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Enhanced adsorption of malachite green dye on chemically modified silica gel

Atul Kumar Kushwaha, Neha Gupta, M.C. Chattopadhyaya*

Environmental Chemistry Research Laboratory, Department of Chemistry, University of Allahabad, Allahabad (U.P.), India

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ABSTRACT

Present work was undertaken to chemically modified silica gel with oxalic and citric acid to enhance its adsorption power for malachite green (MG) dye from aqueous solution. Oxalic acid and citric acid modified silica gel was synthesized thermochemically and characterized by Fourier transform infra red (FT-IR) spectroscopy. The influences of various parameters such as adsorbent dose, pH, initial dye concentration, contact time and temperature on adsorption were studied. The adsorption data was analyzed using the Langmuir and Freundlich isotherm models. Kinetic studies show that the adsorption follows pseudo-second order kinetics and intraparticle diffusion model. Negative values of Gibbs free energy change (ΔG°) show that the adsorption was feasible and spontaneous and positive values of enthalpy change (ΔH°) confirm endothermic adsorption.

Key words: Adsorption; Isotherm; Kinetics; Malachite green; Silica gel; Thermodynamics.

INTRODUCTION

Effluents from several industries (e.g. textile, leather, paper, pulp, plastics, food etc.) contain huge amount of dyes and pigments which are used for colouring their final products [1]. Dyes present in waste water may cause serious environmental pollution problems (e.g. reducing light penetration in water and photosynthesis).

Malachite green (Fig. 1) (MG) is a triphenyl methane dye and used for the colouring cotton, wool, silk, paper, leather etc. It is also used as parasiticide, fungicide, antiprotozoan and antibacterial agent [2]. This dye is recommended for only external applications, its oral consumption is toxic, hazardous and carcinogenic due to presence of nitrogen [3]. It is known to be highly toxic to mammalian cells and acts as a tumor-enhancing agent. It decreases food intake, growth and fertility rates, causes damage to liver, spleen, kidney and heart, inflicts lesions on skin, eyes, lungs and bones. Hence it is necessary to remove it from effluent discharge.

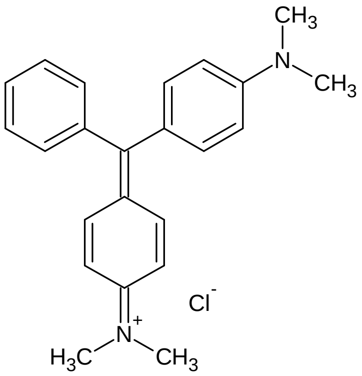
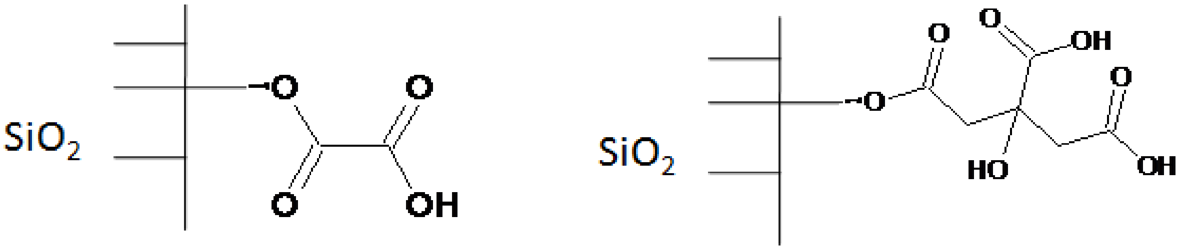


Fig. 1 Molecular structure of malachite green dye

Various processes have been proposed for the removal of dyes from aqueous solution. The important ones are biodegradation, adsorption [4], coagulation and precipitation [5], chemical oxidation, photooxidation [6], membrane separation, and microfiltration [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 MG dye on various adsorbent surfaces such as alumina and silica [8], zeolite [9], activated carbon [10, 11], bagasse fly ash [12], algae [13], agro-industry waste [14], agricultural waste materials [15], nanocomposites [16].

