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Kinetics and mechanism of removal of methylene blue by adsorption on various carbons—a comparative study

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Abstract

The kinetics and mechanism of methylene blue adsorption on commercial activated carbon (CAC) and indigenously prepared activated carbons from bamboo dust, coconut shell, groundnut shell, rice husk, and straw, have been studied. The effects of various experimental parameters have been investigated using a batch adsorption technique to obtain information on treating effluents from the dye industry. The extent of dye removal increased with decrease in the initial concentration of the dye and particle size of the adsorbent and also increased with increase in contact time, amount of adsorbent used and the initial pH of the solution. Adsorption data were modeled using the Freundlich and Langmuir adsorption isotherms and first order kinetic equations. The kinetics of adsorption were found to be first order with regard to intra-particle diffusion rate. The adsorption capacities of indigenous activated carbons have been compared with that of the commercial activated carbon. The results indicate that such carbons could be employed as low cost alternatives to commercial activated carbon in wastewater treatment for the removal of colour and dyes. © 2001 Published by Elsevier Science Ltd. All rights reserved.

Keywords: Adsorption; Methylene blue; Activated carbons—commercial and indigenously prepared; Freundlich and Langmuir adsorption isotherms; Kinetics of adsorption; Intra-particle diffusion; Wastewater treatment—removal of dyes

1. Introduction

Effluents from the dyeing and finishing processes in the textile industry are known to contain colour, high amounts of surfactants, dissolved solids and possibly heavy metals such as Cr, Ni and Cu [1]. The effluents from the dyestuff manufacturing and some similar industries are also generally highly coloured with a large amount of suspended organic solids and hence are the important sources of water pollution. From an environmental point of view, the removal of synthetic dyes is of great concern, since some dyes and their degradation products may be carcinogens and toxic and, consequently, their treatment cannot depend on bio-degradation alone [2,3]. Hence, decolourisation of dye house effluent via the removal of dyes has become an important aspect of textile wastewater treatment.

The environmental issues surrounding the presence of colour in effluent is a continuing problem for dyestuff manufactures, dyers, finishers and water companies, because increasingly stringent colour consent standards are being enforced

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by regulatory bodies to reduce the quality of colour in effluent and water courses. At present, the problem is considered to be solely aesthetic rather than ecotoxicological. Even so, the problem of colour in wastewater is common to many dye houses.

Many studies have been conducted on the toxicity of dyes and their impact on the ecosystem [4,5], as well as the environmental issues associated with the manufacture and subsequent usage of dyes [6,7].

Biological treatment processes are reported to be efficient in the removal of suspended solids and reduction of chemical oxygen demand but are largely ineffective in removing colour from waste water [8]. Hence, investigations have been conducted on physico-chemical methods of removing colour from textile effluent. These studies include the use of coagulants [9], oxidising agents [10], ultra-filtration [11], electro-chemical [12,13] and adsorption [8] techniques. The advantages and disadvantages of each technique have been extensively reviewed [14]. Of these methods, **adsorption** has been found to be an efficient and economic process to remove dyes, pigments and other colourants and also to control the bio-chemical oxygen demand [14]. Activated carbon (AC), inorganic oxides, natural adsorbents (such as clays and clay minerals, cellulosic materials, chitin and chitosan) have been extensively used as adsorbents [15–20].

AC adsorption has been found to be an effective and widely employed means of water and waste water treatment [21]. Despite its prolific use in water and waste water industries, commercial AC (CAC) remains an expensive material. This has led to a search for low-cost materials as alternative adsorbent materials [17,18].

The purpose of this work was to study the kinetics and mechanism of adsorption of methylene blue (MB), on various indigenously prepared ACs (IPACs) from agricultural wastes and to compare their adsorption capacity for the removal of MB under optimum experimental conditions. Thus, this investigation is aimed at to study the kinetics and dynamics of adsorption of a basic dye viz., methylene blue (MB) on CAC and (IPACs) such as bamboo dust carbon (BDC), coconut shell carbon (CSC), groundnut shell carbon (GNSC), rice husk carbon (RHC) and straw carbon (SC) and to find out the possibility of using these carbonaceous materials as low-cost adsorbents for the removal of dyes in general and MB, in particular.

2. Materials and methods

The material commercial AC (CAC) was supplied by E.Merck, India. Raw materials for the preparation of ACs such as bamboo dust, coconut shell, rice husk and straw were procured locally, washed, dried, cut into small pieces and dried. The raw materials were then carbonised (at 300 °C) and steam digested (at 700 °C), acid treated and washed. The materials were finally sieved to discrete particle sizes. IPACs thus produced and CAC were thermally activated at 120 °C for 1 h in an air oven. Methylene blue (MB) supplied by BDH was used as an absorbate and was not purified prior to use. All the other chemicals used in this study were reagent grade and supplied by BDH (India). Double distilled water was employed for preparing all the solutions and reagents.

2.1. Adsorption studies

A stock solution of MB (1000 mg/ l) was prepared and suitably diluted to the required initial concentrations. Adsorption experiments were carried out at room temperature (30±1 °C) under batch mode [22]. The initial concentrations (C_i) of MB were obtained by measuring O.D. at 663 nm (λ max) using Elico UV–visible spectrophotometer (Model: SLI59). Exactly 50 ml of MB solution of known initial concentration (C_i range: 100–400 mg/l) was shaken at the constant agitation speed (200 rpm) with a required dose of AC (range 8–11.6 g/l) for IPACs, except CAC), of a fixed particle size (range: 90–250 μm for ACs except CAC) for a specific period of contact time (range: 5–120 min) in a thermostatic orbit incubator shaker (NEOLAB, India), after noting down the initial pH of the solution (pH = 7.2). The pH of the solutions were adjusted to the required value (range: 2–10) by adding either 1 M HCl or 1 M NaOH solution. After equilibration, the final concentrations (C_f) were measured at 663 nm by spectrophotometeric method (Elico UV visible spectrophoto meter—Model : SL159). The various experimental conditions are given in Table 1. The percentage removal of dye and amount adsorbed (in mg/g) were calculated using the following relationships:

$$\text{Percentage removal} = 100(C_\mathrm{i} - C_\mathrm{f})/C_\mathrm{i} \tag{1}$$

$$\text{Amount adsorbed } (q_\mathrm{e}) = (C_\mathrm{i} - C_\mathrm{f})/m \tag{2}$$

where C_i and C_f are the initial and final concentrations (in mg/l) of dye, respectively and m is the mass of AC (in mg/l). Blanks containing no dye were used for each series of experiments as controls. The average values of duplicate runs were obtained and analysed. Error in data: ± 1–2% for percentage removal ± 0.005–0.01 mg/g for amount adsorbed.

