



## Enhanced adsorption of methylene blue on modified silica gel: equilibrium, kinetic, and thermodynamic studies

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### ABSTRACT

The present work was undertaken to chemically modify silica gel (SG) with citric acid (CA) to enhance its adsorption power for methylene blue (MB) dye from aqueous solution. Citric acid-modified silica gel (CAMSG) was synthesized thermochemically and was characterized by Fourier transform infrared (FT-IR) spectroscopy, scanning electron microscopy (SEM), and elemental analysis. Influences of various parameters such as adsorbent dose, pH, initial dye concentration, contact time, and temperature on adsorption were studied. Equilibrium data were analyzed using Langmuir, Freundlich, and Temkin isotherm models. Kinetic studies show that the adsorption follows pseudo-second-order kinetics and intraparticle diffusion model. Negative values of Gibb's free energy change ( $\Delta G^\circ$ ) show that the adsorption was feasible and spontaneous in nature and the negative values of enthalpy change ( $\Delta H^\circ$ ) confirm exothermic adsorption.

*Keywords:* Adsorption; Isotherm; Kinetics; Methylene blue; Silica gel

### 1. Introduction

Effluents from several industries (e.g. textile, leather, paper, pulp, plastics, food, etc.) contain huge amount of dyes and pigments used for coloring their final products. Dyes present in waste water may cause serious environmental pollution problems (e.g. reducing light penetration in water and photosynthesis). In addition, some dyes are either toxic or mutagenic and carcinogenic.

Methylene blue (MB) (C.I. Basic blue 9) is a cationic dye (Fig. 1). The toxic effects of MB dye are not that acute but it can cause several adverse effects on human beings e.g. it can damage cardiovascular, cen-

tral nervous system, dermatologic, gastrointestinal, genito-urinary, hematologic system, etc. Hence, it is necessary to remove it from effluent discharge.

Various processes have been proposed for the removal of dyes from aqueous solution. The important ones are biodegradation, adsorption/precipitation [1], coagulation–flocculation [2], chemical oxidation [3], biological oxidation [4], electrochemical oxidation [5], membrane separation [6], and ultrafiltration [7]. Among these, the adsorption process is found to be quite suitable, cheap, and effective for the removal of dyes from aqueous solution. A considerable amount of work has also been published in the literatures regarding the adsorption of MB dye on various adsorbent surfaces such as alumina [8], clay [9–11], zeolite

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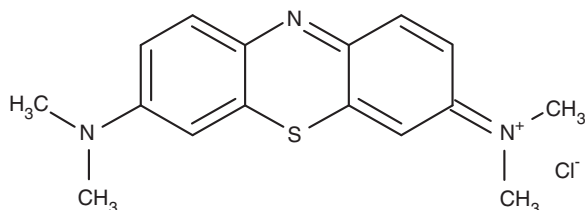


Fig. 1. Molecular structure of MB dye.

[12], peat [13], activated carbon [14], silica [15], organic polymers [16], algae [17], plants wastes [18–20], wood sawdust [21] agricultural waste materials [22,23], nanocomposites [24], organic–inorganic hydrogel composites [25], and nanotubes [26].

Availability of silica is in plenty and its high potential towards the adsorption of organic and inorganic compounds has attracted the attention of many researchers to use it in the removal of pollutants. The presence of –OH groups on the surface of the silica gel (SG) creates a site for the adsorption of cationic dye. In order to get high adsorption, SG was esterified with citric acid (CA) causing an increase in anionic adsorption site (–COO<sup>−</sup>) on SG surface. In the present work, the adsorption properties of the activated silica gel (ASG) (Fig. 2(a)) and citric acid-modified silica gel (CAMSG) (Fig. 2(b)) were investigated with the cationic dye MB as target pollutant from aqueous solution as a function of pH, adsorbent dose, initial dye concentration, contact time, and temperature.

## 2. Methodology

### 2.1. Synthesis of adsorbent

Silica gel G (SG) was obtained from Sigma-Aldrich Chemicals Pvt. Ltd., India. Activation of SG was done by adding 100 mL of 6 M HCl in 20 g of SG and the mixture was allowed to reflux with continuous stirring for 4 h. The resultant material was filtered and washed with deionized water until the pH becomes seven and dried at 150 °C for 5 h. The resulting

material (ASG) was kept in a desiccator for use as an adsorbent.

The SG was modified with CA (Merck, India) by a similar procedure reported by Vaughan et al. [27]. Twenty gram of ASG was added into 0.6 M CA solution (1:12 w/v) in 500 mL flask. The resulting mixture was stirred for 30 min to make slurry, which was poured on stainless steel tray and was kept at 50 °C for 24 h in forced air oven followed by an increase in temperature up to 120 °C, where thermochemical reaction between SG and CA takes place. After cooling, the resulting material was washed with deionized water until the liquid did not turn turbid when 0.1 mol lead (II) nitrate was dropped in. After filtration, the solid was dried in an oven at 70 °C. The resulting material (CAMSG) was kept in a desiccator for use as an adsorbent.

### 2.2. Preparation of cationic dye solutions

MB dye was obtained from Central Drug House Pvt. Ltd., India and was used without further purification. A stock solution of 1,000 mg L<sup>−1</sup> of MB was prepared by dissolving 1 g of MB into 1 L of deionized water. It was subsequently diluted to different concentrations (20, 40, 60, 80, 100, and 150 mg L<sup>−1</sup>) and the pH of dye solutions were maintained by adding 0.1 M HCl or 0.1 M NaOH. The experiments were carried out by taking 50 mL of MB solution and a required amount of adsorbent into 150 mL conical flasks and stirred using a magnetic stirrer (Remi) at a speed of 200 rpm. The adsorption was monitored by determining the concentration of MB in solution by double-beam UV–Visible spectrophotometer (Systronics-2203) at  $\lambda_{\max}$  665 nm.

