

Equilibrium and Dynamic Adsorption of Methylene Blue from Aqueous Solutions by Surface Modified Activated Carbons

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Abstract

The equilibrium and dynamic adsorption of methylene blue from aqueous solutions by activated carbons have been studied. The equilibrium studies have been carried out on two samples of activated carbon fibres and two samples of granulated activated carbons. These activated carbons have different BET surface areas and are associated with varying amounts of carbon oxygen surface groups. The amounts of these surface groups was enhanced by oxidation with HNO₃ and O₂ gas at 350 °C and decreased by degassing at increasing temperatures of 400°, 650° and 950 °C. The adsorption increases on oxidation of the carbon surface and decreases on degassing. The increase in adsorption has been attributed to the formation of acidic carbon-oxygen surface groups and the decrease in adsorption on degassing to their elimination. The dynamic adsorption studies have been carried out on the two granulated activated carbons using two 50 mm diameter glass columns at a feed concentration of 300 mg/L and at different hydraulic loading rates (HLR) and bed heights. The minimum achievable concentrations are comparatively lower while the adsorption capacities are higher for GAC-S under the same operating conditions. The adsorption capacity of a carbon increases with increase in HLR but the rate of increase decreases at higher HLR values.

Keywords : Adsorption, Surface modified activated carbons, Oxidation

1. Introduction

Waste water from dye, textile and paper industries is highly coloured due to the presence of residual dyes. These dyes cause micro toxicity to aquatic life and slow down self purification of streams and lakes by reducing light penetration. The conventional methods such as coagulation and flocculation used for the removal of dyes from water introduce metallic impurities and produce a large amount of sludge which requires further disposal. The sludge free treatments are, therefore, gaining importance. Activated carbon adsorption is one such method which has a great potential for the removal of dyes from waste water. Consequently, a considerable amount of research work is being carried out in this direction.

Graham [1] and Puri [2] studied the adsorption of methylene blue, a cationic dye and two anionic dyes on a graphitised carbon black graphon and on a number of activated carbons. These workers observed that while the adsorption on graphon was related to its BET surface area, it differed appreciably for the activated carbons. This was attributed to the presence of carbon-oxygen groups on the surface of activated carbons.

Sastri [3, 4] and Dai and coworkers [5-7], while studying the influence of solution pH on the adsorption of methylene blue and several anionic dyes on activated carbons observed

that the removal of the dye was a function of the pH and involved ion-exchange mechanism. Al Degs *et al.* [8, 9] investigated the adsorption of three highly reactive dyes used in textile industry and found that the adsorption could not be related to surface area or the surface oxygen groups while Chen and coworkers [10, 11] observed that in the case of methylene blue on Sisal based activated carbon fibres (ACF), the amounts adsorbed and adsorption rates were related to surface properties of the carbons such as surface area, pore size and the concentration of surface functional groups. Tamai [12] also studied the adsorption of methylene blue on ACFs and observed that the adsorption was much larger on the mesoporous ACF than that on the highly microporous ACF. Sasaki *et al.* [13], however, observed that the adsorption depended on the pore size and the electrostatic interaction between the dye molecules and the carbon surface.

Honas and Bakir [14] and Khalil and Girgis [15], found that the adsorption of methylene blue on activated carbons from aqueous solutions followed Langmuir isotherm equation and that the accessible surface area decreased with increase in the degree of activation of the carbon. This was attributed to the development of fine microporosity which was partly inaccessible to methylene blue molecules. Viraghavan and Mikhial [16] observed that the adsorption of a basic and an acidic dye on peat also followed Langmuir adsorption equation.

The removal of the basic dye was better, being 99% compared with 48% of the acidic dye. Lin [17, 18], however found that in the case of a disperse dye the multilayer BET isotherm showed better fit than the monolayer Langmuir model.

Nandi and Walker [19] investigated the adsorption of two basic and two acidic dyes on coals, charcoals and activated carbons and observed that the fraction of the BET surface area covered by the dye depended on the nature of the carbon surface. Dusan *et al.* [20] studied the adsorption of several dyes from waste water on peat and charcoal using a dynamic system. The breakthrough curves showed that while peat columns were able to remove sufficient amounts of basic red dye, the charcoal showed smaller adsorption values. Guzel [21] studied the effect of carbon surface acidity on the adsorption of methylene blue and metanil yellow by activated carbons. The adsorption of methylene blue was much larger compared to that of metanil yellow. It has been suggested that the methylene blue molecules (a cationic dye) are attracted by the acidic carbon surface while those of metanil yellow (an anionic dye) are repelled.

The present studies on the adsorption of methylene blue have been carried out from two points of view: their removal from waste water and the characterisation of the activated carbon surfaces for their surface area, microporous character and their polarity. The paper has been divided into two parts: the equilibrium adsorption and the dynamic adsorption. The former studies determine the parameters involved in the adsorption of dyes and the mechanism of adsorption, while the latter studies examine the effect of loading rate and bed height on the dynamic adsorption characteristics for the removal of methylene blue by activated carbons.

2. Experimental

The activated carbons used in these investigations are two samples of granulated activated carbons GAC-E and GAC-S and two samples of activated carbon fibres ACF-307 and ACF-310. The granulated activated carbons are commercial grade peat based extruded carbons activated with steam. These samples were supplied by Norit N.V. Netherlands. The fibrous activated carbons are pitch based materials supplied by Ashland Petroleum Company, Kentucky, U.S.A.