3. Results and discussion

The adsorption experiments were carried out at different experimental conditions (Table 1) and the results obtained are discussed below.

3.1. *Effect of initial concentration*

The effect of initial concentration of dye on the extent of removal of MB (in terms of percentage removal) on various adsorbents viz., CAC, BDC, CSC, GNSC, RHC, and SC was studied and the relevant data are given in Table 2. The percentage removal was found to decrease exponentially, while the amount adsorbed increased exponentially with the increase in initial concentration of MB. This indicates that there exist reductions in immediate solute adsorption, owing to the lack of available active sites required for the high initial concentration of Methylene blue (MB). Similar results have been reported in literature on the extent of removal of dyes [19,20], metal ions [22], and carboxylic acids [23]. Although the adsorption capacities of IPACs are less, still they could be employed as low-cost adsorbents as alternatives to CAC for the removal of dyes in general and MB, in particular. The percentage removal of MB by SC is 99.2. SC is found to have adsorption capacity almost equal to that of CAC. Hence, among the IPACs SC is the best low cost adsorbent material.

Table 1
Experimental conditions for the various of adsorption experiments for the removal of MB dye on ACs

Variation	[Dye] initial (ppm)	Contact time (min)	Dose (g l^{-1})	Initial pH	Particle size of IPACs (μm)
I Initial concentration (C_i)	600–900	35	2	7.2	90
	100–200	35	10		
i. CAC	100–200	35	10		
ii. BDC	100–200	35	10		
iii. CSC	200–400	35	10		
iv. GNSC	200–300	35	10		
v. RHC					
vi. CAC					
II Contact time	CAC—600[a] BDC, CSC, GNSC } 100[a] RHC, SC } 200[a]	5–120	10	7.2	90
III Dose	Optimum[a]	35	IPACs = 8–11.6 (CAC = 1–3)	7.2	90
IV Initial pH	Optimum[a]	35	CAC = 2 IPACs = 10	2–10	90
VI Particle size of IPACs	Optimum[a]	35	IPACs = 10	7.2	90–250

[a] Optimum C_I refers to the initial concentration of dye at which maximum removal of MB was noticed.

3.2. Adsorption isotherms

The adsorption data were analysed with the help of the following linear forms of Freundlich and Langmuir isotherms [24]:

$$\text{Freundlich isotherm}: \quad \log q_e = \log k_f + (1/n)\log C_e \qquad (3)$$

$$\text{Langmuir isotherm}: \quad (C_e/q_e) = (1/Q_o b) + (C_e/Q_o) \qquad (4)$$

where log k_f is roughly a measure of the adsorption capacity and $1/n$, is an indicator of adsorption effectiveness; q_e is the amount of dye adsorbed per unit mass of adsorbent (in mg/g) and C_e is the equilibrium concentration of dye (in mg/l), Q_o and b are the Langmuir constants, which are the measures of monolayer (maximum) adsorption capacity (in mg/g)and energy of adsorption (in g/l), respectively. The values of Freundlich and Langmuir parameters were obtained respectively, from the linear correlations between the values of (i) log q_e and log C_e and (ii) (C_e/q_e) and C_e. The adsorption isotherms parameters along with the correlation coefficients are presented in Table 3. The observed statistically significant (at 95% confidence level) linear relationships as evidenced by the r-values (close to unity) indicate the applicability of these two adsorption isotherms and the

Table 2
Effect of initial concentration of MB on the extent of removal by adsorption on ACs at 30 °C[a]

Carbon	Parameter	Concentration (in ppm)					
CAC	C_o	600	650	700	750	800	850
	C_e	29.9 (99.6)[b]	32.4 (99.5)	34.8 (99.4)	37.3 (99.3)	39.7 (99.2)	42.2 (99.1)
BDC	C_o	100	125	150	175	200	
	C_e	3.8 (96.2)	5.9 (95.3)	8.3 (94.5)	10.7 (93.9)	13.9 (93.1)	
CSC	C_o	100	125	150	175	200	225
	C_e	3.5 (96.5)	4.5 (95.9)	6.6 (94.5)	8.8 (93.7)	9.2 (93.4)	10.8 (92.8)
GNSC	C_o	100	125	150	175	200	
	C_e	3.6 (96.4)	5.0 (96.0)	7.9 (94.7)	10.1 (94.2)	12.0 (94.0)	
RHC	C_o	200	250	300	350	400	
	C_e	1.8 (99.1)	2.6 (98.9)	4.7 (98.4)	7.1 (97.9)	9.4 (97.6)	
SC	C_o	200	225	250	275	300	
	C_e	1.7 (99.2)	1.9 (99.1)	2.3 (99.0)	3.0 (98.8)	3.5 (98.6)	

[a] Initial pH = 7.2, dose: CAC = 2 g/l, IPACs = 10 g/l, particle size: 90 μm, contact time: 5–120 min, speed = 200 rpm.
[b] Values given in the parentheses are % removal of MB.

Table 3
The Freundlich and Langmuir parameters of adsorption isotherms[a]

Parameter	CAC	BDC	CSC	GNSC	RHC	SC
Freundlich isotherm						
Intercept	6.737	0.683	0.620	0.698	1.220	1.193
Slope (1/*n*)	0.288	0.514	0.677	0.524	0.378	0.519
Correlation coefficient (*r*)	0.998	0.999	0.993	0.994	0.995	0.985
Langmuir isotherm						
Q_o	980.3	143.2	277.9	164.9	343.5	472.1
B	0.479	0.120	0.091	0.128	0.358	0.389
Correlation coefficient (*r*)	0.997	0.994	0.948	0.983	0.995	0.991
R_L	0.001	0.083	0.001	0.072	0.002	0.013

[a] Data given in Table 2 are used. pH = 7.4, dose: CAC = 2 g/l, IPAC = 10 g/l, speed = 200 rpm, contact time: 5–120 min, particle size: 90 μm.

monolayer coverage on adsorbent surface. Freundlich and Langmuir isotherm plots are shown in Figs. 1 and 2. The monolayer adsorption capacities of the adsorbents are found to be of the order:

BDC < GNSC < CSC < RHC < SC << CAC

Among the IPACs, the SC and RHC are observed to possess high adsorption capacity and hence they could be employed as low-cost adsorbents as alternatives to CAC, for the removal of dyes in general and MB, in particular. Further, the essential characteristics of the Langmuir isotherm can be descried by a **separation factor** R_L; which is defined by the following Eq. [25]:

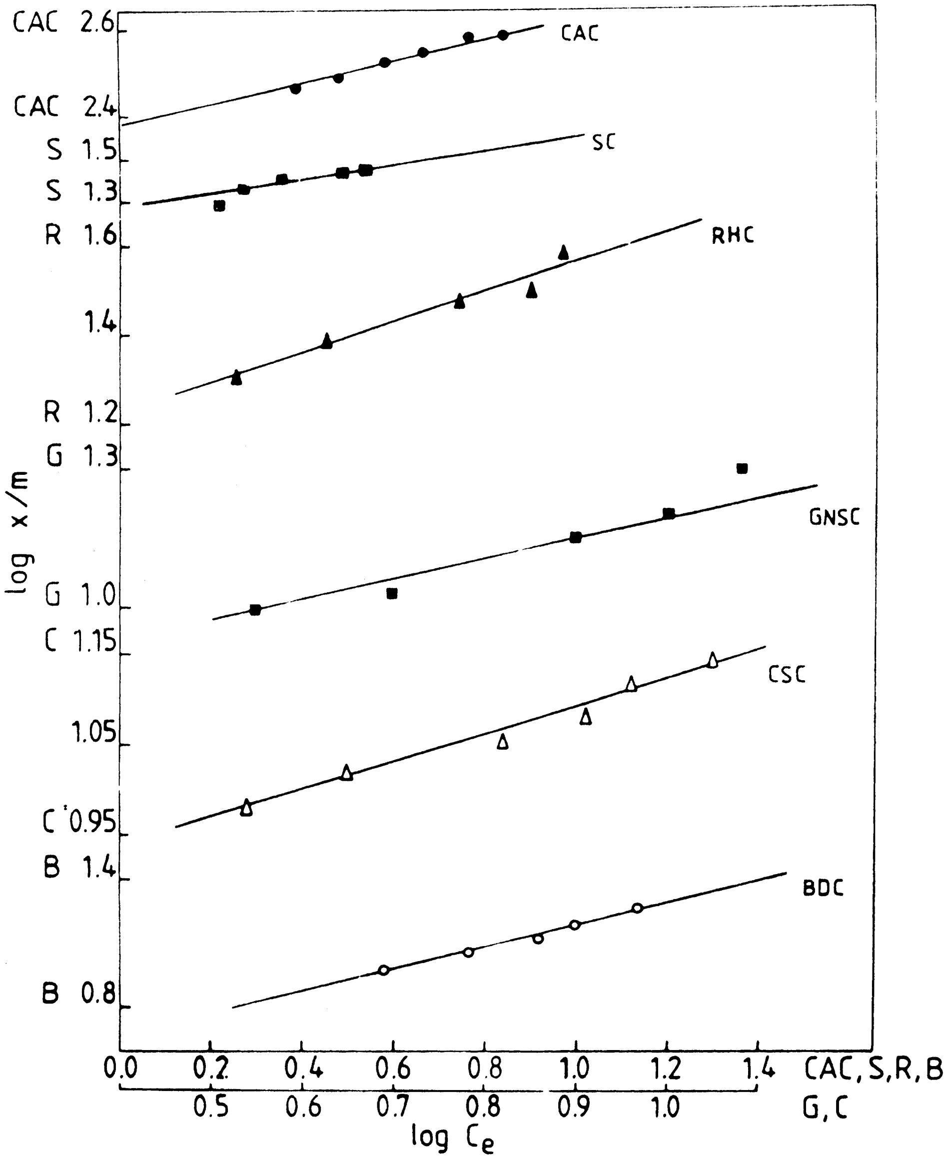

Fig. 1. Freundlich isotherms for the removal of MB by adsorption on various ACs.

$$R_L = 1/(1 + b\ C_i) \quad (5)$$

where C_i is the initial concentration of dye (in ppm or mg/l) and b is the Langmuir constant (in g/l). The value of separation factor R_L, indicates the nature of the adsorption process as given below:

R_L value	Nature of adsorption process
$R_L > 1$	Unfavourable
$R_L = 1$	Linear
$0 < R_L < 1$	Favourable
$R_L = 0$	Irreversible

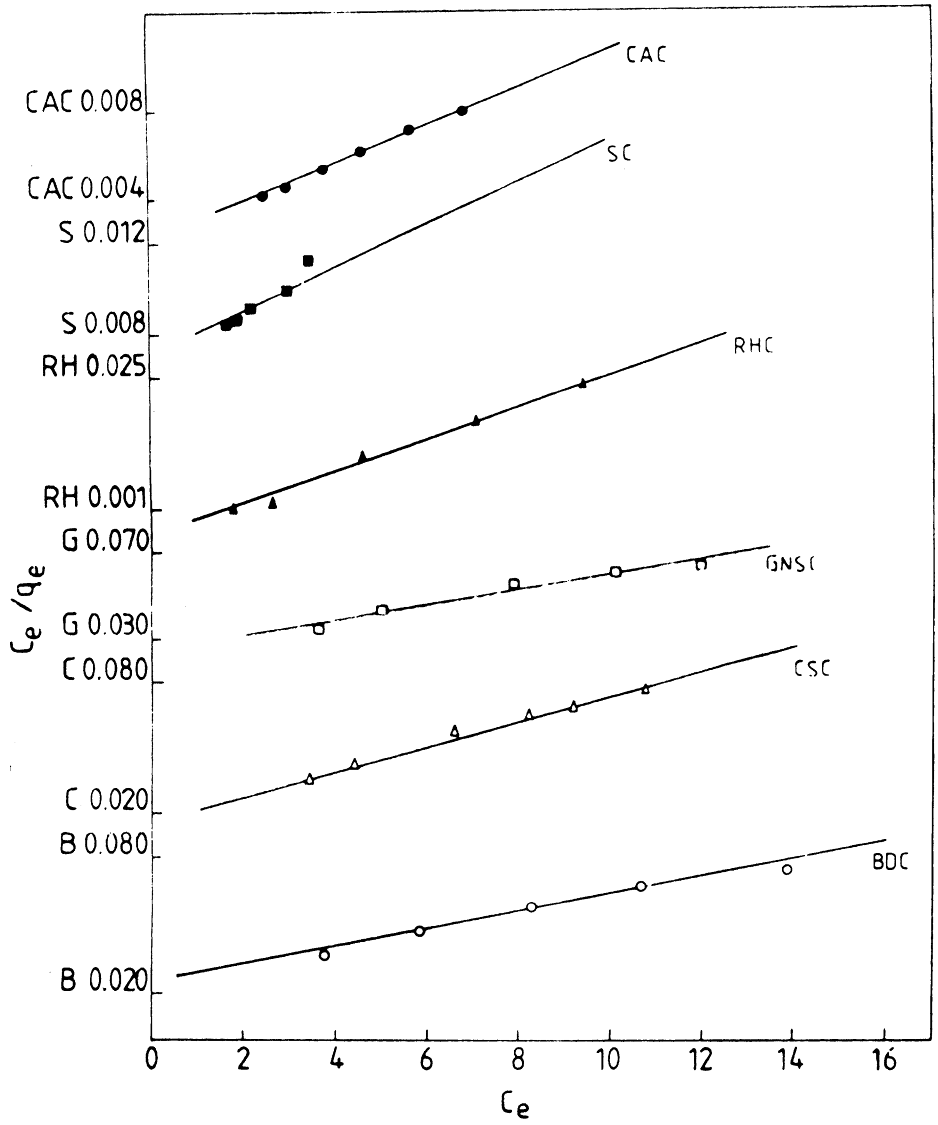

Fig. 2. Langmuir isotherms for the removal of MB by adsorption on various ACs.