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 removal of pollutants. The presence of –OH groups on the surface of the silica gel (SG) create site for adsorption of cationic dye. In order to get high adsorption, SG was esterified with oxalic acid (OA) and citric acid (CA), increase anionic adsorption site ($-COO^-$) on SG surface. In the present work, the adsorption properties of the activated silica gel (ASG), oxalic acid modified silica gel (OAMSG) (Fig. 2a) and citric acid modified silica gel (CAMSG) (Fig. 2b) were investigated with the cationic dye MG as target pollutant from aqueous solution as a function of pH, adsorbent dose, initial dye concentration, contact time and temperature.



a ***b***

Fig. 2 (a) Oxalic acid modified silica gel (b) Citric acid modified silica gel

EXPERIMENTAL SECTION

Synthesis of adsorbent

Silica gel G (SG) was purchased from Sigma Aldrich Chemicals Pvt. Ltd., India. Activation of SG was done by adding 6M HCl (100 mL) 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 become 7 and dried at 150 °C for 5 hours [17]. Resulting activated silica gel (ASG) was kept in dessicator for use as adsorbent.

The activated silica gel was modified with oxalic and citric acid by similar procedure reported by Vaughan et al. [18]. The 20 g of ASG was taken in 500 mL flask and 0.6 M oxalic or citric acid solution was added (1:12 w/v of silica gel / oxalic or citric acid). Resulting mixture was stirred for 30 min to make the slurry, which was poured on stainless steel tray and was kept at 50 °C for 24 h. in forced air oven followed by increase in temperature up to 120 °C, where thermochemical reaction between silica gel and oxalic or citric acid takes place. After cooling the resulting material was washed with deionized water until the liquid did not turn turbidity when 0.1 mol lead nitrate was added drop wise. After filtration solid was dried in oven at 70 °C. Resulting materials (OAMSG, CAMSG) were kept in dessicator for use as adsorbent.

Preparation of cationic dye solutions

MG dye was obtained from Merck Pvt. Ltd., India and was used without further purification. Stock solution (1000 mgL^{-1}) of MG was prepared by dissolving 1 g of MG into 1 L of deionised water. The experimental solution of desired concentration was obtained by successive dilution of stock solution. The pH of all these solutions was maintained by adding 0.1 M HCl or 0.1 M NaOH. The experiments were carried out by taking 50 mL of MG solution and required amount of adsorbent into 150 mL conical flasks and stirred on magnetic stirrer (Remi) at the speed of 200 rpm. The adsorption was monitored by determining the concentration of MG in solution using double beam UV-Visible spectrophotometer (Systronics -2203) at λ_{max} 617 nm.

Percentage of dye removal and quantity of MG adsorbed on adsorbent at the time of equilibrium (q_e) was calculated using Eq. 1 and 2 respectively.

$$\% \text{ MG removal} = 100\,(C_0 - C_e) / C_0 \qquad (1)$$
$$q_e = (C_0 - C_e)\,V / W \qquad (2)$$

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

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

RESULTS AND DISCUSSION

FT-IR study

The FT-IR spectra of ASG, OAMSG and CAMSG were recorded by spectrophotometer (ABB-FTLA2000) using KBr disc method and are shown in Fig. 3.

The spectra of ASG showed a band at 1027 cm^{-1} due to asymmetric stretching of Si–O–Si and corresponding symmetric stretching was observed at 805 cm^{-1}. The Si–O–Si bending mode was positioned at 499 cm^{-1}. The peak at 3473 cm^{-1} and 1594 cm^{-1} was due to stretching and bending mode of O-H groups present in silica, respectively. The FT-IR spectra of OAMSG and CAMSG shows a band around 1740 cm^{-1} which was due to stretching of C=O group of ester and confirms esterification of ASG with oxalic and citric acid.