The as-received activated carbons were oxidized with nitric acid and gaseous oxygen at 350 °C [22, 23] to increase the amounts of carbon-oxygen surface groups. The oxidized carbon samples were degassed at 400°, 650°, and 950 °C to gradually eliminate varying amounts of these surface oxygen groups. The amounts of these surface groups were determined by evacuating the as-received, oxidized and degassed carbons at gradually increasing temperatures upto 950 °C and analyzing the gases evolved. The details of the degassing and evacuating procedures have been published

elsewhere [24-26]. However, brief descriptions are given below.

2.1. Degassing of the carbon

About 5 g. of the oxidized carbon sample was spread in thin layers about 5 inches long in a platinum boat which was placed in a tube furnace. The tube furnace was connected to a Hyvac Cenco vacuum pump capable of giving vacuum of the order of 3×10^{-2} mmHg. The temperature of the furnace was allowed to rise gradually to the degassing temperature and kept at that temperature until the evolution of gases ceases almost completely. After degassing at the required temperature, the carbon sample was allowed to cool in vacuum to room temperature to avoid reformation of the carbon-oxygen surface groups and was then transferred to stoppered bottles flushed with nitrogen. These sample are referred to as degassed samples in the text.

2.2. Determination of Carbon-Oxygen Surface Groups

The carbon-oxygen groups present on the as-received, oxidized and degassed carbon samples were determined by evacuating one gram portion of each sample at gradually increasing temperatures upto 950 °C. The carbon sample, dried at 120 °C and contained in a platinum boat is placed in a resistance tube furnace. The temperature of the furnace was allowed to rise gradually in steps of 50 °C to ensure complete elimination of the gas at the previous temperature. The carbon-oxygen surface groups decompose into CO₂, CO and water vapour which are measured using usual analytical procedures. The details of the procedures are already published [27, 28].

2.3. Equilibrium Adsorption of Methylene Blue

200 mg portions of the carbon sample were weighed in borosil glass stoppered bottles and mixed with 20 ml solutions of methylene blue of different concentrations. The suspensions were placed in an air thermostat for 24 hrs with vigorous shaking. A time of 24 hrs. was found sufficient for the attainment of equilibrium. The amount adsorbed was determined using a spectrophotometer at a wavelength of 620 nm.

2.4. Dynamic Adsorption of Methylene Blue

The dynamic adsorption studies of methylene blue from aqueous solutions were carried out on the two granulated activated carbons GAC-E, and GAC-S. The experimental set up consists of two glass columns of 50 mm diameter and 750 mm length connected in series. The activated carbon under study is saturated with water overnight to remove entrapped air and was packed in the glass column prefilled with water and supported on perforated plates. Methylene blue solution of known concentration was prepared and pumped into an overhead tank with overflow for maintaining a constant head. This ensures a constant influent flow rate

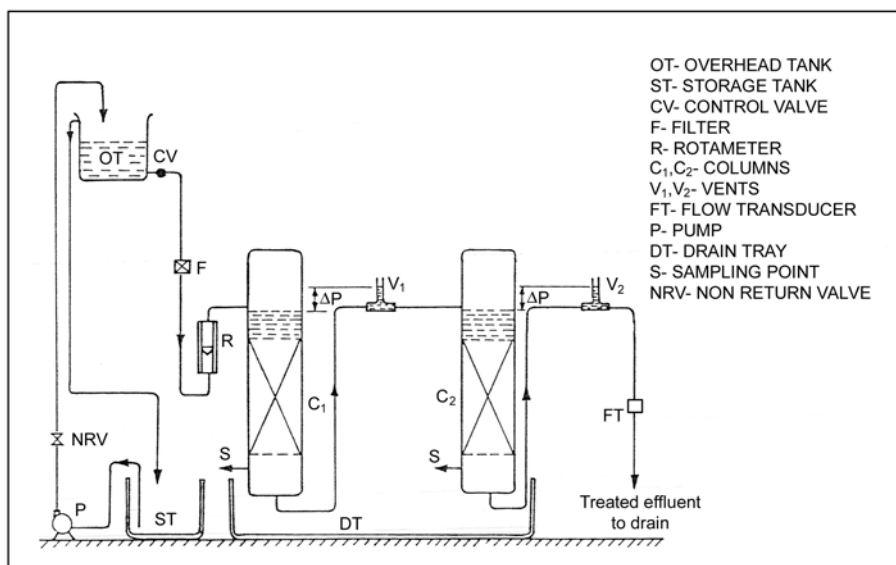


Fig. 1. Experimental set up for column studies.

throughout the experiment because the solution from the overhead tank is gravity fed to the first column. Fig. 1 shows the schematic of the experimental set up. The outlet from the first column (column 1) forms the feed to the second column (column 2). The outlet from the second column leads to a drain tank. An online filter to remove suspended impurities, a control valve to regulate the flow and a rotameter to monitor the flow rate are installed in the feed tank. A pressure equalizing arrangement is used to maintain the solution level within the column. The effluent from both the columns is collected at regular intervals and analysed.