In the present study, the values of R_L (Table 3) computed are observed to be in the range of 0–1, indicating that the adsorption process is favorable for all these low-cost adsorbents (IPACs).

3.3. Effect of contact time

The effect of contact time on the amount of dye adsorbed was investigated at the optimum initial concentration of dye (Table 1) and the data are presented in Table 4. The extent of removal (in terms of q_e) of MB by these ACs was found to increase, reach a maximum value with increase in contact time. In some cases it decreases with the increase in contact time after, 90 min which may be due to a desorption process. The relative increase in the extent of removal of dye after 35 min of contact time is not significant and hence it is fixed as the optimum contact time. Similar results have been reported in literature for the removal of dyes [19,20], metal ions [22] and carboxylic acids [23].

In batch type adsorption systems, monolayer of adsorbate is normally formed on the surface of adsorbent [26] and the rate of removal of adsorbate species from aqueous solution is controlled primarily by the rate of transport of the adsorbate species form the exterior/outer sites to the interior sites of the adsorbent particles [27,28].

3.4. Kinetics of adsorption

The plots of q_t vs t for all the MB-adsorbent systems are found to be exponential indicating the first order nature of the adsorption process (Fig. 3). In order to find out whether the adsorption process followed first order kinetics the following generalised first order kinetic equation proposed by Annadurai and Krishnan [19] was employed

$$1/q_t = (k/q_{max})(1/t) + 1/q_{max} \tag{6}$$

where q_t is the amount of dye adsorbed (in mg/g) at various time t, q_{max} is the maximum adsorption capacity and k is the first order rate constant for the adsorption process (in min^{-1}). Linear correlations of $1/q_t$ vs $1/t$ were made and the results are given in Table 5.

The kinetics and dynamics of adsorption of MB on various ACs have been studied by applying the following kinetic equations proposed by Natarajan and Khalaf—as cited by Kannan and Vanangamudi [29], Lagergeren—as cited by Trivedi et al. [30] and Bhattacharya and Venkobachar [31].

Natarajan and Khalaf equation:

$$\log\ (C_i/C_f) = (k/2.303)t \tag{7}$$

Lagergren equation:

$$\log\ (q_e - q_t) = \log\ q_e - (k_{ad}/2.303)t \tag{8}$$

Bhattachara and Venkobachar equation:

$$\log\ [1 - U(T)] = (k_{ad}/2.303)t \tag{9}$$

where C_i and C_t are the concentration of dye (in mg/l) at time, zero and at time t, respectively; q_e and q_t are the amount of dye adsorbed per unit mass of the adsorbent (in mg/g) at equilibrium time and time t, respectively. $U(T)=[(C_i-C_t)/(C_i-C_e)]$; C_e = equilibrium dye concentration (in mg/l) and k and k_{ad} are the adsorption rate constants (in min^{-1}). The values of log (C_i/C_t), log $(q_e - q_t)$ and log $[1-U(T)]$ were correlated with time. The values of first order rate constants and correlation coefficient (r-value) are given in Table 5. All the linear correlations were found to be statistically significant (as evidenced by r-values close to unity) at 95% confidence level and indicate the applicability of these kinetic equations and the first order nature of the adsorption process of MB on various adsorbents. The value of k_{ad} calculated from the Bhattacharya and Venkobachar equation are found to be close to that computed from Lagergren equation for any given adsorbent. The rate of adsorption k_{ad} is found to be high in SC (0.034 min^{-1}) and low in BDC (0.023 min^{-1}). Lagergren plots, Bhattacharya and Venkobachar plots are shown, respectively, in Figs. 4 and 5.

3.5. Intra-particle diffusion model

The adsorbate species are most probably transported from the bulk of the solution in to the solid phase through intra-particle diffusion/transport process, which is often the rate limiting step in many adsorption process, especially in a rapidly stirred batch reactor [26,32].

The possibility of intra-particle diffusion was explored by using the intra-particle diffusion model [33].

$$q_t = k_p t^{1/2} + C \tag{10}$$

where q_t is the amount of dye adsorbed at time t; C is the intercept and k_p is the intra-particle diffusion

Table 4
Effect of contact time on the amount of dye adsorbed (q_e in mg/g) at 30 °C[a]

No.	Contact time (min.)	CAC	BDC	CSC	GNSC	RHC	SC
1	5	293.5	9.06	9.06	9.25	19.41	19.20
2	10	293.9	9.17	9.25	9.34	19.48	19.36
3	15	294.3	9.25	9.32	9.43	19.57	19.48
4	20	294.5	9.38	9.44	9.48	19.65	19.60
5	25	294.5	9.45	9.51	9.55	19.72	19.70
6	30	294.7	9.53	9.56	9.60	19.77	19.78
7	35	296.3	9.62	9.58	9.64	19.83	19.82
8	40	297.1	9.74	9.60	9.69	19.89	19.82
9	45	297.3	9.74	9.65	9.72	19.89	19.88
10	90	298.0	9.74	9.68	9.72	19.89	19.88
11	120	298.4	9.66	9.68	9.70	19.89	19.88

[a] C_I = optimum, dose: CAC = 2 g/l, IPACs = 10 g/l, particle size: 90 μm, speed = 200 rpm, initial pH = 7.2. Optimum C_I refers to the initial concentration of dye at which maximum removal of MB was noticed.

