.6
800	1100	910	1.0	1098.9

Table 9: Langmuir's constants for the adsorption of n-butyric acid on GAC evacuated at different temperatures (105°C, 300°C and 800°C)

Evacuated adsorbent (°C)	Slope (1/b)	b (μmol/g)	Intercept (1/ab)	a (L/g)
105	2750	360	3.0	925.9
300	1500	660	1.0	1515.1
800	900	1000	0.5	2000.0

Nomenclature:

GAC = Granular Activated Charcoal.

L = Liter.

g = gram

mol = moles

μ = micro.

ln = natural log

Experimental

Sample selection, reagents and solutions:

Commercial grade charcoal in granular form was selected as an adsorbent for the present study.

The sample was leached with 0.1 N HNO₃ and 0.1 N HCl (1:1) for removing inorganic

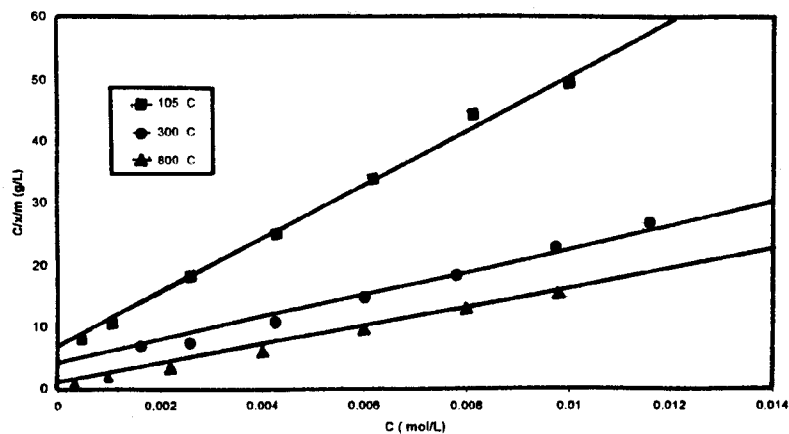


Fig. 14: Langmuir's plots for the adsorption of acetic acid on activated charcoal evacuated at different temperature (105°C, 300°C, and 800°C).

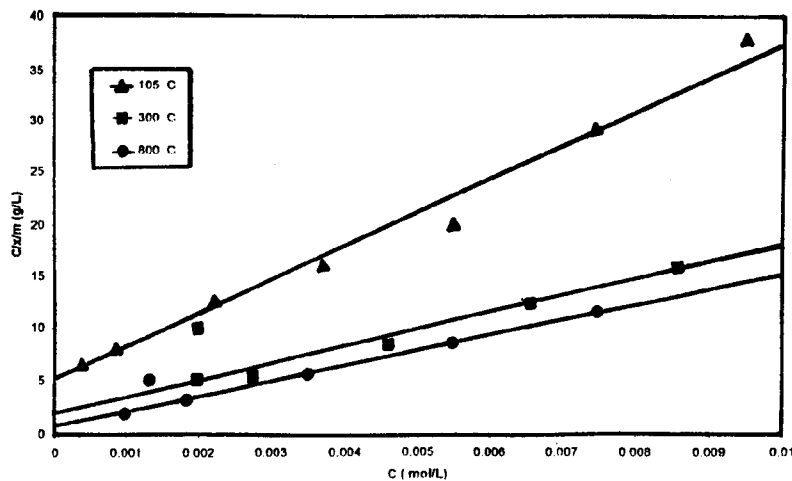


Fig. 15: Langmuir's plots for the adsorption of Propionic acid on activated charcoal evacuated at different temperature (105°C, 300°C, and 800°C).

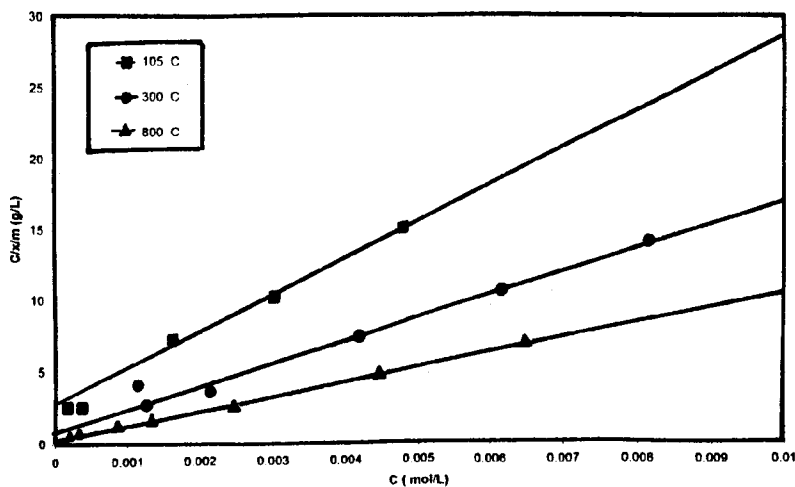


Fig. 16: Langmuir's plots for the adsorption of n-butyric acid on activated charcoal evacuated at different temperature (105°C, 300°C, and 800°C).

contents. The slurry was allowed to stand for 24 hours, at room temperature with infrequent aging. Filtered and washed the sample with distilled water until it shows no acidity. Dried the resulted sample in air dried oven (at 105°C), cooled and stored for extraction.