The percentage of dye removal and quantity of MB adsorbed on adsorbent at the time of equilibrium ( $q_e$ ) was calculated by Eqs. (1) and (2), respectively.

$$\% \text{ MB removal} = 100 (C_0 - C_e)/C_0 \quad (1)$$

$$q_e = (C_0 - C_e)V/W \quad (2)$$

where  $C_0$  and  $C_e$  are the initial and the equilibrium concentrations (mg/L) of MB in solution,  $q_e$  is quantity of MB adsorbed on the adsorbent at the time of equilibrium (mg/g),  $V$  is volume (L) of solution, and  $W$  is mass of adsorbent (g) taken for experiment.

Batch experiments were carried out to determine the effects of pH, adsorbent dose, initial dye concentration, contact time, and temperature by varying the parameter under study and keeping other parameters constant.

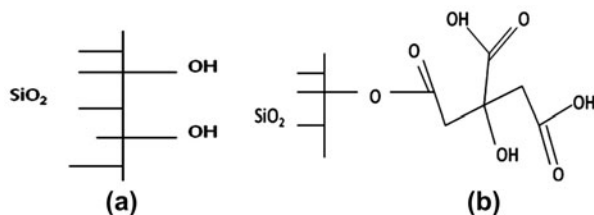


Fig. 2. Activated SG (a) and CAMSG (b).

### 3. Results and discussion

#### 3.1. Characterization of adsorbents

The Fourier transform infrared (FT-IR) spectra of ASG and CAMSG were recorded by FTLA2000 spectrophotometer using KBr disc method and are shown in Fig. 3. FT-IR spectra of ASG showed a band at  $1,027\text{ cm}^{-1}$  which was due to asymmetric stretching of Si–O–Si and the corresponding symmetric stretching was observed at  $805\text{ cm}^{-1}$ . The peak at  $3,473$  and  $1,594\text{ cm}^{-1}$  was due to the stretching and bending of O–H groups and water molecules present in silica. The FT-IR spectra of CAMSG showed a band around  $1,740\text{ cm}^{-1}$  formed due to stretching of C=O group of ester which confirms esterification of ASG with CA. The significant change was observed in surface morphology of ASG after its modification with CA as shown in scanning electron microscopy (SEM) images of ASG (Fig. 4(a)) and CAMSG (Fig. 4(b)). The elemental analysis of ASG and CAMSG was performed by Elementar Vario EL III, and wt.% of C in ASG and CAMSG was found to be 0.51 and 8.62%, respectively.

#### 3.2. Influence of initial pH

The influence of pH on the adsorption of MB dye solution was studied over a range of pH 3–11. As shown in Fig. 5, the adsorption of MB increased from 25 to 77% on ASG and from 30 to 96.4% on CAMSG, while the pH increased from 3 to 7. At lower pH values, the hydrogen ion competes with MB dye and most of the hydroxyl groups of ASG and carboxyl of CAMSG exist in the form of –OH and –COOH, respectively, which reduces the adsorbed amounts for MB dye. At higher pH values, more  $\text{O}^-$  and  $\text{COO}^-$  ions occur, which may enhance electrostatic attraction,

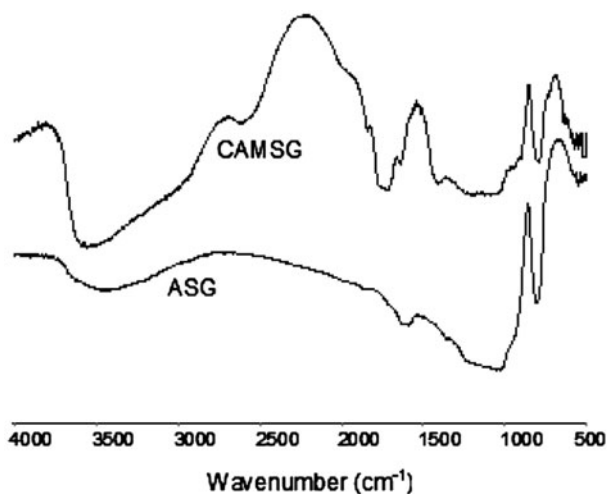


Fig. 3. FT-IR spectra of ASG and CAMSG.

hence the adsorption capacity of the adsorbent for MB dyes increases. The MB adsorption on CAMSG was not much significantly increased after pH 7. So pH 7 was used for further experiments. Higher % removal shown by CAMSG was due to the presence of more anionic ( $\text{COO}^-$ ) (acidic) (Eq. (3)) adsorption site than ASG (Eq. (4)).

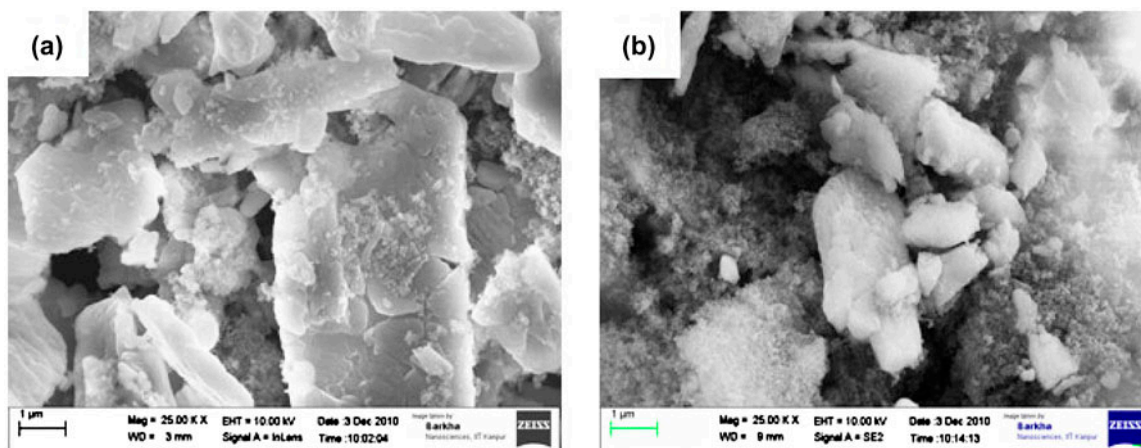
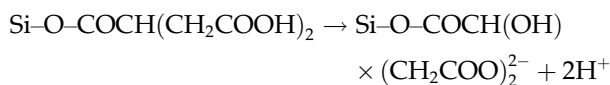
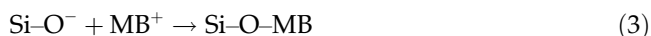
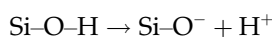