Table 5
Statistical results of the application of the kinetic equations and models for MB–adsorbent systems[a]

Parameter	Activated carbon					
	CAC	BDC	CSC	GNSC	RHC	SC
I. Natarajan and Khalaf equation						
$10k$	2.148	1.443	1.684	3.123	2.477	2.355
r-Value	0.939	0.986	0.980	0.999	0.988	0.993
II. Lagergren equation						
$10k_{ad}$	3.008	2.250	2.623	2.431	3.317	3.443
r-Value	0.911	0.992	0.992	0.956	0.991	0.993
III. Bhattacharya and Venkobachar equation						
$10k_{ad}$	3.008	2.250	2.623	2.431	3.317	3.443
r-Value	0.911	0.953	0.994	0.956	0.991	0.993
IV. Intraparticle diffusion model						
$10k\mu$	14.412	3.733	2.945	2.464	2.734	3.639
Intercept	292.1	8.661	8.828	9.009	19.119	18.867
r-Value	0.932	0.993	0.983	0.999	0.997	0.987
V. Log (% removal) vs log (time)						
Slope	0.539	0.0339	0.0251	0.0233	0.0119	0.0166
Intercept	2.463	1.930	1.941	1.948	1.978	1.970
r-Value	0.950	0.965	0.974	0.988	0.976	0.993

[a] Data given in Table 4 are used.

rate constant (in mg $\text{min}^{1/2}$/g). The values of q_t were found to be linearly correlated with values of $t^{1/2}$. The k_p values were calculated by using correlation analysis (Table 5). The r-values are close to unity indicating the application of this model. This reveals the presence of intra-particle diffusion process [26,33]. The calculated values of k_p is maximum for BDC (0.37) and minimum for GNSC (0.25)—MB systems. The intra-particle diffusion plots are given in Fig. 6. The values of intercept (Table 5) give an idea about the boundary layer thickness, i.e. the larger the intercept, the greater is the boundary layer effect [20].

The correlation of the values of log (% removal) and log (time) also resulted in linear relationships, which also indicate that the process of intra-particle diffusion is taking place in these adsorption systems. (Table 5). The divergence in the value of slope from 0.5 indicate the presence of intra-particle diffusion process as one of the rate limiting

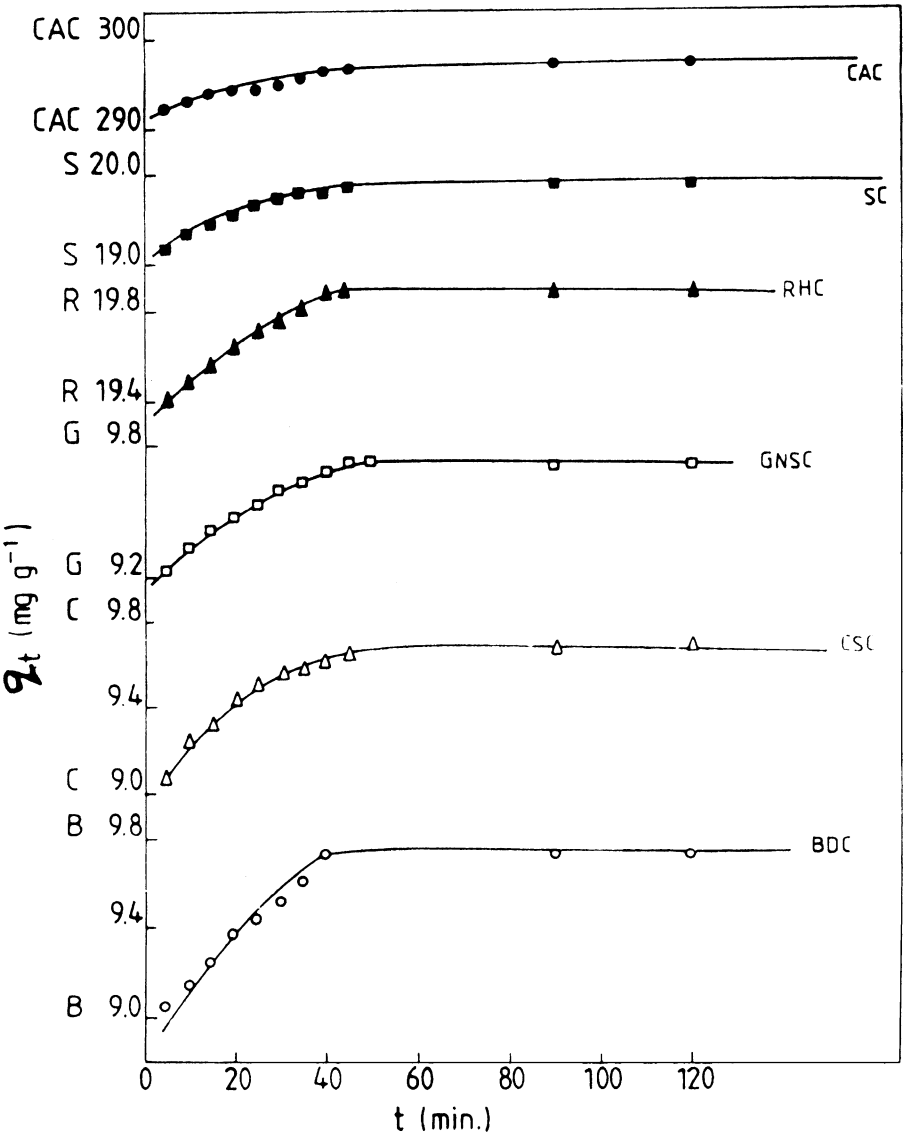

Fig. 3. First order kinetic plots for the removal of MB by adsorption on various ACs.

steps, besides many other processes controlling the rate of adsorption, all of which may be operating simultaneously [20,27].

3.6. *Effect of dose of adsorbent*

The effect of dose of adsorbent on the amount of dye adsorbed was studied (Table 6). The equilibrium value of amount adsorbed was observed to decrease with increase in dose. The percentage removal of MB (given in parentheses in Table 6) increased with the increase in dose of adsorbent. This may be due to the increase in availability of surface active sites resulting from the increased dose and conglomeration of the adsorbent [34]. The increase in the extent of removal of MB is found to be insignificant after a dose 10 g/l for various IPACs and 2.0 g/l for CAC, which are fixed as the optimum doses of adsorbent. The amount of dye adsorbed was observed to vary

