



# Kinetics and Equilibrium Study for the Adsorption of Methylene Blue Dye on *Azadirachta indica* Activated Carbon

<sup>1</sup>G. Vijayalakshmi, <sup>1</sup>B. Ramkumar and <sup>2</sup>S. Chandra Mohan

<sup>1</sup>PG and Research Department of Chemistry, Government Arts College, Tiruchurappalli-620022, Tamil Nadu, India

<sup>2</sup>Division of Phytochemistry, Shanmuga Centre for Medicinal Plants Research, Thanjavur-613007, Tamil Nadu, India

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**Corresponding Author:**

S. Chandra Mohan,  
Division of Phytochemistry,  
Shanmuga Centre for Medicinal Plants  
Research, Thanjavur-613007,  
Tamil Nadu, India

## ABSTRACT

Methylene Blue (MB) can cause some harmful effects and difficult to decolorize due to its complex structure. So, the main purpose of the present study was to remove MB by activated carbon, prepared from *Azadirachta indica* waste biomass material. In the present study, adsorption of MB on activated carbon obtained from *Azadirachta indica* has been investigated by batch adsorption method. The percentage removal of dye has been optimized by studying the initial concentration of the dye, adsorbent dosage, adsorption time and pH (2-11). The experimental data were found to be well fitted to Langmuir isotherm. Three kinetics models including Natarajan and Khalaf equation, Lagergren equation, Bhattacharya and Venkobachar equation were selected to follow the adsorption processes. Kinetic studies showed that the adsorption followed Lagergren first order kinetic model. The present study indicated that activated carbon obtained from *Azadirachta indica* is an effective adsorbent of MB dye.

**Key words:** Activated carbon, kinetic studies, adsorption isotherms, methylene blue, neem carbon

## INTRODUCTION

Textile and dyeing industry are among important sources for the continuous pollution of the aquatic environment because they produce approximately 5% of them end up in effluents. The textile and dyeing industries effluents are discarded into rivers, ponds and lakes; they affect the biological life various organisms<sup>1-3</sup>. Dye-containing effluents are undesirable wastewaters because they contain high levels of chemicals, suspended solids and toxic compounds<sup>4,5</sup>. Colour causing compounds can react with metal ions to form substances which are very toxic to aquatic flora and fauna and cause many water borne diseases<sup>6-8</sup>. Adsorption process has been found to be superior technique for treating dye effluents due to simplicity and insensitivity to toxic substance. Although the activated carbon<sup>9,10</sup> was most effective for adsorption of dye, but it has some disadvantages such as (i) high adsorbent cost, (ii) problems of regeneration and difficulties of separation of powdered activated carbon from waste water for regeneration are expensive and hence increasing need for equally effective but commercially low cost sorbents. A wide variety of materials such as animal bone meal<sup>11</sup>, black tea leaves<sup>12</sup>, cocoa<sup>13</sup>, almond shell<sup>14</sup>, mango leaves<sup>15</sup>, saw dust<sup>16</sup>. Methylene blue is one of cationic dyes that most frequently used in industry<sup>17</sup>. Concerning the quantity

and its harmful impacts, it was necessary to make efforts to reduce the dye components before discharging to environment. The removal of methylene blue from wastewater were reported by using numerous methods such as liquid-liquid extraction, reverse osmosis, advanced oxidation process, electro coagulation, electrochemical oxidation, ozonation and membrane filtration. However, adsorption method offers some advantages due to its simple design, high efficiency and low costs with un hazardous by products<sup>18</sup>. The present investigation deals with studies on the removal of dye Methylene Blue (MB) by adsorption on activated carbon Vembu Sulphuric acid Activated Carbon (VSAC) and Vembu Phosphoric acid Activated Carbon (VPAC).

## MATERIALS AND METHODS

**Adsorbate:** Methylene blue ( $C_{16}H_{18}ClN_3S$ ), was obtained from BDH (India).

**Adsorbents:** The Vembu tree (*Azadirachta indica*) waste biomass material was collected from Trichy, Tamil Nadu, the collected plant material was washed and air dried for 15-20 days. The dried material was cut into small pieces for further chemical modification. The ground material was mixed with equal amount of concentrated phosphoric acid/sulphuric acid and stirred for 30 min. The acid-plant material slurry was placed in a beaker and dried at 80°C in a hot air-oven. After 24 h, the thermo chemical reaction between acid and plant materials, it was proceeding by raising the oven temperature to 120°C for 90 min. After cooling, the resulting carbon washed with distilled water until a constant pH of the slurry reached. The wet carbon material was dried at 110°C and sieved into discrete particle size and stored. The adsorbent after phosphoric acid treatment was designated as VPAC and sulphuric acid treated adsorbent designated as VSAC. A stock solution of dye with known concentration (1000 ppm) was prepared. It is diluted to get different required initial concentration of the dye and used in the adsorption experiments. All the chemicals used throughout the study were supplied by so fine chemicals, E.Merck, India etc., double distilled water was used for preparing all of the solutions and reagents. The initial pH was adjusted with prepared 0.1 M HCl or 0.1 M NaOH. All the adsorption experiments were carried out at room temperature ( $30 \pm 1^\circ C$ )<sup>19</sup>.