Fig. 4. SEM images of ASG (a) and CAMSG (b).

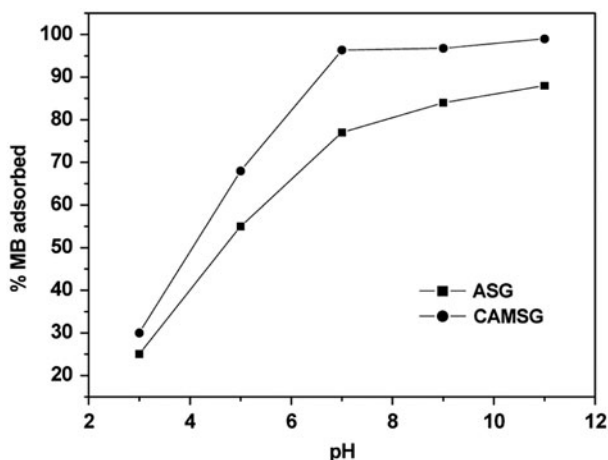
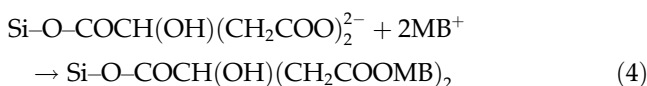


Fig. 5. Influence of pH on adsorption of MB on ASG and CAMSG (adsorbent dose: 2 g/L; initial MB concentration: 100 mg/L; contact time: 100 min; temperature: 303 K).



### 3.3. Effect of adsorbent dose

The effect of adsorbent dose on adsorption was studied using different amounts of adsorbent dosage in the range of 0.5–4 g/L. As shown in Fig. 6, by increasing adsorbent dose frequently from 0.5 to 4 g/L, the adsorption of MB on ASG increased from 40 to 85% and in case CAMSG, it increased from 55 to 97%

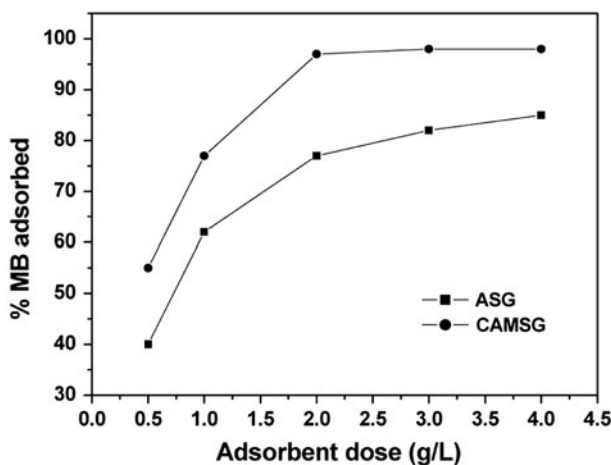


Fig. 6. Influence of adsorbent dose on adsorption of MB on ASG and CAMSG (pH: 7; initial MB concentration: 100 mg/L; contact time: 100 min; temperature: 303 K).

on increasing the dose from 0.5 to 2 g/L. The increase in % adsorption with increase of adsorbent dose was due to the greater availability of the adsorption binding sites. Further increase of adsorbent dose of CAMSG did not cause any significant change because equilibrium was achieved between solution and the solid phase.

### 3.4. Effect of initial dye concentration

To observe the effect of initial dye concentration on adsorption, experiments were conducted over the wide range of initial dye concentrations (20–150 mg/L). Fig. 7 shows that the adsorption of MB decreases from 87.5 to 58.6% and from 98.6 to 96% for ASG and CAMSG, respectively, on increasing the initial dye concentration from 20 to 150 mg/L. The decrease in % MB adsorption with increase in MB concentration is very little in case of CAMSG, which is because of the availability of a large number of adsorption sites. The decrease in % MB adsorption is more in case of ASG due to the availability of lesser number of adsorption sites.

### 3.5. Adsorption isotherms

The analysis of the adsorption process requires relevant adsorption equilibria for understanding the adsorption process better. Adsorption equilibrium describes the nature of adsorbate–adsorbent interaction. In the present study, the equilibrium data were analyzed using the Langmuir, Freundlich, and Temkin isotherm models.

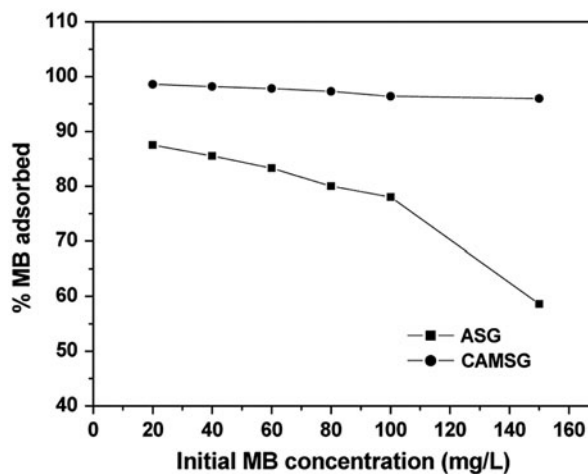


Fig. 7. Influence of initial MB concentration on adsorption of MB on ASG and CAMSG (adsorbent dose: 2 g/L; pH: 7; contact time: 100 min; temperature: 303 K).