The leached sample was extracted in sohxlet apparatus (for the removal of organic compounds) using cyclohexane as a solvent for 24 hours. After extraction the dried sample was subjected to evacuation. Some portion of the extracted sample was evacuated in vacuum oven (model precision 919 USA) for 24 hours at 105°C. Cooled the sample in vacuum oven and was then stored.

The vacuum dried adsorbent was transferred to a silica (SiO₂) tube and evacuated in the tube furnace (model, Cat, No;FS. 215 Gallenkamp England) at elevated temperature (300°C and 800°C) separately for 24 hours. A 1/2 horse power vacuum pump was used for the evacuation (degassing). Cooled the sample in the furnace and stored in a clean dry bottle and sealed under nitrogen atmosphere.

Measurement of surface area of granular activated charcoal:

The surface area of granular activated charcoal was determined by C.W. Snow's iodine adsorption method [42].

Procedure:

Measured one gram of each GAC sample (i.e., evacuated at 105°C, 300°C, 800°C) and placed separately in conical flask with 5 ml of Iodine solution, capped the flasks with rubber stopper. The mixture was shaken occasionally for two hours. After 2 hours, added 45ml of distilled water and left for one hour. Titrated 20 ml clear supernatant solution with 0.0394N Na₂S₂O₃.5H₂O solution. The surface area was determined by using the formula i.e. 12.5 × (24-V). The same experiment was repeated three times.

Whereas

V = volume of Na₂S₂O₃.5H₂O used.

Time study for optimum uptake:

Time study for all samples evacuated at 105°C, 300°C, and 800°C was conducted by taking 0.5gm of GAC sample and 50cm³ of adsorbate (Formic, Acetic, Propionic and n-Butyric acids) of 0.005M and 0.01M in conical flask separately and stoppered tightly. Stirred the reaction mixture for different periods (1/2, 1, 2, 4, 6 and 8 hours) using magnetic stirrers. The experiment was conducted in a thermostatically controlled bath at 25°C. pH of the slurry was noted before and after adsorption using pH meter. Filtered the slurry (Wattman pore size 11.6cm), discarding the first 5ml of the filtrate. The amount of acid remaining was determined through titration against standard NaOH (0.0056M & 0.011M) solutions. The amount adsorbed (moles/gm) was then calculated using the following formula.

$$\text{Amount adsorbed (moles/gm)} = \frac{C_0 - C_1 \times V}{W}$$

Whereas,

C₀ = Initial concentration (moles/L)

C₁ = Equilibrium concentration (moles/L)

V = Volume of adsorbate (L)

W = Amount of Adsorbent (g)

The same formula was used for all adsorbate studies.

It was observed through a series of experiments that the time of 4 hours was sufficient to attain equilibrium. Similar procedure was followed for all carboxylic acids.

Uptake study at constant temperature:

Batch experiments were carried out in thermo stated beakers (25°C). 0.5gm of vacuum dried (105°C, 300°C and 800°C) evacuated samples with 50cm³ of aqueous solution of carboxylic acids of different concentration i.e. Formic acid (0.001M – 0.012M), Acetic acid (0.001M – 0.016M), Propionic acid (0.001M – 0.014M), n-Butyric acid (0.001M – 0.016M) in conical flasks and stirred at a constant

temperature of 25°C on magnetic stirrers for four hours. Filtered the slurry through filter paper. The remaining amount of acids was determined through titration, against standard NaOH (0.002M – 0.0095M). The amount adsorbed (moles/gm) was calculated, using the above mentioned formula.

Conclusion

The following most vital conclusion was drawn from the study.

After evacuating the Charcoal at high temperature (800°C) the efficiency of Granular Activated Charcoal for aliphatic organic acids adsorption was enhanced two folds compared to other samples evacuated at lower temperature. Therefore the organic acids can be effectively removed from aqueous system after evacuating the sample at high temperature. The amount of adsorption of organic acid constantly increases as the homologous series is ascends, from formic acid to n-butyric acid which is in conformity with Traube rule. Further the optimum equilibrium for all aliphatic organic acids was also found to be achieved within four hours times and the linear form of Freundlich's and Langmuir's isotherms were applied to the isotherms data and found to obey it well.

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