**Characterization of adsorbent:** Physicochemical characteristics of the adsorbent were studied as per the standard testing methods<sup>20</sup>. The surface morphology of the

adsorbent were visualised via Scanning Electron Microscopy (SEM). The diameter of the composite range was 10  $\mu m$ .

**Effect of initial concentration:** In order to study the effect of initial concentration of the dye by VSAC and VPAC, all the other parameters except initial concentration of dye solutions are kept constant in all bottles. Different initial concentrations of the dye were maintained (for VSAC 100-550 ppm and for VPAC 200-650 ppm). The bottles were placed in a mechanical shaker and shaken vigorously for 30 min. Then, the Optical Density (OD) of the filtrates was measured by using uv-visible spectrophotometer (model: 207). The corresponding equilibrium concentration ( $C_e$ ) was obtained from the standard curve. The readings, the percentage removal and amount adsorbed ( $q_e$  in  $mg L^{-1}$ ) were calculated. The optimum initial concentration was determined<sup>21</sup>.

**Effect of contact time:** In order to study the effect of contact time on the removal of dye by adsorption on VPAC and VSAC, the batch type adsorption experiments were carried out at constant dose of adsorbents and optimum initial concentration at room temperature (30°C) at solution pH and the particle size. All the bottles containing required dose of adsorbents (VSAC and VPAC) were placed in a mechanical shaker. About 50 mL of the dye solution of required optimum initial concentration ( $C_i$ ) was added to each bottle. A stop watch was started simultaneously to note the time. The bottles were withdrawn at different time intervals viz., 5, 10, 15, 20, 25, 30, 35, 40, 45 and 50 min and then the dye solutions was filtered. The initial concentration ( $C_e$ ) of the dye solution was obtained by measuring its optical density (OD). The optimum contact time for the adsorbents (VSAC and VPAC) was fixed as 30 min<sup>22</sup>.

**Effect of dose of adsorbent:** To study the effect of dose of adsorbent on the removal of dye by adsorption on VSAC and VPAC the contact time, initial concentration, pH and temperature are kept constant in all bottles. Different weight of adsorbent where maintained (for VSAC 50-140 mg and for VPAC 150-240 mg). The experiments were carried out of following the general procedure for batch adsorption studies at the optimum initial concentration and contact time for the dye. The equilibrium concentration ( $C_e$ ) of dye solutions was determined. The maximum amount of adsorbent required for maximum removal of dye was determined and fixed as the optimum dose of adsorbent. The percentage removal and amount adsorbed ( $q_e$ ) were calculated<sup>22</sup>.

**Effect of pH:** The other process parameters like initial concentration of dye, contact time and dose of VSAC and VPAC kept constant in all the bottles. The pH of the solution was altered by adding 0.1 M hydrochloric acid and sodium hydroxide from pH 2 to 11. In each case, after the addition of acid or base, the initial pH of the solution was measured by using digital pen pH meter (Hanna instrument, Portugal). After shaking the solutions up to the optimum contact (30 min), the equilibrium concentration of dye solutions ( $C_e$ ) were determined as usual by spectrophotometer method. The percentage removal of dye was calculated using Eq. 1<sup>23</sup>.

**Effect of particle size:** At a particle size range 45-300  $\mu$  the values of amount adsorbed linearly increases with the decrease in particle size of the adsorbent. Decrease in the particle size would lead to increase in surface area and the increase in the adsorption opportunity at the outer surface of the ACs. Besides adsorption at the outer surface of the carbon there is also the possibility of intra-particle diffusion from the outer surface into the pores of the material.

**Adsorption experiments:** An accurately weighed quantity of the dye (MB) was dissolved in double distilled water to prepare the stock solution (1000 mg L<sup>-1</sup>). The percentage purity of the dye was taken into consideration while preparing the stock solutions. Adsorption experiments were carried out at room temperature (30 $\pm$ 1 $^\circ$ C) under batch mode<sup>24</sup>. Experimental solutions of desired concentration were obtained by successive dilution. All the other chemicals used in this study were of reagent grade and obtained commercially. Double distilled water was employed for preparing all the solutions and reagents. Thermostatic incubator shaker (Neolab, India) was used to maintain the temp (30 $\pm$ 1 $^\circ$ C). The concentrations of the MB solution was analyzed by measuring its absorbance at  $\lambda_{max} = 544$  nm using UV-Visible Spectrophotometer (ELICO Semi Micro Spectrophotometer, (Model, No. 207) India.