3.5.1. Langmuir isotherm model

The saturated monolayer isotherm can be represented by Eq. (5):

$$Q_e = Q_m b C_e / (1 + b C_e) \tag{5}$$

The linearized form of Eq. (5) can be written as [28]:

$$C_e / q_e = 1 / b Q_m + C_e / Q_m \tag{6}$$

where  $q_e$  is the adsorption density (mg/g) at equilibrium of MB dye,  $C_e$  is the equilibrium concentration (mg/L) of the dye in solution,  $Q_m$  is the monolayer adsorption capacity (mg/g), and  $b$  is the Langmuir constant related to the free energy of adsorption (L/mg). The values of  $Q_m$  and  $b$  were calculated from the slopes ( $1/Q_m$ ) and the intercepts ( $1/bQ_m$ ) of the linear plots of  $C_e/q_e$  vs.  $C_e$  (Fig. 8) and are given in Table 1. Linear plots of  $C_e/q_e$  vs.  $C_e$  show that the adsorption isotherm of MB on ASG and CAMSG follows the Langmuir isotherm model. Table 1 shows higher  $Q_m$  value for adsorbent CAMSG which indicates a higher monolayer adsorption capacity for MB than ASG.

3.5.2. Freundlich isotherm model

Freundlich isotherm can be expressed as follows [29]:

$$Q_e = K_f C_e^{1/n} \tag{7}$$

The linearized form of Eq. (7) can be written as follows:

Table 1

Isotherm parameters for MB dye adsorption on ASG and CAMSG

Isotherm parameters	ASG	CAMSG
<i>Langmuir parameters</i>		
$Q_{max}$ (mg/g)	71.42	125.0
$b$ (L/mg)	0.055	0.242
$R^2$	0.994	0.994
<i>Freundlich parameters</i>		
$K_f$ (mg/g (mg/L) <sup>-1/n</sup> )	4.933	24.14
$N$	1.459	1.644
$R^2$	0.986	0.987
<i>Temkin parameters</i>		
$B$	15.28	13.72
$b$ (J/mol)	159.4	183.6
$A$ (L/g)	5.87	0.676
$R^2$	0.980	0.981

$$\ln q_e = \ln K_f + (1/n) \ln C_e \tag{8}$$

where  $K_f$  and  $n$  are Freundlich constants related to adsorption capacity [ $\text{mg g}^{-1} (\text{mg L}^{-1})^{-1/n}$ ] and adsorption intensity of adsorbents. The values of  $K_f$  and  $n$  were calculated from the intercepts ( $\ln K_f$ ) and the slopes ( $1/n$ ) of the plots  $\ln q_e$  vs.  $\ln C_e$  (Fig. 9) and results are presented in Table 1. Linear plots of  $\ln q_e$  vs.  $\ln C_e$  show that the adsorption isotherm of MB on ASG and CAMSG also fitted well in the Freundlich isotherm model. Table 1 shows that higher  $K_f$  value for CAMSG that indicates a higher adsorption capacity for CAMSG and a value of  $n > 1$  indicates favorable adsorption conditions [30,31].

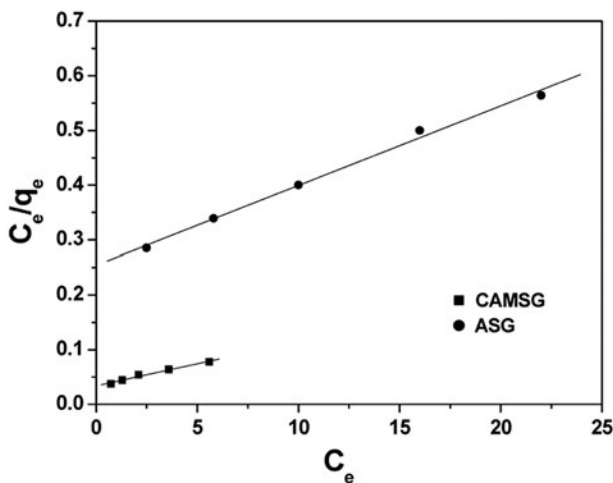


Fig. 8. The Langmuir plots for the adsorption of MB on ASG and CAMSG.

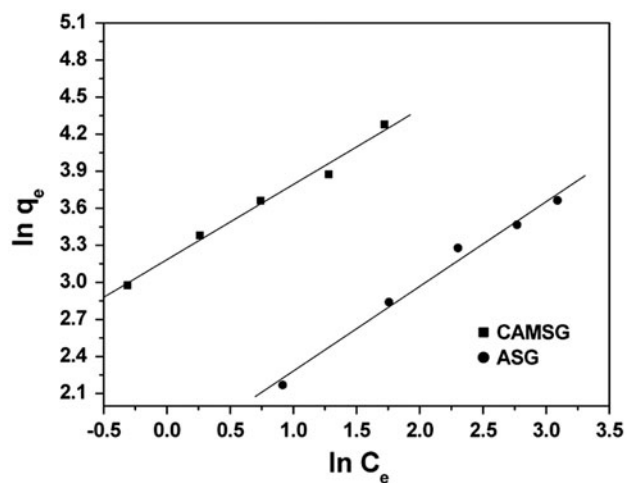


Fig. 9. The Freundlich plots for the adsorption of MB on ASG and CAMSG.