3. Results and Discussion

3.1. Equilibrium Adsorption Studies

3.1.1. Influence of pH on the Adsorption

It has been observed by several workers [4, 5, 29] that the pH of the carbon sample is an important factor that determines the adsorption of cationic or anionic dyes from aqueous solutions. Consequently the influence of pH on the adsorption of methylene blue was studied and is presented in Fig. 2. The pH of the solution was controlled by the addition of HCl or NaOH. The uptake of the dye at pH below 3 is small in both the granulated as well as fibrous activated carbons. However, when the pH of the solution is enhanced, a maximum in adsorption is obtained at pH of 4. At higher pH values the uptake of the dye is found to decrease. This is due to the fact that a change in pH of the solution results in a change in the carbon surface charge being different at different pH values [30]. A sudden increase in the adsorption of methylene blue in the pH range 2 and 4 indicates that the

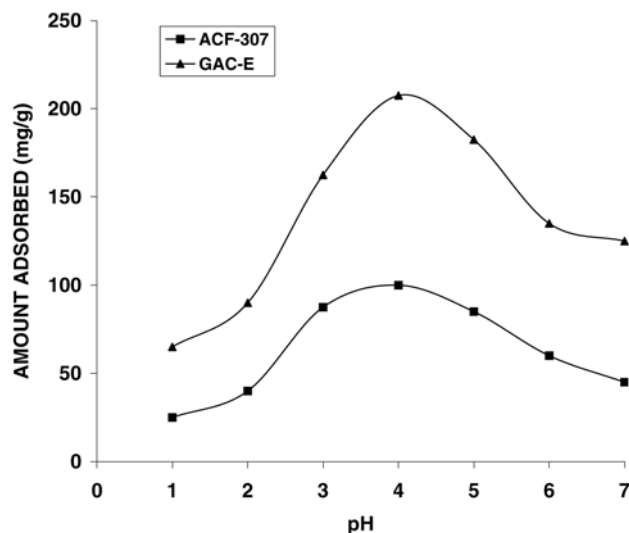


Fig. 2. Effect of solution pH on the adsorption of Methylene Blue.

zero point charge (ZPC) of the carbon surface lies between these pH values. Kim and coworkers [31] in their studies on the electrosorption of Co(II) ions on modified activated carbon fibres observed a value of 3.1 as the ZPC for the carbon. At pH values lower than the ZPC there is excessive protonation of the carbon surface which gives it a positive charge. This enhances the electrostatic repulsive interactions between the carbon surface and the positively charged methylene blue cations resulting in lower adsorption. As the pH of the solution is increased beyond ZPC the carbon surface becomes negatively charged. This results in electrostatic attractive interactions between the carbon surface and the dye cations thus increasing the adsorption. At higher pH

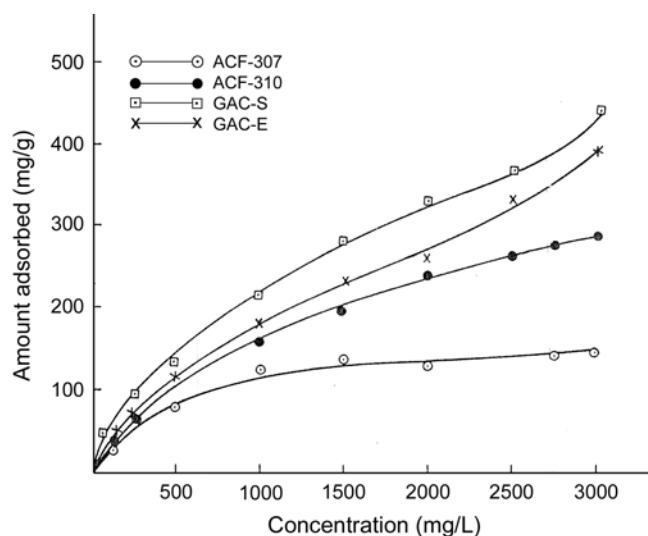


Fig. 3. Adsorption isotherms of Methylene Blue on as received activated carbons.

values, the preponderance of OH^- ions in the solution generates a competition between the carbon surface and the solution OH^- ions for the methylene blue cations which results in a decrease in the adsorption.

3.1.2. Adsorption Isotherms

The adsorption isotherms of methylene blue from aqueous solutions on the four samples of activated carbons in the concentration range 20~3000 mg/L are presented in Fig. 3. All equilibrium studies have been carried out at pH-4. The isotherms are generally Langmuir in shape in case of the activated carbon fibres (ACF-307 and ACF-310) but show a larger increase in adsorption at higher concentrations in the case of granulated activated carbons (GAC-E and GAC-S). The adsorption is larger in the case of granulated carbons compared with the fibrous carbons. The maximum amount of adsorption is about 450 mg/g for GAC-S and only 150 mg/g for ACF-307. This large difference in adsorption cannot be attributed to differences in BET surface area alone (cf. Table 1) since GAC-E which has about the same surface area (1190 m^2/g) as ACF-310 (1184 m^2/g), adsorbs appreciably larger amounts of methylene blue. This, however, may be attributed to the differences in the microporous character and the chemical nature of the carbon surface. As the

Table 2. Surface areas and Gases evolved on degassing different as-received activated carbons at 950 °C

Sample Identification	Oxygen evolved as (g/100 g)			
	CO_2	CO	H_2O	Total
ACF-307	1.00	5.30	1.30	7.60
ACF-310	1.90	4.20	1.40	7.50
GAC-S	2.10	1.05	1.24	4.39
GAC-E	2.13	1.66	1.33	5.12

granulated and fibrous activated carbons have been prepared using different source raw materials and using different preparation procedures. The amount of oxygen evolved as CO_2 and CO, as determined by evacuation at 950 °C is shown in Table 2. It is apparent that the carbons are associated with varying amounts of different carbon-oxygen surface groups.