Exactly 50 mL of dye solution of known initial concentration ( $C_i$ ) was shaken at constant agitation speed (200 rpm) with required dose of adsorbent of a fixed particle size (90 micron) for a specific period of contact time. The pH of the dye solution was adjusted by adding either 1 M HCl (or) 1 M NaOH solution and the pH values of dye solutions were noted with digital pen pH meter (Hanna instruments, Portugal). After equilibration, the final concentration ( $C_f$ ) of MB was measured by using a UV-Visible Spectrophotometer

(ELICO-Semi micro spectrophotometer, Model No. 207 India). The values of percentage removal of dye and amount adsorbed ( $q$  in mg g<sup>-1</sup>) were calculated using the following relationships<sup>25</sup>:

$$\text{Percentage removal} = 100 (C_i - C_e)/C_i \quad (1)$$

$$\text{Amount adsorbed (q)} = (C_i - C_e)/m \quad (2)$$

where,  $C_i$  and  $C_e$  are the initial and equilibrium (final) concentration of dye (in mg L<sup>-1</sup>), respectively and  $m$  is the mass of adsorbent, in g L<sup>-1</sup>.

## RESULTS AND DISCUSSION

**Characterization of adsorbents:** The surface morphology of the VSAC and VPAC adsorbents were visualized via Scanning Electron Microscopy (Fig. 1). Porous active centers clearly visualized in Fig. 1a and 1c. Figure 1b and 1d showed MB completely adsorbed VSAC and VPAC active sites.

**Effect of initial concentration:** The effect of initial concentration of dye on the extent of removal of MB (in terms of percentage removal) on VSAC and VPAC adsorbent was shown in Fig. 2. At different initial concentrations of the dye (for VSAC 100-550 ppm (300 ppm) and for VPAC 200-300 ppm (400 ppm) at fixed dose of adsorbent (VSAC and VPAC) and contact time (30 min). From the figure the percentage removal of dye was found to decrease with increase of initial concentration of MB. This indicated that there exists a reduction immediate solute adsorption, owing to the lack of available active sites required for the high initial concentration of MB. Similar results have been reported in literature on the extent of removal of dyes<sup>26</sup>. At lower concentrations, all dye molecules present in the adsorption medium could interact with the binding sites, therefore higher percentage of removal was obtained. This is already reported in literature<sup>26,27</sup>.

**Effect of contact time:** The effect of contact time on the amount of dye adsorbed ( $q$ , in mg g<sup>-1</sup>) was studied at the optimum initial concentration of dye (Fig. 3). The amount of MB adsorbed by these carbons was increased and reached a constant value with the increase in contact time<sup>28</sup>. The decrease in the removal of dye adsorbed after reaching a constant value (in some cases) may be due to the desorption process. The increase in extent of removal of dye after a particular contact time is less and hence it was fixed as the optimum contact time.