3.5.3. Temkin isotherm model

The derivation of the Temkin isotherm assumes that the fall in the heat of adsorption is linear rather than logarithmic, as implied in the Freundlich equation. The Temkin isotherm can be expressed by Eq. (9) [32]:

$$Q_e = B \ln A + B \ln C_e \tag{9}$$

where  $B = RT/b$ ,  $b$  is the Temkin constant (J/mol) related to adsorption heat,  $T$  is the absolute temperature (K),  $R$  is the gas constant (8.314 J/(mol K)), and  $A$  is the Temkin isotherm constant (L/g).  $B$  and  $A$  can be calculated from the slopes ( $B$ ) and intercepts ( $B \ln A$ ) of the plot of  $q_e$  vs.  $\ln C_e$  (Fig. 10). The Temkin constants  $B$ ,  $b$ , and  $A$  together with the  $R^2$  values are shown in Table 1. The heat of adsorption of all the molecules in the layer would decrease linearly with coverage due to adsorbate/adsorbate interactions.

3.6. Adsorption kinetics

Adsorption kinetics were studied for adsorption of MB of initial concentration range, 20, 40, 60, 80, and 100 mg/L on ASG and 40, 60, 80, 100, and 150 mg/L on CAMSG. Figs. 11 and 12 show that the rate of adsorption decreases with increase in time and after 100 min, equilibrium was achieved.

Several kinetic models have been proposed to clarify the mechanism of a solute adsorption from aqueous solution onto an adsorbent. The rate constant of adsorption was determined from the pseudo-first-order rate expression (Eq. (10)) [33] given by Lagergren:

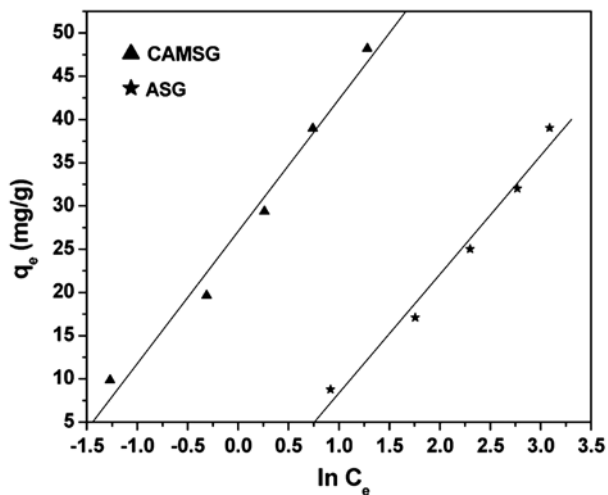


Fig. 10. The Temkin plots for the adsorption of MB on ASG and CAMSG.

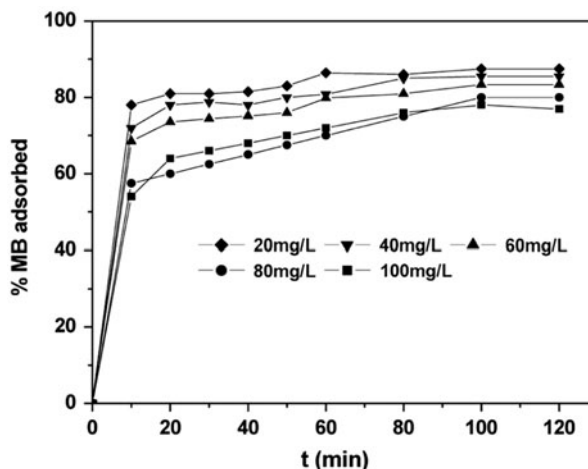


Fig. 11. Sorption kinetics of MB on ASG (adsorbent dose: 2 g/L; pH: 7; temperature: 303 K).

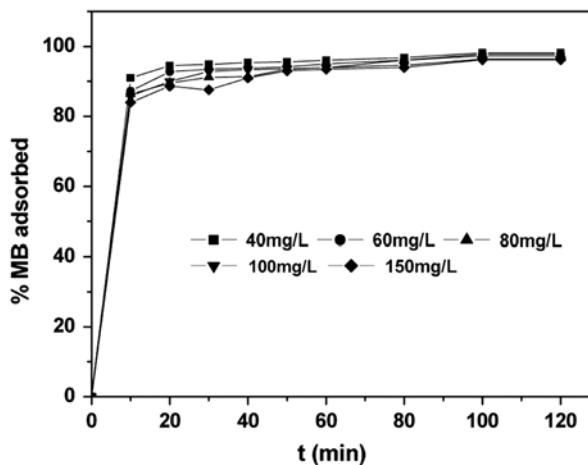


Fig. 12. Sorption kinetics of MB on CAMSG (adsorbent dose: 2 g/L; pH: 7; temperature: 303 K).

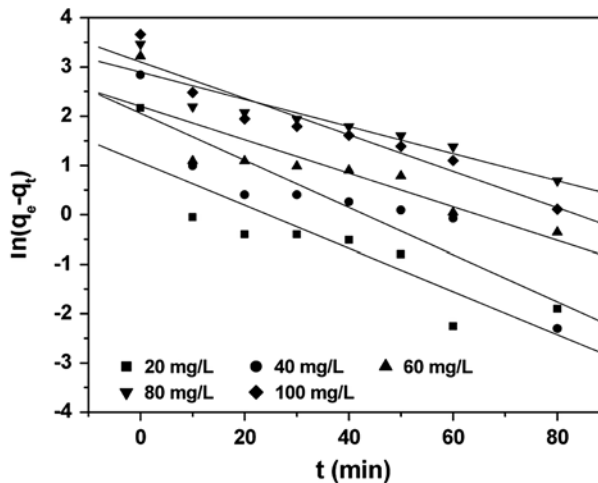


Fig. 13. Pseudo-first-order kinetics plots for adsorption of MB on ASG (adsorbent dose: 2 g/L; pH: 7; temperature: 303 K).