The linear Langmuir plots for adsorption on the four samples are shown in Fig. 4. The BET surface area and the surface areas occupied by methylene blue molecules calculated from these linear Langmuir plots taking 1.19 nm^2 as the molecular area of methylene blue molecules are given in Table 1. It is seen that only about 50~60% of the BET surface area is available for the adsorption of methylene blue

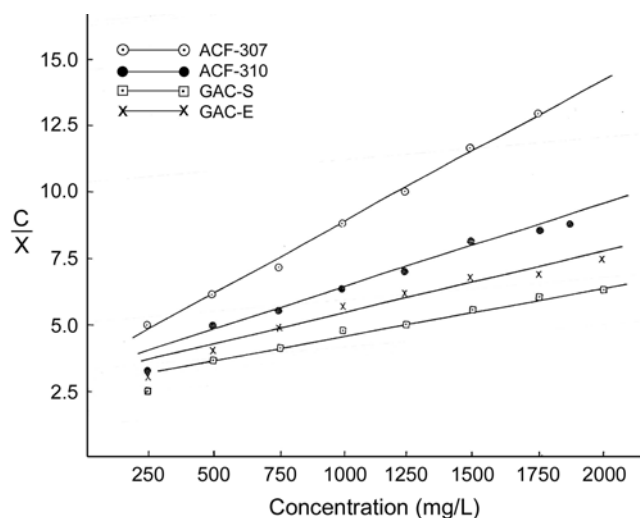


Fig. 4. Linear Langmuir plots for as received activated carbons.

Table 1. Fraction of BET surface are occupied by methylene blue for different activated carbons

Sample Identification	BET (N ₂) Surface area (m^2/g)	Monolayer capacity X_m (from linear Langmuir plots) (mg/g)	Surface area covered by Methylene Blue (m^2/g)	% BET Area Covered
ACF-307	910	200	451	49.5
ACF-310	1184	300	676	57.1
GAC-E	1190	454	1123	94.3
GAC-S	1256	556	1253	99.7

in the case of activated carbon fibres while almost the entire BET surface area is available for adsorption in the case of granulated activated carbons. This indicates that about 50~60% of the BET surface area in the case of activated carbon fibres is present in the form of extremely fine micropores which are not accessible to the larger methylene blue molecules. On the other hand, almost all the pores in granulated carbons have larger pore diameter and are available for the adsorption of methylene blue. This, however, may not be completely true since the presence of surface carbon-oxygen groups in these carbons may also be influencing the adsorption of methylene blue and a part of this adsorption may take place at the sites provided by these surface groups.

3.1.3. Influence of carbon-oxygen surface groups on the adsorption

It is well known that associated oxygen on the carbon surface is present in the form of two types of surface groups (cf. Table 2): one which are evolved as CO_2 on evacuation in the temperature range $350^\circ\text{--}750^\circ\text{C}$. These surface groups are acidic in character and are postulated as carboxyls and lactones [22-28, 32, 33]. These acidic oxygen groups produce negatively charged sites on the carbon surface. The other oxygen groups are evolved as CO on evacuation in the temperature range $500\text{--}950^\circ\text{C}$. These groups have been postulated to be quinones which are neutral in character and tend to render the carbon surface hydrophobic. Further more, the amounts of these both types of surface groups can be enhanced by oxidation of the carbon surface and decreased on degassing the oxidized carbons.

In order, to examine the influence of these surface groups, on the adsorption of methylene blue, two of the activated carbons namely ACF-307 and GAC-E were oxidized with

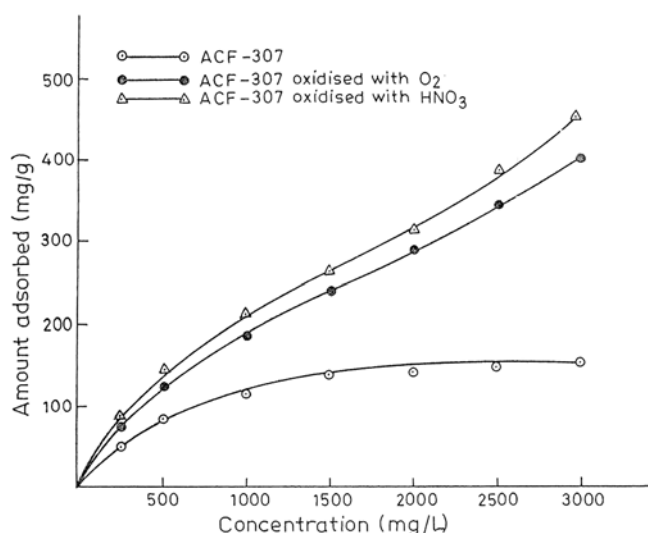


Fig. 5. Adsorption isotherms of Methylene Blue on ACF-307 before and after oxidation.

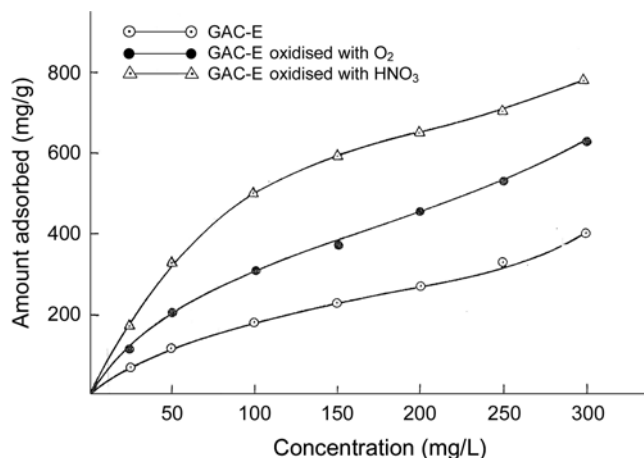


Fig. 6. Adsorption isotherms of Methylene Blue on GAC-E before and after oxidation.

nitric acid in the liquid phase and with oxygen gas at 350°C . The adsorption isotherms on the oxidized samples are presented in Fig. 5 for ACF-307 and in Fig. 6 for GAC-E. It is evident that the oxidation of both ACF-307 and GAC-E with nitric acid or with oxygen gas results in an increase in the adsorption of methylene blue. The increase in adsorption in both the carbons is larger when the oxidation is carried out with nitric acid. This increase in adsorption and the larger adsorption on oxidation with nitric acid can be attributed to the formation of larger amounts of carbon-oxygen groups. As nitric acid is a stronger oxidative treatment, it can give rise to the formation of larger amounts of carbon-oxygen surface groups. This is apparent from the amounts of oxygen evolved as CO_2 and CO from the oxidized samples as shown in Table 3.