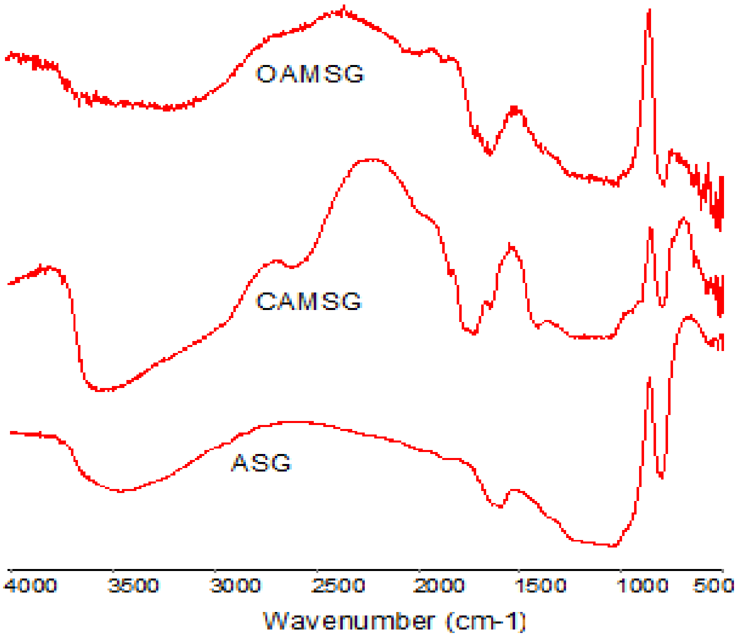


Fig. 3 FT-IR spectra of ASG, OAMSG and CAMSG

Influence of pH

The influence of pH on adsorption of MG dye was studied over the pH range 3-11. For this 60 mg/L of MG solution containing 2 g/L adsorbent was used and the temperature was maintained at 303 K and the contact time kept 30 min.

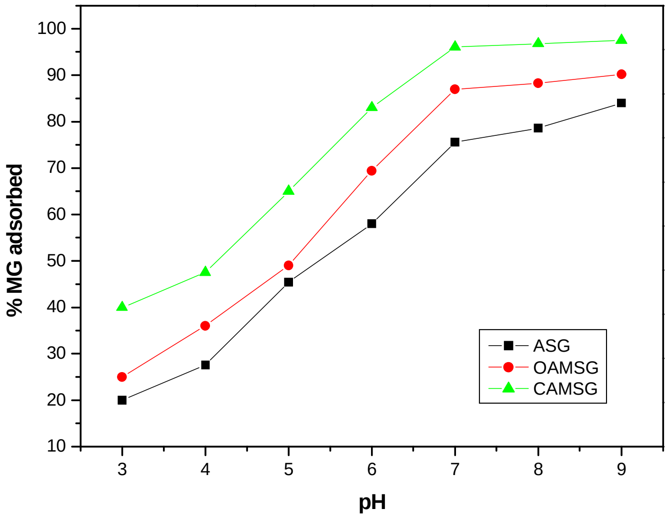


Fig. 4 Influence of pH on adsorption of MG dye on ASG, OAMSG and CAMSG

As shown in Fig. 4, the adsorption of MG increased from 20 to 75.6 % on ASG, 25 to 87 % on OAMSG and 40 to 96.1 % on CAMSG while pH increased from 3 to 7. At lower pH values, hydrogen ion competes with MG dye and most of the hydroxyl groups of ASG and carboxyl of OAMSG and CAMSG exist in the form of –OH and –COOH respectively, which reduce the adsorption of MG dye. At higher pH values, more $–O^-$ and $–COO^-$ ions occur, which may enhance electrostatic attraction and the adsorption capacity of adsorbent for MG dye. Higher % removal shown by CAMSG was due to presence of more anionic ($–COO^-$) adsorption sites.

Further increase in pH causes degradation of dye due to formation of soluble hydroxyl complexes [19]. Therefore, all subsequent studies were carried out at pH 7.

Effect of adsorbent dose

The effect of adsorbent dose on adsorption was studied using different amount of adsorbent dosage in the range of 0.5 g/L to 4 g/L keeping the initial concentration of MG at 60 mg/L while the pH was fixed at 7, temperature at 303 K with contact time 30 min.