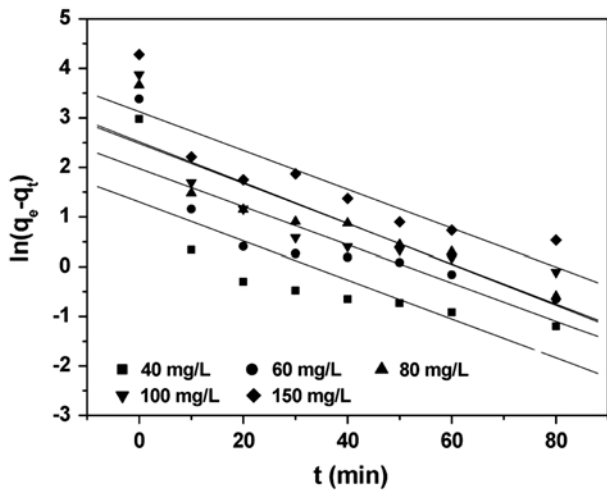


Fig. 14. Pseudo-first-order kinetics plots for adsorption of MB on CAMSG (adsorbent dose: 2 g/L; pH: 7; temperature: 303 K).

$$\ln(q_e - q_t) = \ln q_e - k_{ad}t \tag{10}$$

where  $q_e$  and  $q_t$  are the amount of MB adsorbed at equilibrium and at time  $t$  (mg/g), respectively, and  $k_{ad}$  ( $\text{min}^{-1}$ ) is rate constant of adsorption. The values of the  $k_{ad}$  and  $q_e^{cal}$  were calculated from the slopes ( $-k_{ad}$ ) and the intercepts ( $\ln q_e$ ) of the plots of  $\ln(q_e - q_t)$  vs.  $t$  (Figs. 13 and 14), respectively, and are reported in Table 2. As shown in Table 2, the values of regression correlation coefficients ( $R^2$ ) are not close to unity and a large difference in the values of  $q_e^{cal}$  and  $q_e^{exp}$  for both the adsorbents concluded that the

pseudo-first-order model is not suitable to describe the kinetic profile of the adsorption.

The pseudo-second-order adsorption kinetics [33] may be written as Eq. (11):

$$t/q_t = 1/k_2q_e^2 + t/q_e \tag{11}$$

where  $k_2$  is the rate constant of adsorption ( $\text{g/mg min}$ ),  $q_e$  and  $q_t$  are the amount of MB adsorbed at equilibrium and at time  $t$  (mg/g), respectively. The values of  $k_2$  and  $q_e^{cal}$  were calculated from the intercepts ( $1/k_2q_e^2$ ) and the slopes ( $1/q_e$ ) of the plots of  $t/q_t$  vs.  $t$ . (Figs. 15 and 16), respectively, and are reported in Table 2. The results show that the values of regression correlation coefficients ( $R^2$ ) are close to unity and the values of  $q_e^{cal}$  and  $q_e^{exp}$  are almost equal which confirm that the adsorption of MB on to ASG and CAMSG follows a pseudo-second-order kinetic model.

The mechanism of adsorption can be explained by an intraparticle diffusion model [34]. The equation for intraparticle diffusion can be expressed by Eq. (12):

$$Q_t = k_i t^{0.5} + C \tag{12}$$

where  $k_i$  is the intraparticle diffusion constant ( $\text{mg/g min}^{0.5}$ ) and the intercept ( $C$ ) reflects the boundary-layer effect. The values of  $k_i$  were calculated from the slopes ( $k_i$ ) of the plots of  $q_t$  vs.  $t^{0.5}$  (Figs. 17 and 18), and are presented in Table 2.

Table 2 shows that the rate constant for intraparticle diffusion ( $k_i$ ) increased with the increasing initial MB dye concentration. The driving force of diffusion

Table 2  
Kinetic parameters for MB dye adsorption on ASG and CAMSG

Initial dye concentration	$q_e^{exp}$	Pseudo-first-order			Pseudo-second-order			Intraparticle diffusion		
		$q_e^{cal}$	$k_{ad}$	$R^2$	$q_e^{cal}$	$k_2$	$R^2$	$k_i$	$C$	$R^2$
ASG										
20 mg/L	8.75	2.89	0.043	0.762	8.77	0.067	0.998	0.138	7.382	0.916
40 mg/L	17.10	7.80	0.047	0.818	17.54	0.029	0.999	0.409	13.25	0.860
60 mg/L	25.00	9.00	0.034	0.744	25.64	0.014	0.997	0.616	18.84	0.956
80 mg/L	32.00	18.0	0.027	0.859	32.25	0.0055	0.986	1.321	18.09	0.975
100 mg/L	39.00	22.0	0.037	0.912	40.00	0.0054	0.994	1.669	23.26	0.945
CAMSG										
40 mg/L	19.63	3.60	0.039	0.618	20.00	0.021	0.994	0.171	17.91	0.879
60 mg/L	29.35	7.20	0.038	0.684	29.41	0.015	0.993	0.379	25.62	0.853
80 mg/L	38.95	12.40	0.041	0.791	40.00	0.015	0.999	0.619	32.85	0.983
100 mg/L	48.20	11.97	0.040	0.701	50.00	0.010	0.997	0.678	41.76	0.842
150 mg/L	72.20	22.70	0.039	0.763	71.42	0.010	0.994	1.277	59.75	0.928

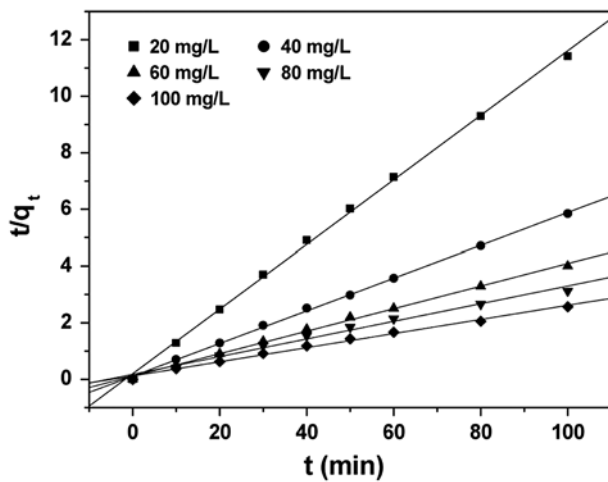


Fig. 15. Pseudo-second-order kinetics plots for adsorption of MB on ASG (adsorbent dose: 2 g/L; pH: 7; temperature: 303 K).