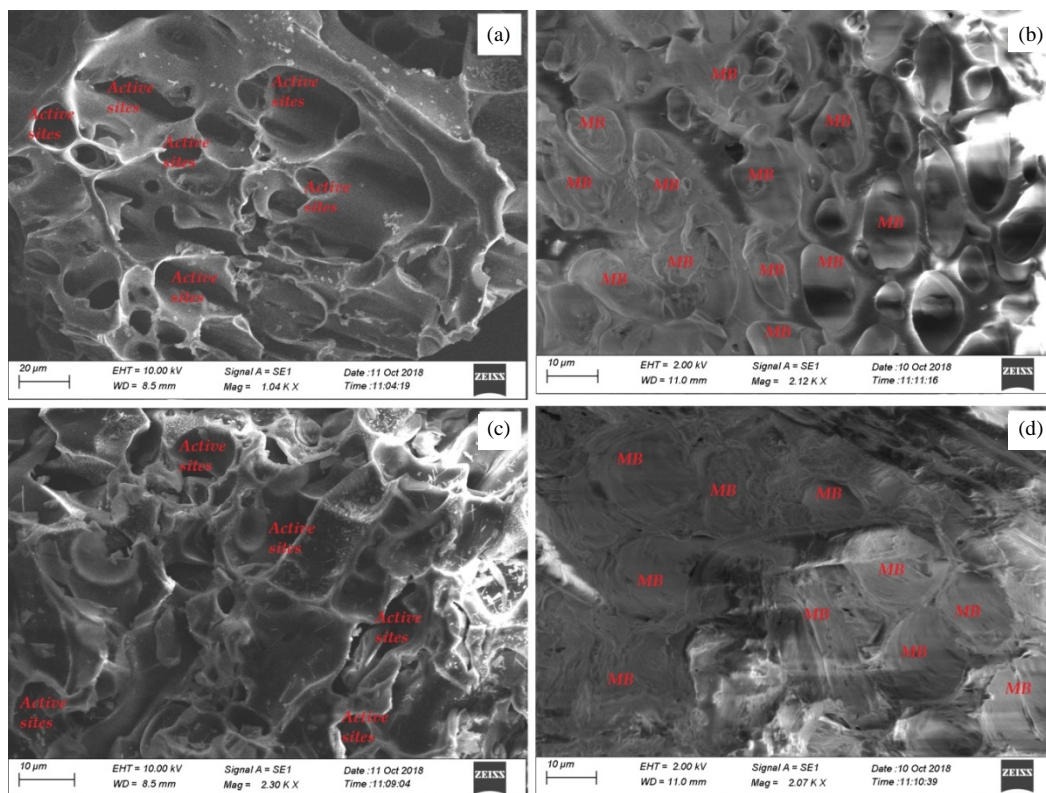


Fig. 1: SEM micrographs of (a) Pure VSAC, (b) MB adsorbed by VSAC, (c) Pure VPAC and (d) MB adsorbed by VPAC

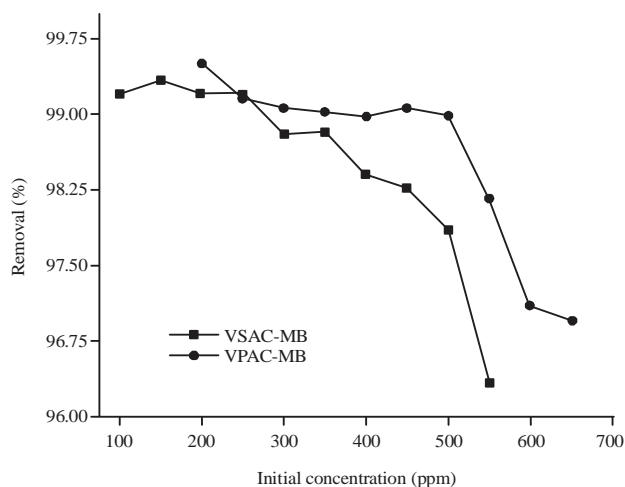


Fig. 2: Effect of initial concentration

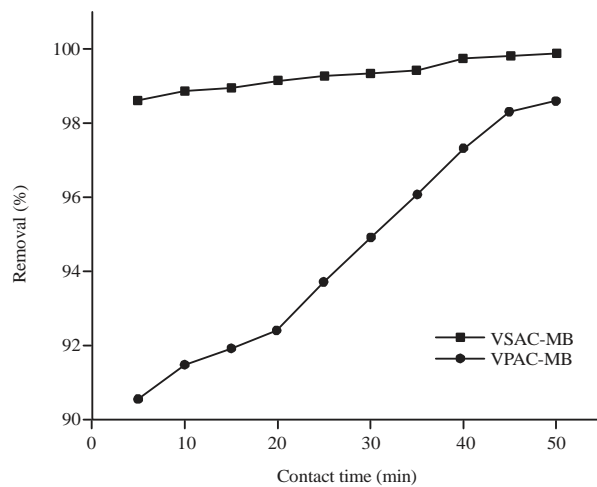


Fig. 3: Effect of contact time

**Effect of dose:** The relative extent of removal of MB (in terms of  $q$ ) is found to be insignificant beyond the dose  $2 \text{ g L}^{-1}$  for adsorbents, which fixed as the optimum dose of adsorbent. The amount of dye adsorbed was observed to vary exponentially in accordance with a fractional power term of

the dose of adsorbent i.e.,  $(\text{dose})^{-n}$  where  $n = \text{fraction}$ . The plots of  $\log(\text{dose})$  vs  $\log(\% \text{ removal})$  are found to be linear ( $r \approx 1.0$ ). The value of %R increased exponentially with increase in dose of adsorbent (Fig. 4). This may be due to the increase in availability of surface active sites resulting from the