In order to examine whether it is the total amount of the associated oxygen which influences the adsorption of methylene blue or a part thereof, the oxidized ACF-307 and GAC-E were degassed at gradually increasing temperatures of 400° , 650° and 950°C , and the adsorption isotherms determined again. The adsorption isotherms on the degassed

Table 3. Gases evolved on degassing different as-received and oxidized activated carbons at 950°C

Sample Identification	Oxygen evolved as (%)			
	CO_2	CO	H_2O	Total
ACF-307				
As-received	1.00	5.30	1.30	7.60
HNO_3 -oxidised	12.90	7.47	2.40	22.77
O_2 -oxidised	3.11	7.71	1.20	12.02
GAC-E				
As-received	2.13	1.66	1.33	5.12
HNO_3 -oxidised	12.40	6.20	1.92	20.52
O_2 -oxidised	3.17	5.97	1.26	10.40

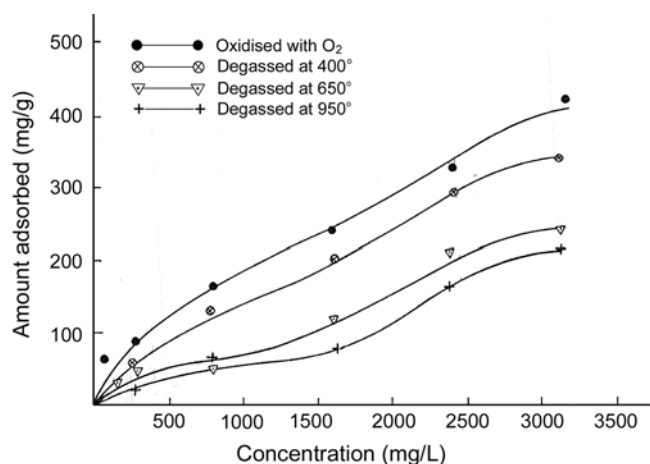


Fig. 7. Adsorption isotherms of Methylene Blue on ACF-307 oxidised with nitric acid before and after degassing at different temperatures.

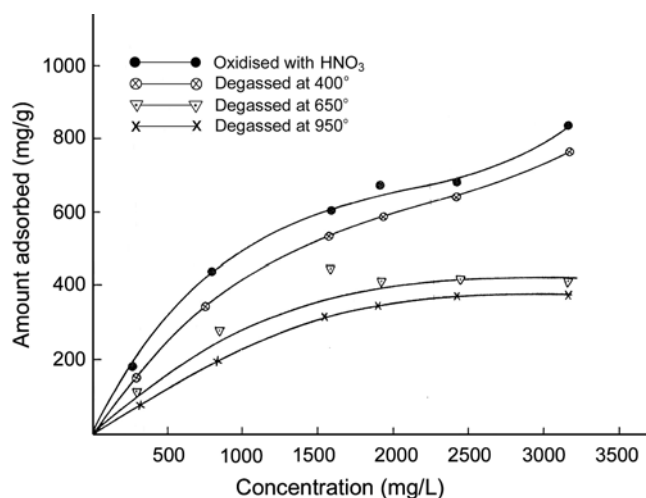


Fig. 9. Adsorption isotherms of Methylene Blue on GAC-E oxidized with nitric acid before and after degassing at different temperature.

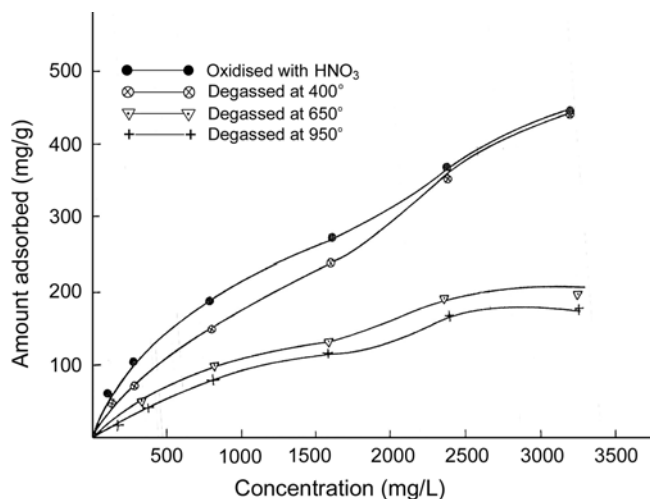


Fig. 8. Adsorption isotherms of Methylene Blue on ACF-307 oxidised with oxygen gas before and after degassing at different temperatures.