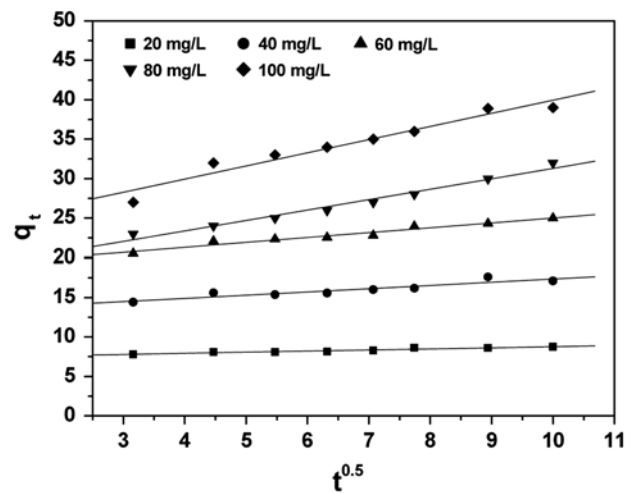


Fig. 17. Intraparticle diffusion plots for the adsorption of MB from aqueous solution on ASG (adsorbent dose: 2 g/L; pH: 7; temperature: 303 K).

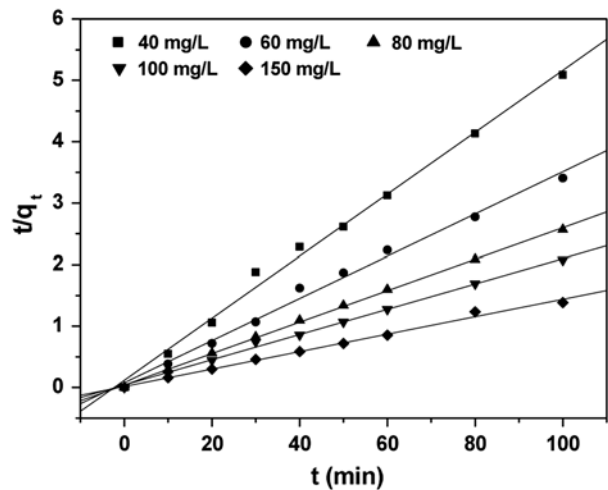


Fig. 16. Pseudo-second-order kinetics plots for adsorption of MB on CAMSG (adsorbent dose: 2 g/L; pH: 7; temperature: 303 K).

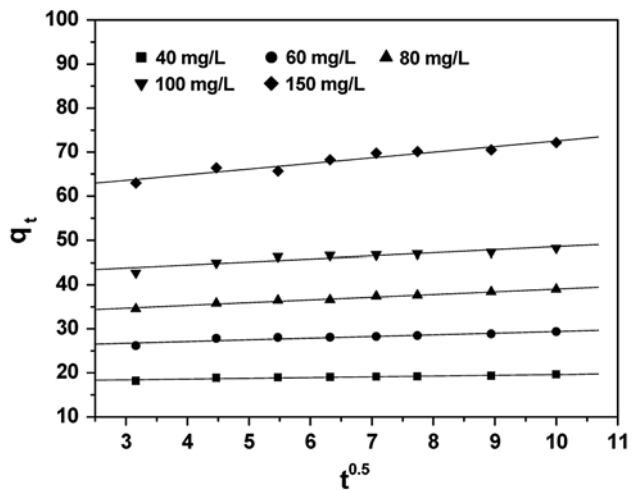


Fig. 18. Intraparticle diffusion plots for the adsorption of MB from aqueous solution on CAMSG (adsorbent dose: 2 g/L; pH: 7; temperature: 303 K).

is very important for adsorption processes. The increase of the initial dye concentration results in an increase in the driving force, which will increase the diffusion rate of MB [35]. Figs. 17 and 18 revealed that the lines of plots are not passing through the origin. Table 2 shows that the values of  $C$  increase with an increase in the initial concentration of MB. Larger the value of  $C$ , greater is the contribution of the surface adsorption in the rate-limiting step, confirms the presence of both surface adsorption and intraparticle diffusion [36].

### 3.7. Thermodynamic studies

To observe the effect of temperature on the adsorption of MB on ASG and CAMSG, experiments were conducted at three different temperatures 303, 313, and 323 K. It was observed that the adsorption decreases with increasing temperature for both the adsorbents which indicates that a low temperature favors MB adsorption onto ASG and CAMSG adsorbent. This may be due to a tendency for the MB molecules to escape from the solid phase to the bulk phase with an increase in temperature of the solution.