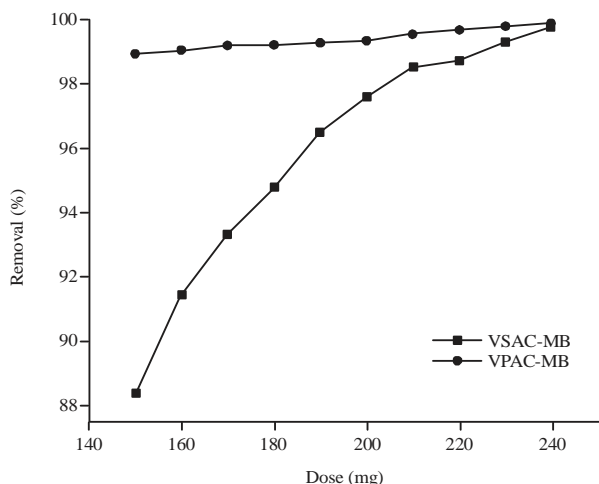


Fig. 4: Effect of dose

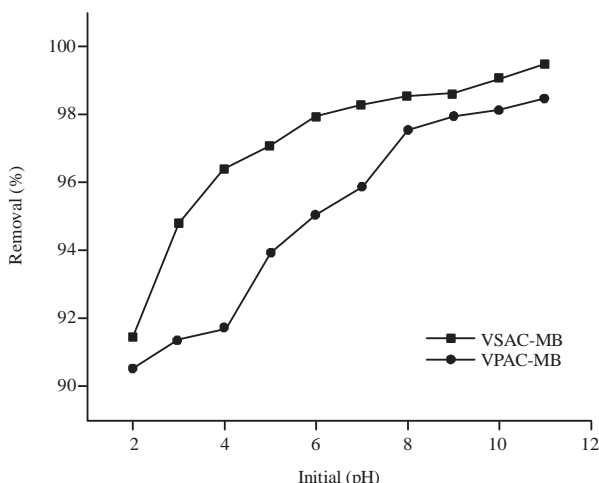


Fig. 5: Effect of initial pH

increased dose and conglomeration of the adsorbent<sup>26</sup>. This suggests that the adsorbed species/solute may be either blocked the access to the internal pores or cause particles to aggregate and thereby resulting in decrease in the availability of active sites for adsorption<sup>29</sup>. Similar observations have been noticed for the removal of dyes<sup>30,31</sup>.

**Effect of initial pH:** The effect of initial pH of the dye solution on the amount of dye adsorbed was studied by varying initial pH of dye solution and keeping the other process parameters as constant. The high and low initial pH of the dye solution increased the amount of dye solution adsorbed (Fig. 5). This result is in harmony with the literature reports<sup>32</sup>, the final pH of the dye (MB) solution after adsorption was found by decreases slightly (range: 0.3-0.5 pH units), due to adsorption

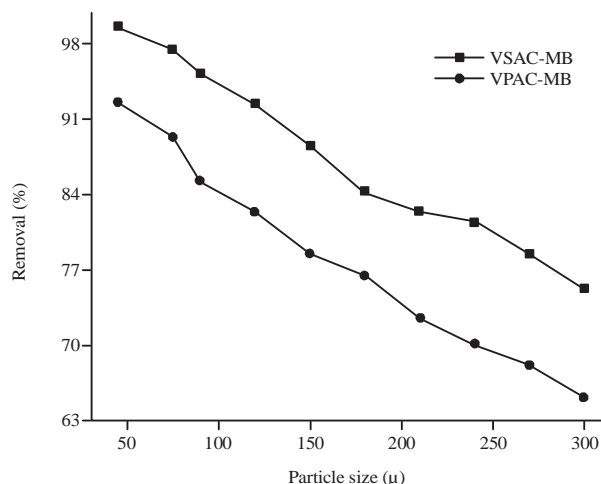


Fig. 6: Effect of particle size

of the neutral form of dye molecule. The change in initial pH values of dye solution significantly affect the adsorption characteristics of anionic dye indicating that removal of MB (neutral dye) is enhanced by acidic solution<sup>33</sup>. Similar type of behaviour is also reported for the adsorption of the dye at different adsorbents<sup>34</sup>.

**Effect of particle size:** The effect of particle size on the amount of MB dye adsorbed was studied by varying only the particle size of ACs as, 45, 75, 90 to 300 microns (Fig. 6), but VSAC was not used since its particle size is uniform and constant at 90 micron. The amount of MB 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. There exists a linear relationship between the amount of dye adsorbed and particle size, as evidenced by the r - value close to unity. Similar observations were reported for the adsorption of dyes<sup>35-37</sup>.