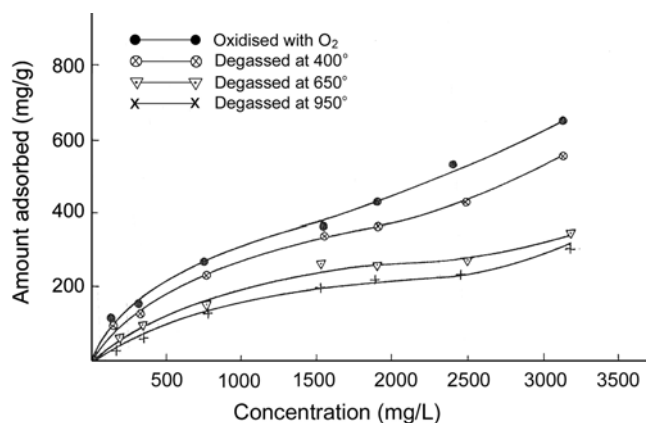


Fig. 10. Adsorption isotherms of Methylene Blue on GAC-E oxidized with oxygen gas before and after degassing at different temperatures.

samples are presented in Fig. 7 and 8 for the oxidized ACF-307 and in Fig. 9 and 10 for the oxidized GAC-E. It is interesting to note that the adsorption decreases continuously as the temperature of degassing is enhanced in all the carbons. Furthermore, there is a definite pattern in the decrease in adsorption with increase in the temperature of degassing. When the oxidized carbons are degassed at 400 °C, there is only a small decrease in adsorption but when the oxidized carbons are degassed at 650 °C, the adsorption shows a considerable decrease. A further decrease in adsorption, although very small is observed on increasing the degassing temperature to 950 °C in all the carbon samples.

The disposition of the acidic (CO_2 -evolving) and non-acidic (CO -evolving) surface groups for the degassed carbon samples is recorded in Table 4 for ACF-307 and in Table 5

Table 4. Gases evolved on degassing different Oxidised and Degassed ACF-307 carbon samples at 950 °C

Sample Identification	Oxygen evolved as (g/100 g)			
	CO_2	CO	H_2O	Total
ACF-307				
HNO ₃ oxidised and then degassed at (°C)	12.90	7.47	2.40	22.77
400	10.85	7.35	0.85	19.05
650	2.15	6.86	0.12	9.13
950	–	Traces	–	–
Oxygen oxidised and then degassed at (°C)	3.11	7.71	1.20	12.02
400	2.95	7.65	0.82	11.42
650	0.42	7.25	0.21	7.88
950	–	Traces	–	–

Table 5. Gases evolved on degassing different oxidised and degassed GAC-E carbon samples at 950 °C

Sample Identification	Oxygen evolved as (g/100 g)			
	CO ₂	CO	H ₂ O	Total
GAC-E				
HNO ₃ oxidised	12.40	6.20	1.92	20.52
oxidised and then degassed at (°C)				
400	10.85	5.92	1.02	17.79
650	2.15	6.86	0.12	9.13
950	Traces	Traces	Traces	Traces
Oxygen oxidised	3.17	5.97	1.26	10.40
oxidised and then degassed at (°C)				
400	2.86	5.56	1.00	9.42
650	0.58	4.78	0.62	5.98
950	–	Traces	–	–

for GAC-E. It is evident that degassing at 400 °C results only in a small decrease in the amount of acidic surface groups (upto 15%) while degassing at 650 °C causes elimination of about 80~90% of the acidic surface groups although these degassed samples retain most of their non-acidic surface groups. When the oxidized carbon samples are degassed at 950 °C, the carbon-oxygen surface groups are removed almost completely.

It is apparent, therefore, that the adsorption of methylene blue from aqueous solutions by activated carbons is influenced largely by the presence of acidic surface groups, the non-acidic surface groups having little or no effect.

3.1.4. Mechanism of Adsorption

When an oxidized activated carbon is placed in an aqueous solution, the acidic surface groups present on the carbon surface undergo ionization producing H⁺ ions which are directed towards the liquid phase leaving the carbon surface with negatively charged COO⁻ sites. The carbon surface of the oxidized carbons, therefore, behaves as negatively charged. Larger the number of acidic groups on the carbon surface, greater will be the negative charge on the carbon surface. This enhances the electrostatic attractive interactions between the negatively charged carbon surface and the positively charged methylene blue cations thereby increasing the adsorption. On degassing the activated carbons at increasing temperatures, the acidic surface groups are gradually eliminated from the carbon surface and this results in a decrease in the concentration of negatively charged sites which in turn decreases the adsorption of methylene blue. Thus the adsorption of methylene blue is much smaller on the 650 °C degassed carbon samples than on the 400 °C-degassed carbon samples because the former have lost between 80~90% of the acidic surface groups

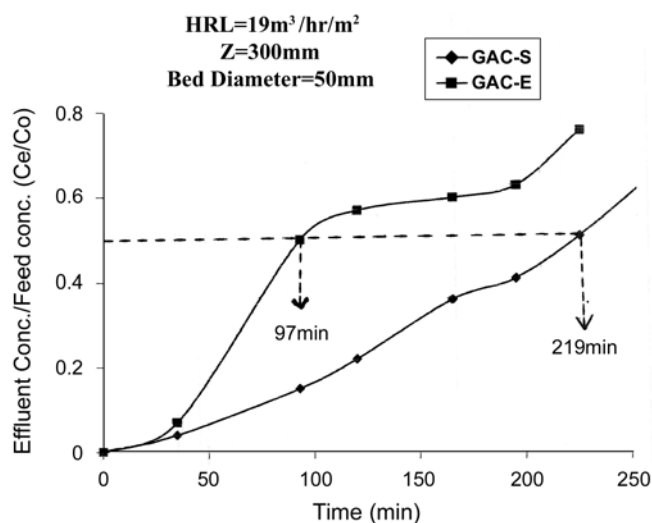
compared with the latter which had lost only 10~15% of the acidic surface groups. When the oxygen is removed almost completely on degassing at 950 °C, the carbon surface loses its negative character almost completely, thereby decreasing still further the adsorption of methylene blue. The adsorption of methylene blue in the case of 950 °C-degassed carbon samples may be attributed to take place in the microporous structure. Graham (1) and Puri (2) have shown that the adsorption of cationic and anionic dyes on graphon – a graphitised carbon black which is devoid of any carbon oxygen surface groups is determined by its microporous structure.