Table 3  
Thermodynamic parameters for MB dye adsorption on ASG and CAMSG

Initial dye concentration	$\Delta H^\circ$ (kJ/mol)	$\Delta S^\circ$ (J/mol/K)	$\Delta G^\circ$ (kJ/mol)		
			303 K	313 K	323 K
ASG					
20 mg/L	-41.769	-121.55	-4.939	-3.723	-2.508
40 mg/L	-39.616	-115.64	-4.577	-3.420	-2.248
60 mg/L	-34.228	-99.35	-4.124	-3.131	-2.137
80 mg/L	-25.873	-73.72	-3.535	-2.798	-2.061
100 mg/L	-21.782	-61.62	-3.111	-2.494	-1.878
CAMSG					
40 mg/L	-43.440	-109.82	-10.164	-9.066	-7.968
60 mg/L	-44.953	-116.31	-9.711	-8.547	-7.384
80 mg/L	-41.894	-107.66	-9.273	-8.196	-7.119
100 mg/L	-36.714	-94.11	-8.198	-7.257	-6.316
150 mg/L	-39.408	-103.50	-8.047	-7.012	-5.977

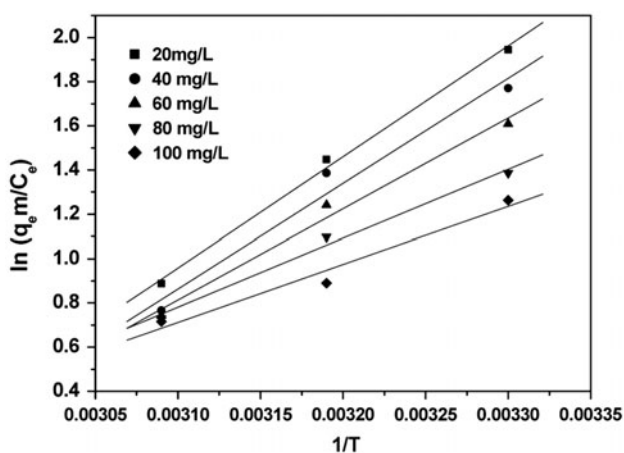


Fig. 19. The plots of  $\ln(q_e m/C_e)$  vs.  $1/T$  for adsorption of MB on ASG (adsorbent dose: 2 g/L; pH: 7; time 100 min).

A similar observation was also reported in the study on the sorption of cadmium onto oxidized granular-activated carbon [37].

Thermodynamic parameters such as enthalpy ( $\Delta H^\circ$ ), entropy ( $\Delta S^\circ$ ) and Gibb's free energy ( $\Delta G^\circ$ ) were determined by Eqs. (13) and (14) [38].

$$\ln(q_e m/C_e) = \Delta S^\circ / R - \Delta H^\circ / RT \quad (13)$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (14)$$

where  $m$  is the adsorbent dose (g/L),  $C_e$  is the equilibrium concentration (mg/L) of the MB in solution,  $q_e$  is the amount of MB adsorbed at equilibrium (mg/g),

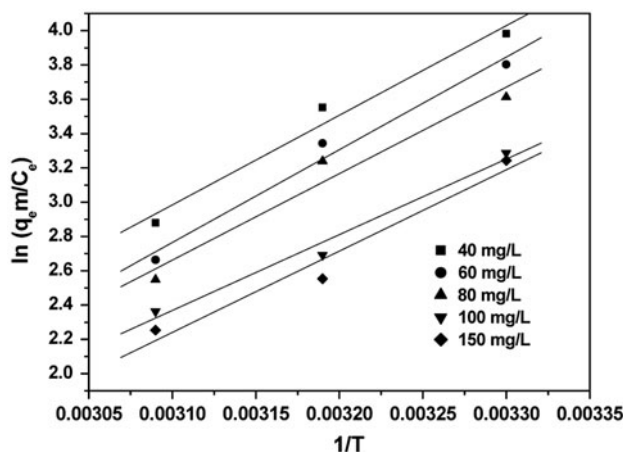


Fig. 20. The plots of  $\ln(q_e m/C_e)$  vs.  $1/T$  for adsorption of MB on CAMSG (adsorbent dose: 2 g/L; pH: 7; time: 100 min).

and  $q_e m$  is the solid phase concentration (mg/L) at equilibrium.  $R$  is the gas constant (8.314 J/mol/K) and  $T$  is the temperature (K).  $\Delta H^\circ$ ,  $\Delta S^\circ$ , and  $\Delta G^\circ$  are changes in enthalpy (J/mol), entropy (J/mol/K), and Gibb's free energy (J/mol), respectively.

The values of  $\Delta H^\circ$  and  $\Delta S^\circ$  were determined from the slopes ( $-\Delta H^\circ/R$ ) and the intercept ( $\Delta S^\circ/R$ ) of the plots of  $\ln(q_e m/C_e)$  vs.  $1/T$  (Figs. 19 and 20). The  $\Delta G^\circ$  values were calculated using Eq. (14). The values of thermodynamic parameters are presented in Table 3. Negative values of  $\Delta G^\circ$  indicate that the adsorption process is feasible and spontaneous in nature. Negative values of  $\Delta H^\circ$  suggest the exothermic nature of adsorption and the negative values of  $\Delta S^\circ$  describe the randomness at the adsorbent–solution interface decreased during the adsorption. The  $\Delta H^\circ$  values obtained for the adsorption of MB on ASG and CAMSG are in the range of  $-21.78$  to  $-41.76$  kJ/mol and  $-39.40$  to  $-44.95$  kJ/mol, respectively, which indicate the presence of both physical and chemical adsorption mechanism. However, the chemisorption was more predominant on CAMSG than ASG.

#### 4. Conclusions

The present study shows that the CAMSG is a potential adsorbent for the effective removal of MB dye from aqueous solution. The pH 7 and temperature 303K was found to be optimum for adsorption study. The removal% of MB dye increased from 75 to 95% after chemical modification of SG with CA. Equilibrium study shows that the adsorption of MB on ASG and CAMSG are fitted well in Langmuir and Freundlich isotherm models. Kinetics study shows that the rate of adsorption decrease with increase in

time and equilibrium was achieved within 100 min of contact time. It was found that the pseudo-second-order kinetics fitted better than the pseudo-first-order kinetics. Two mechanisms intraparticle diffusion and surface sorption were found to be involved in the rate-determining step of the sorption of the MB dye from solution. The thermodynamic study shows that the adsorption process was exothermic and spontaneous in nature for both the adsorbents.

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