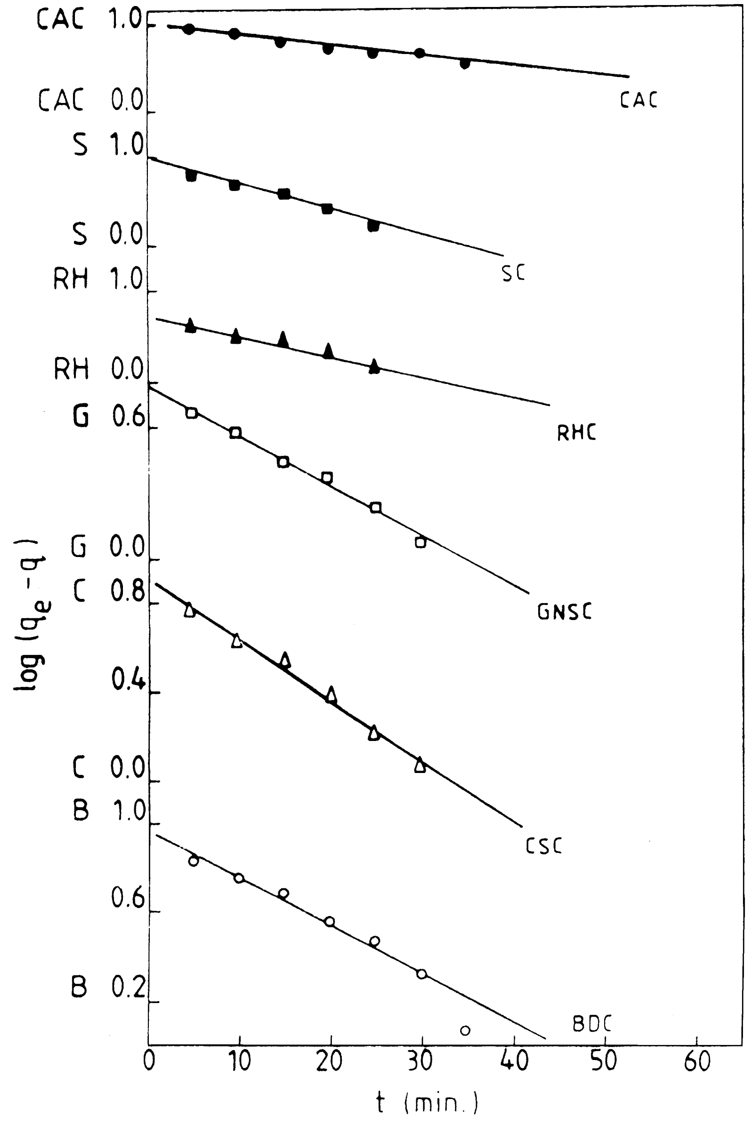

Fig. 4. Lagergren plots for the removal of MB by adsorption on various ACs.

Table 6
Effect of dose of AC on the amount of MB adsorbed (q_e, in mg/g)[a]

Dose of CAC (g/l)	q_e	Dose of IPACs (g/l)	Amount adsorbed (q_e)				
			BDC	CSC	GNSC	RHC	SC
1.0	296.45 (99.4)[b]	8.0	11.14 (89.1)[b]	11.19 (89.5)	10.80 (87.1)	11.15 (89.2)	10.89 (87.1)
1.2	247.45 (99.5)	8.8	10.45 (92.0)	10.52 (92.6)	10.18 (91.0)	10.67 (93.9)	10.34 (91.0)
1.4	212.43 (99.6)	9.6	9.79 (94.1)	9.80 (94.1)	9.78 (95.0)	10.08 (96.8)	9.90 (95.0)
1.6	186.09 (99.6)	10.0	9.62 (96.2)	9.65 (96.5)	9.64 (98.3)	9.82 (98.2)	9.83 (98.3)
1.8	165.64 (99.7)	10.8	9.12 (98.5)	9.04 (98.8)	9.17 (99.0)	9.19 (99.3)	9.76 (100.0)
2.0	149.25 (99.8)	11.6	8.62 (100.0)	8.62 (100.0)	8.62 (100.0)	8.62 (100.0)	8.62 (100.0)

[a] pH = 7.2, temperature: 30 ± 1 °C, contact time: 35 min, particle size: 90 μm.
[b] The values of percentage removal are given in parentheses.

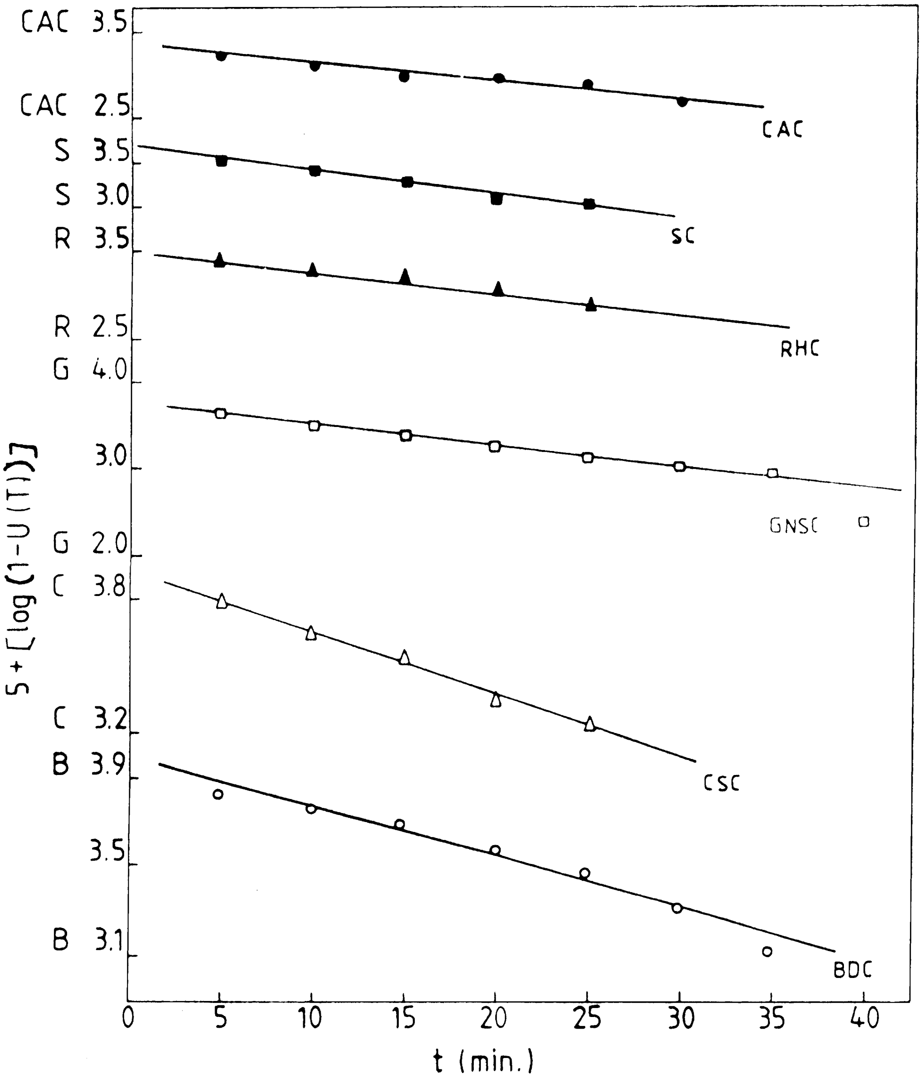

Fig. 5. Bhattacharya and Venkobachar plots for the removal of MB by adsorption on various ACs.