3.2. Dynamic Adsorption Studies

In the dynamic adsorption studies, the adsorbent (activated carbon) is loaded in columns which form a bed through which the aqueous solution of the adsorbate is passed. During its passage through the bed, the solution continuously meets a fresh part of the adsorbent and tends to establish a new equilibrium. However, as the time of contact with a given part of the adsorbent is limited, a true equilibrium is never attained.

The operating variables in such investigations are the hydraulic loading rate (HLR) which is the volume flow rate of inlet solution per unit cross sectional area of the adsorbent bed, the bed height (Z), the feed concentration (C₀), the bed diameter and the activated carbon grade. The values of these parameters used in these investigations are:

Hydraulic Loading Rate (HLR)	:20~40 m ³ /hr/m ²
Bed height (Z)	:150~600 mm.
Bed diameter	:50 mm
Feed concentration	:200 mg/L
Activated carbons	:GAC-E and GAC-S

**Fig. 11.** Breakthrough curves for Methylene Blue on GAC-E and GAC-S activated carbons.

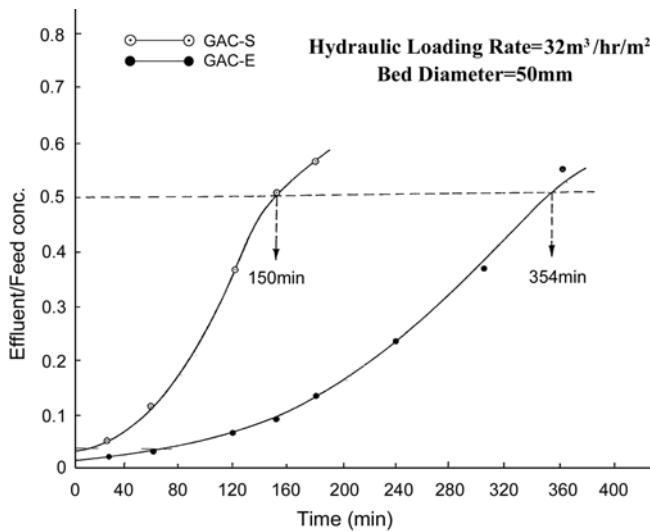


Fig. 12. Breakthrough curves for Methylene Blue on GAC-E and GAC-S activated carbons.

As it can be seen the feed concentration and the bed diameter have been kept constant in these experiments.

The breakthrough curves for methylene blue showing the effluent concentration at different time intervals for the two carbons at HLR $19 \text{ m}^3/\text{hr}/\text{m}^2$ and with a bed height $Z = 300$ are shown in Fig. 11. It is seen from the shapes of the two curves that the effluent concentration rises very slowly in the beginning but increases considerably after the slow period. The period of slow rise and the breakthrough time, t_b , are longer for GAC-S than for GAC-E. It is also seen that the later half of the breakthrough curves i.e. the portion after the

breakthrough appears to be similar in shape as the first half i.e. the portion before the breakthrough so that for the experimental purposes it is sufficient to operate the column upto breakthrough point to understand the adsorption behaviour. Similar breakthrough curves at HLR $= 32 \text{ m}^3/\text{hr}/\text{m}^2$ and a bed height of 300 mm are shown us Fig. 12. It is seen that with increase in HLR both the break through time and the adsorption capacity of the carbon are enhanced considerably. The variation in minimum achievable concentration, C_e with bed height for the two carbons is shown in Fig. 13. The minimum achievable concentration decreases as the bed height increases. At 150 mm bed height C_e is 30 mg/L for GAC-E and only 13 mg/L for GAC-S. This indicates that the adsorption zone height is higher for GAC-S than GAC-E. With increasing bed height, there is a sharp fall in C_e to around 1 mg/L for GAC-E and 0.03 mg/L for GAC-S at a bed height of 600 mm.

The adsorption capacities of the two activated carbons for methylene blue obtained from the breakthrough time t_b were calculated using the equation:

$$\text{Adsorption capacity (mg/g)} = \frac{t_b \cdot Q \cdot C_o}{m}$$

where Q is the liquid flow rate in litres per hr, C_o is the concentration of the methylene blue in the feed solution and m is the mass of the carbon. These adsorption capacities are plotted against the hydraulic loading rate in Fig. 14. The adsorption capacity increases with increase in HLR but the rate of increase decreases at higher loading rates and tends to be maximum around $35 \text{ m}^3/\text{hr}/\text{m}^2$ HLR. (cf. Table 6). Extrapolation of the curves shows that the maximum in adsorption capacity for GAC-E is about 85 mg/g corresponding to HLR of $36 \text{ m}^3/\text{hr}/\text{m}^2$ while that GAC-S is around 185 mg/g corresponding to a HLR of approximately $42 \text{ m}^3/\text{hr}/\text{m}^2$. The difference in adsorption capacities of the two activated