**Adsorption isotherm:** In order to determine the adsorption potential, the study of sorption isotherm is essential in selecting an adsorbent for the removal of dyes<sup>38</sup>. The adsorption data were analyzed with the help of Freundlich<sup>39</sup> and Langmuir<sup>40</sup> isotherms.

$$\text{Freundlich isotherms: } \log q = \log k + (1/n) \log C_e \quad (3)$$

$$\text{Langmuir isotherms: } (C_e/q) = (1/Q_0 b) + (C_e/Q_0) \quad (4)$$

where, k and 1/n are the measures of adsorption capacity and intensity of adsorption, respectively. q is the amount dye adsorbed per unit mass of adsorbent (in mg g<sup>-1</sup>) and C<sub>e</sub> is the

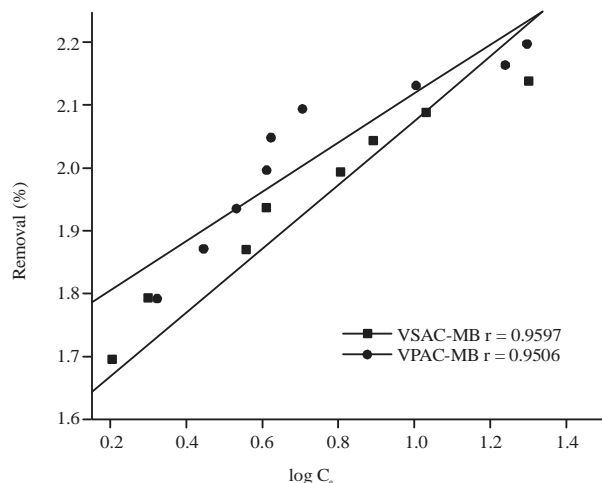


Fig. 7: Freundlich adsorption isotherm for the removal of MB onto VSAC and VPAC

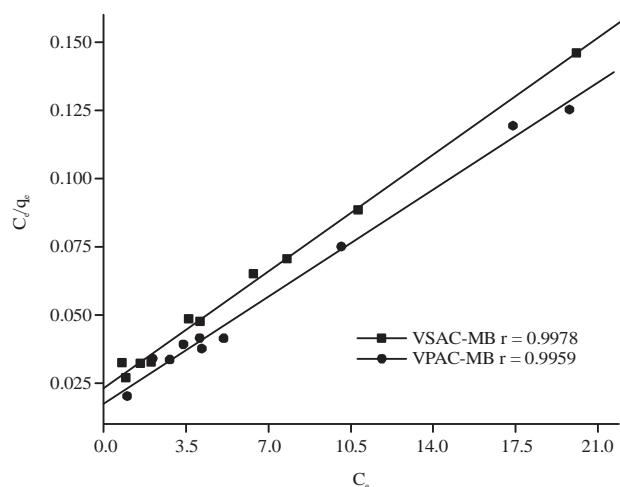


Fig. 8: Langmuir adsorption isotherm for the removal of MB onto VSAC and VPAC

equilibrium concentration of dye (in mg L<sup>-1</sup> or ppm); Q<sub>0</sub> and b are Langmuir constants, which are the measures of monolayer adsorption capacity (in mg g<sup>-1</sup>) and surface energy (in g L<sup>-1</sup>), respectively. The adsorption data were fitted to the isotherm equations by carrying out correlation analysis and the values of slope (1/n and 1/Q<sub>0</sub>) and intercept (log K and 1/Q<sub>0</sub>b) were obtained.

The values of Freundlich and Langmuir constants obtained from the linear correlation between the values of (i) log q<sub>e</sub> and log C<sub>e</sub> (ii) (C<sub>e</sub>/q<sub>e</sub>) and C<sub>e</sub>. They are found to be linear (Fig. 7 and 8). The applicability of Langmuir isotherm indicates the formation of mono-layer and also nature of adsorption

Table 1: Results of correlation analysis on testing the applicability of Adsorption isotherm

S.No	Parameters	VSAC	VPAC
1	<b>Freundlich isotherm</b>		
	Slope (1/n)	0.348	0.457
	Intercept (logk)	18.25	9.452
	r-value	0.9597	0.9506
2	<b>Langmuir isotherm</b>		
	Slope (1/Q <sub>0</sub> )	0.087	0.079
	Intercept1 (Q <sub>0</sub> b)	57.26	45.26
	r-value	0.9978	0.9959
	Q <sub>0</sub> (mg g <sup>-1</sup> )	157.25	78.26
	b (g L <sup>-1</sup> )	5.782	6.254
	R <sub>L</sub> = 1/(1+C <sub>0</sub> b)	0.028	0.023

process. In order to compare the validity of each model a normalised standard deviation, Δq(%) is calculated using the following equation:

$$\Delta q (\%) = 100 \times [ (\sum [(q_t^{exp} - q_t^{cal})/q_t^{exp}]^2) / (n - 1) ]^{1/2} \quad (5)$$

where, the superscripts, exp. and cal. are the experimental and calculated values of q<sub>t</sub> viz., the amount adsorbed at different time t and n is the number of measurements. The Δq (%) values are also given in Table 1. Based on the low values of Δq (%), it is concluded that the adsorption of MB can best be described by the Langmuir adsorption isotherm. This indicates the applicability of Langmuir isotherm and the mono-layer coverage on the surface. The mono-layer adsorption capacities (Q<sub>0</sub>) of the adsorbents are found to be the order:

$$VPAC < VSAC$$

Adsorption capacity of VPAC is better and nearer to VSAC. Further, the essential characteristics of the Langmuir isotherm can be described by a separation factor, R<sub>L</sub>, which is defined by the following equation<sup>41</sup>:

$$R_L = [1 / (1 + bC_i)] \quad (6)$$

where, R<sub>L</sub> is the separation factor, C<sub>i</sub> and b are the initial concentration of dye (in mg L<sup>-1</sup> or in ppm) and Langmuir constant (in g L<sup>-1</sup>). The value of R<sub>L</sub>, indicates the shape of the isotherm and nature of the adsorption process as given below:

R <sub>L</sub> value	Nature of adsorption process
R <sub>L</sub> > 1	Unfavourable
R <sub>L</sub> = 1	Linear
0 < R <sub>L</sub> < 1	Favourable
R <sub>L</sub> = 0	Irreversible

In the present study, the value of  $R_L$  (0.028 and 0.023) indicated that the adsorption process is favourable for this low cost adsorbent.

**Kinetics of adsorption:** The kinetics and dynamics of adsorption of MB these two adsorbents have been studied by applying the various first order kinetic equations, proposed by Natarajan-Khalaf as cited by Kannan and Vanangamudi<sup>25</sup>, Lagergren as cited by Trivedi<sup>42</sup> and Bhattacharya-Venkobachar<sup>43</sup>.

$$\text{Natarajan and Khalaf equation: } \log ( C_t / C_i ) = ( k / 2.303 ) t \quad (7)$$

$$\text{Lagergren equation: } \log ( q_e - q_t ) = \log q_e - ( k / 2.303 ) t \quad (8)$$

$$\text{Bhattacharya and Venkobachar equation: } \log [ 1 - U ( T ) ] = - ( k / 2.303 ) t \quad (9)$$

where,  $k$  is the first order rate constant ( $\text{min}^{-1}$ ) for adsorption of MB.  $C_i$  and  $C_t$  are the concentration of dye (in  $\text{mg L}^{-1}$  or ppm), 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  $\text{mg g}^{-1}$ ) and at time  $t$ , respectively.

Where

$$U ( T ) = [ ( C_i - C_t ) / ( C_i - C_e ) ] \quad (10)$$

where,  $C_e$  is an equilibrium concentration of OG ( $\text{mg L}^{-1}$ ). The values of (i)  $\log ( C_t / C_i )$ , (ii)  $\log ( q_e - q_t )$  and (iii)  $\log [ 1 - U ( T ) ]$  are linearly correlated with time ( $t$ ). The values of first order rate constant ( $k$ ),  $\Delta q$  (%) and correlation co-efficient ( $r$ -value) are given in Table 2. All the linear correlations are found to be statistically significant, indicating the applicability of these kinetic equations and the first order nature of the adsorption process of MB on these adsorbents. Natarajan and Khalaf kinetic plot for the removal of MB are shown in Fig. 9. The rate of adsorption ( $k$ -value) for VSAC and VPAC are obtained from Lagergren equation and it is found to be almost equal with the value obtained from Bhattacharya and Venkobachar equation (Fig. 10). Hence any one of these kinetic equations could be used in future to calculate  $k$ -value for the adsorption of dyes. Lagergren plots are shown in Fig. 11, based on the high  $r$ -values, which are close to unity and low  $\Delta q$  (%) values, it is concluded that the Lagergren equation is applicable to the kinetics of adsorption of MB.

The high values of correlation co-efficient ( $r$ -values) indicate the applicability of first order kinetic model for the adsorption of MB onto VSAC and VPAC. The  $r$ -values and

Table 2: Results of correlation analysis of adsorption data

S. No.	Parameters	Values	
		VSAC	VPAC
1	<b>Natarajan and Khalaf equation</b>		
	Correlation coefficient ( $r$ )	0.9757	0.9602
	$10^2 k$ ( $\text{min}^{-1}$ )	36.45	25.14
2	<b>Lagergren equation</b>		
	Correlation coefficient ( $r$ )	0.9755	0.9473
	$10^2 k$ ( $\text{min}^{-1}$ )	17.25	9.455
3	<b>Bhattacharya and Venkobachar equation</b>		
	Correlation coefficient ( $r$ )	0.9252	0.9635
	$10^2 k$ ( $\text{min}^{-1}$ )	25.45	12.56
	$\Delta q$ (%)	25.48	12.45