exponentially in accordance with the fractional power term of the dose of adsorbent i.e. $(\text{dose})^{-n}$, where n = fraction (n-values: CAC = 0.991, BDC = 0.690, GNSC = 0.598, CSC = 0.676, RHC = 0.638 and SC = 0.541). The plots of log q_e vs log (dose) are found to be linear (r = 1.0). This suggests that the adsorbed species/solute may either block the access to the internal pores or cause particles to aggregate and thereby resulting in the availability of active sites for adsorption.

3.7. Effect of initial pH

The effect of initial pH of the dye solution on the amount of dye adsorbed was studied by varying the initial pH under constant process parameters. The results are shown in Fig. 7. The increase in initial pH increases the amount of dye adsorbed. The final pH of the solution was found to decrease slightly (by 0.3–0.5 pH units) after adsorption of MB as MB^+ cationic form with the

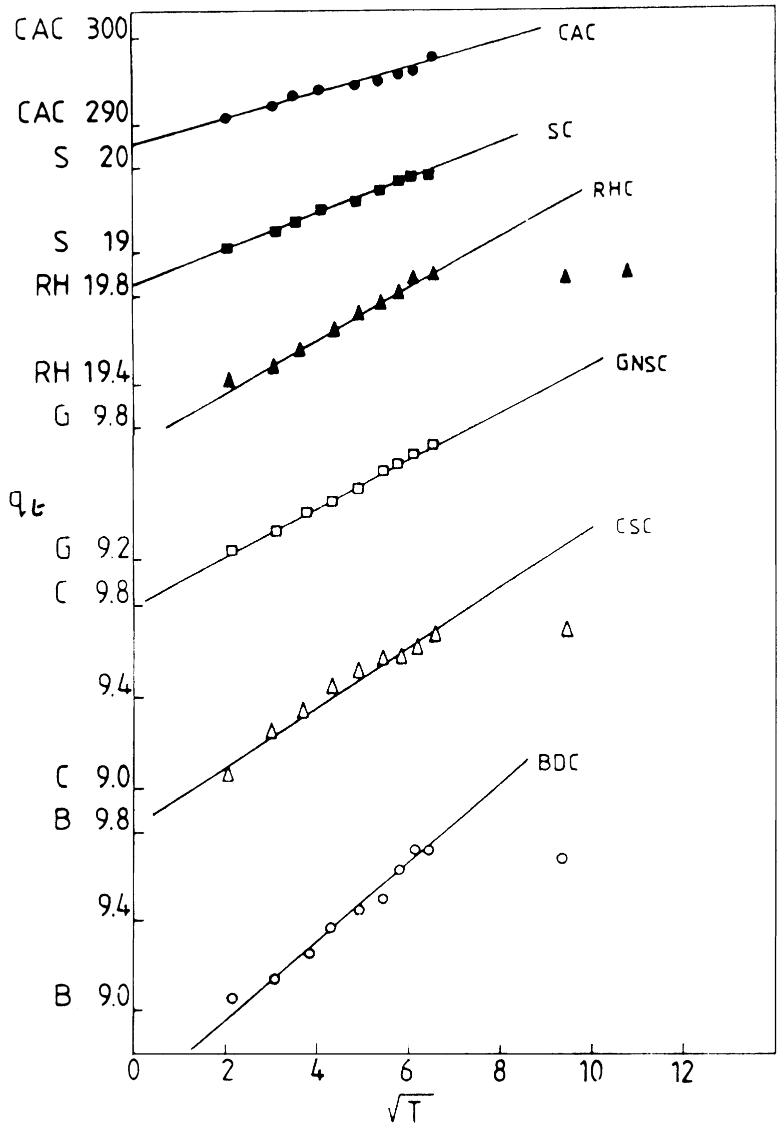

Fig. 6. Intra-particle diffusion plots for the removal of MB by adsorption on various ACs.

release of H^+ ion from the active site of the adsorbent surface. The results are in harmony with the literature reports [19,20].

3.8. Effect of particle size of IPACs

The effect of particle size of IPACs (except CAC) on the amount of dye adsorbed was studied for indigenously prepared ACs. The amount of dye adsorbed increases with the decrease in particle size of the adsorbent. This is due to the increase in available surface area with the decrease in particle size. The effect of particle size on the amount of dye by various IPACs is shown in Fig. 8. There exists a linear relationship between the amount of dye adsorbed and particle size, as evidenced by the *r*-values close to unity (*r*-value for ACs: BDC =0.998, CSC=0.989, GNSC=0.948, RHC=0.94 and SC=0.958). Similar observations have been reported for the adsorption of dyes [19,20].