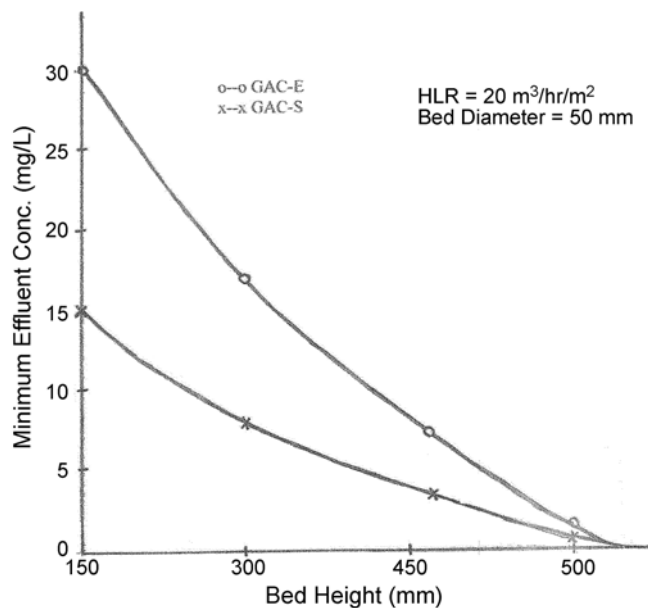


Fig. 13. Variation in minimum effluent concentration with Bed Height.

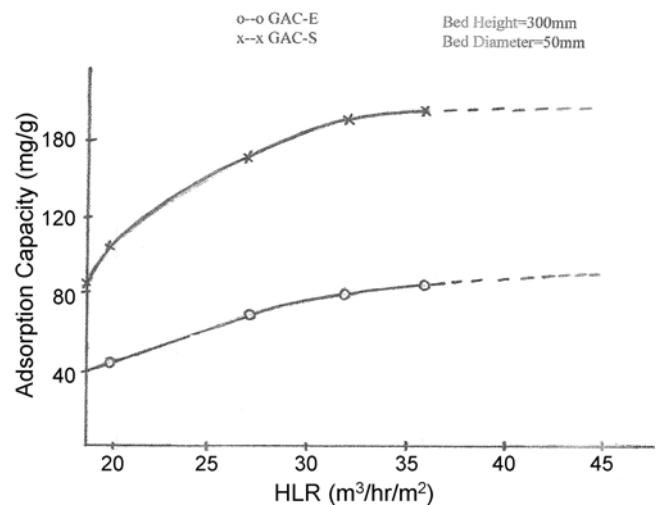


Fig. 14. Adsorption Capacity Vs Hydraulic Loading Rate.

Table 6. Variation in Adsorption Capacity with Hydraulic Loading rate
Z = 300 mm

Hydraulic Loading rate, HLR (m ² /hr/m ²)	Adsorption Capacity (mg/g)	
	GAC-S	GAC-E
19	–	40
20	105	45
27.2	140	66
32	–	80
36	173	–
42	185	85
	(Extrapolation value)	(Extrapolation value)

carbons is higher at higher HLRs in the range studied. In general, the adsorption capacity of GAC-S is nearly twice of that for GAC-E.

The difference in the breakthrough behaviour of the two activated carbons observed in Fig. 11 and 12 shows that GAC-S has better adsorption characteristics than GAC-E. This can be attributed partly to the large surface area and partly to the larger amount of associated oxygen (carbon oxygen surface groups) in the case of GAC-S. The relatively lower values of minimum effluent concentration for GAC-S compared to GAC-E (cf Fig. 13) is also due to its better adsorption characteristics due to which a greater proportion of the dye gets adsorbed at any point leading to smaller concentration in the treated effluent. Fig. 13 also indicates that the adsorption zone is about 600 mm in length since the minimum effluent concentration tends to become more or less constant for bed heights beyond this length.

The increase in adsorption capacity with increasing HLR may be attributed to the dynamics of the carbon column adsorption process. The change in HLR effects the overall resistance to mass transfer which is a non-linear summation of the pore particle interphase and fluid resistances. At low HLRs laminar flow conditions prevail. There is nearly a stationary film of liquid covering the particles across which the mass transfer has to take place. This high resistance leads to lower mass transfer rates and, therefore, results in smaller adsorption. As the HLR is increased, the interphase resistance decreases resulting in an increase in the rate of mass transfer and hence in an increase in the adsorption capacity. Beyond a certain optimum HLR, the rate of increase in the adsorption capacity tends to decrease due to the decreased residence time of the solution within the bed and lower time available for mass transfer. The optimum HLR from the present studies has been found to be around 40 m³/hr/m².

4. Conclusions

Adsorption of methylene blue from aqueous solutions by

activated carbons follows Langmuir adsorption isotherm equation. The methylene blue molecules cover only 50% of the BET surface area in the case of activated carbon fibres while whole of the BET area is available for adsorption in the case of granulated carbons. This indicates that about 50% of the BET surface area in the case of ACFs is present in the form of fine micropores which are inaccessible to larger methylene blue molecules. The adsorption increases on oxidation of the carbons due to the formation of acidic surface groups and decreases on degassing when these surface groups are eliminated. The acidic surface groups on ionization in aqueous solutions render the carbon surface negatively charged and thereby enhance the attractive electrostatic interactions between the carbon surface and the positively charged cations of the dye. The adsorption and the breakthrough time both increase with increase in hydraulic loading rate. The adsorption capacity tends to be maximum around an HLR 35 m²/hr/m². The minimum achievable concentration decreases as the bed height increases.

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