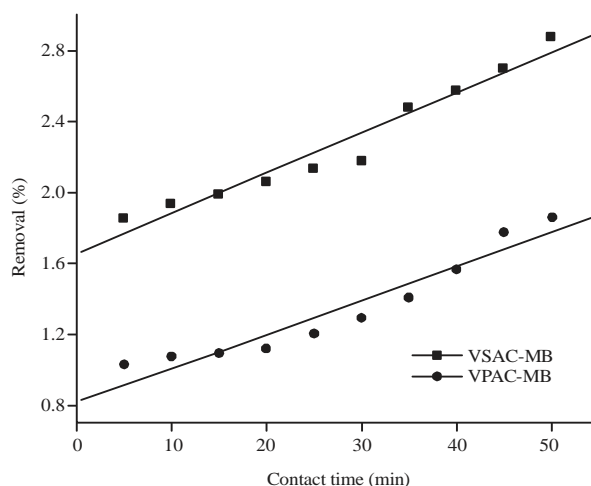


Fig. 9: Natarajan and Khalaf kinetic plot for the removal of MB on VSAC and VPAC

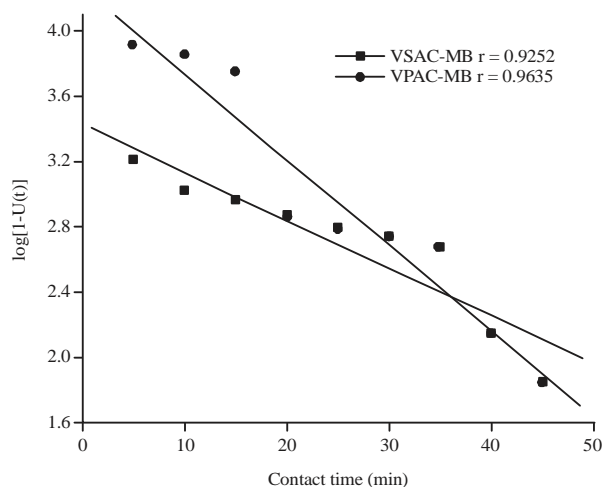


Fig. 10: Bhattacharya-Venkobachar kinetic plot for the removal of MB on VSAC and VPAC



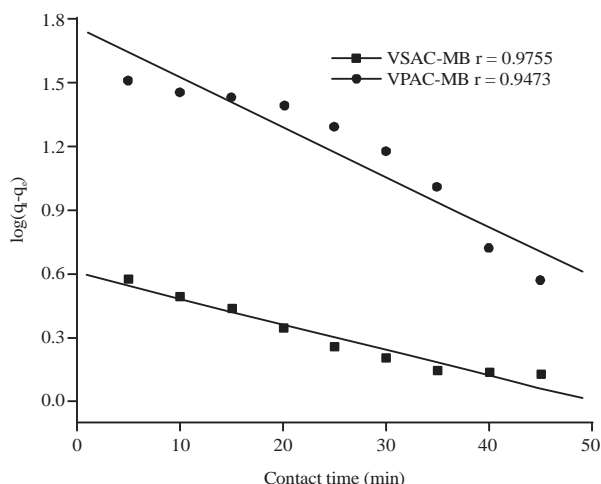


Fig. 11: Lagergren plot for the removal of MB on VSAC and CPAC

k-values (Table 2) obtained from Lagergren (first order) equation for all the adsorbent are found to be almost equal with the values obtained from Bhattacharya and Venkobachar equation. Hence, any one of these kinetic equations could be used to calculate the first order rate constant for adsorption of dyes.

In order to compare the validity of each model more efficiently a normalised standard deviation,  $\Delta q$  (%) is calculated using the following equation:

$$\Delta q (\%) = 100 \times \left\{ \frac{\sum [(q_t^{\text{exp.}} - q_t^{\text{cal.}}) / q_t^{\text{exp.}}]^2}{(n - 1)} \right\}^{1/2} \quad (11)$$

where, the superscripts, exp. and cal. are the experimental and calculated values of  $q_t$  viz., the amount adsorbed at different time  $t$  and  $n$  is the number of observations. The  $\Delta q$  (%) values are also given in Table 2.

Based on the low values of  $\Delta q$  (%), it was concluded that the adsorption of MB can best be described by the Lagergren first order kinetic model.

## CONCLUSION

The present study shows that VSAC and VPAC were effective adsorbents for the removal of MB from aqueous solution. Adsorption followed the Langmuir isotherms. Based on the low values of  $\Delta q$  (%), it was concluded that the adsorption of MB can best be described by the Langmuir adsorption isotherm. Among the various models described, the adsorption of MB can best be described by the Lagergren first order kinetic model. The results would be useful for the fabrication and designing of waste water treatment plants for

the removal of dye. Since the raw material is freely available in large quantities of the treatment method, seems to be economical.

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