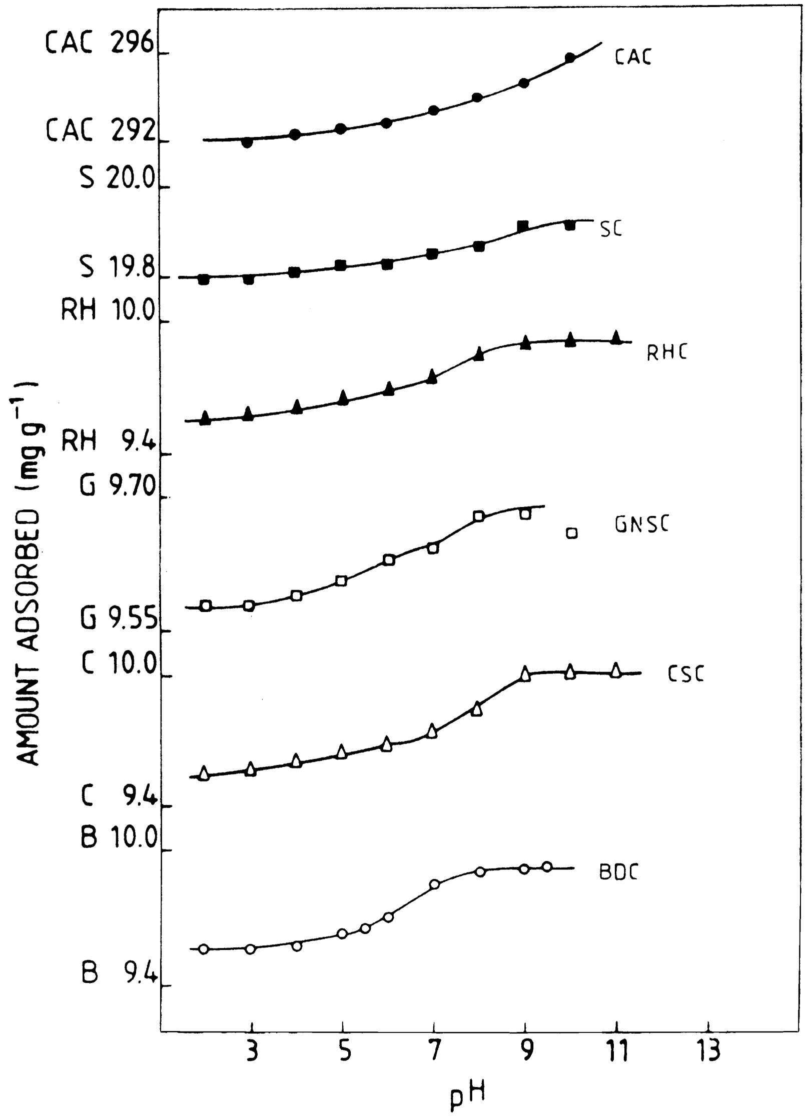

Fig. 7. Effect of pH on the amount of MB adsorbed on various ACs.

3.9. Mechanism of adsorption

The removal of MB by adsorption on various ACs was found to be rapid at the initial period of contact time and then to become slow and stagnate with the increase in contact time. The removal of MB by adsorption on surface of ACs was due to MB as MB^+ cationic form. The mechanism for the removal of dye by adsorption may be assumed to involve the following four steps [34]:

- Migration of dye from bulk of the solution to the surface of the adsorbent (AC)
- Diffusion of dye through the boundary layer to the surface of the adsorbent.
- Adsorption of dye at an active site on the surface of AC, and
- Intra-particle diffusion of dye into the interior pores of the AC particle.

The boundary layer resistance will be affected by the rate of adsorption and increase in contact time, which will reduce the resistance and increase the mobility of dye during adsorption. Since, the uptake of dye at the active sites of AC is a rapid process, the rate of adsorption is mainly governed

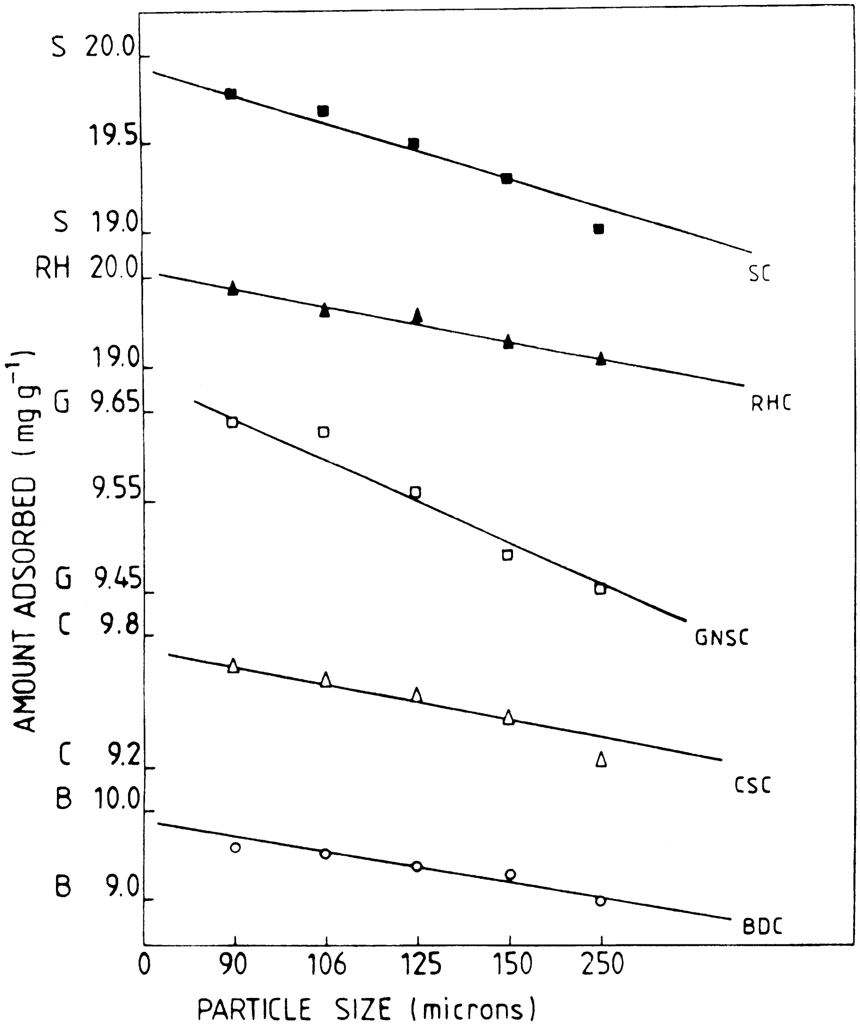

Fig. 8. Effect of particle size on amount of MB adsorbed by various indigenously prepared ACs.

by either liquid phase mass transfer rate or intra-particle mass transfer rate [34]. The applicability of intra-particle diffusion model indicates, that it is the rate-determining step.

3.10. Relative adsorption capacity

The increasing order of relative adsorption capacity of various ACs compared to that of CAC calculated from Q_0 values under optimum experimental conditions is:

BDC < GNSC < CSC < RHC < SC < CAC

Relative adsorption capacity values of various carbons for adsorption of MB are; CAC = 100; BDC = 7.20; GNSC = 7.50; CSC = 8.16; RHC = 37.57; and SC = 42.60. Among the IPACs the SC has the maximum adsorption capacity and BDC has the minimum adsorption capacity. Cost-wise the IPACs are nearly **five times cheaper** than the CAC. Hence, the IPACs are cost effective adsorbent materials for the removal of dyes/colour.

4. Conclusion

MB is found to adsorb strongly on the surface of carbons. The equilibrium adsorption is practically achieved in 35 min. The results suggest that pore diffusion is more important. Adsorption behaviour is described by a monolayer Langmuir type isotherm. The adsorption process is found to be first order with intra-particle diffusion as one of the rate determining steps. The present study concludes that the IPACs could be employed as low-cost adsorbents as alternatives to CAC for the removal of colour and dyes from water and wastewater, in general and for the removal of MB, in particular.

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