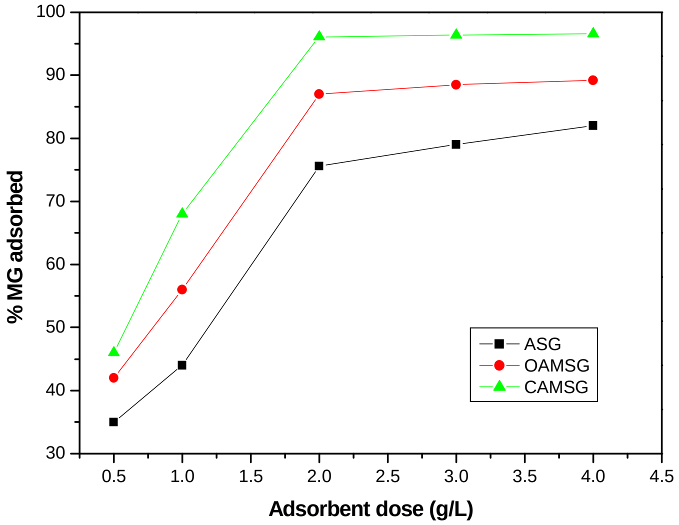


Fig. 5 Effect of adsorbent dose on adsorption of MG on ASG, OAMSG and CAMSG

As shown in Fig. 5 by increasing adsorbent dose from 0.5 to 4 g/L the adsorption of MG increases from 35 to 82 % on ASG and 42 to 89.2 % on OAMSG. Adsorbent dose increased from 0.5 to 2 g/L, adsorption of MG on CAMSG increased from 46 to 96.1 %. This increase is 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 solid phase.

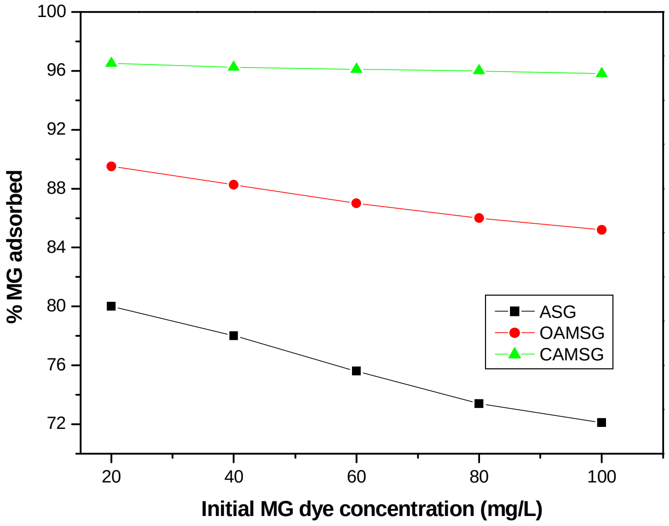


Fig. 6 Influence of initial MG concentration on adsorption of MG on ASG, OAMSG and CAMSG.

Influence 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 (20-100 mg/L) at constant adsorbent dose (2 g/L), pH (7), temperature (303 K) and contact time (30 min). The Fig. 6 shows that the % removal of MG decreases with increasing initial MG dye concentration. The adsorption of MG decreases from 80 to 72.1 %, 89.5 to 85.2 and 96.5 to 95.8 % for ASG, OAMSG and CAMSG, respectively on increasing initial dye concentration from 20 to 100 mg/L. This decrease in % adsorption of MG is due to lesser availability of the adsorption site.

Adsorption isotherms

The analysis of the sorption process requires the relevant adsorption equilibria for better understanding the adsorption process. Sorption equilibrium describes the nature of adsorbate-adsorbent interaction. In the present study the equilibrium data were analyzed using the Langmuir and Freundlich isotherms.

Langmuir isotherm model

The saturated monolayer isotherm can be represented by following Eq. 5

$$q_e = Q_m b C_e/(1 + bC_e) \qquad (3)$$

The linearized forms of Eq. 3 can be written as follows [20]

$$C_e / q_e = 1/bQ_m + C_e/Q_m \qquad (4)$$

where q_e is the adsorption density (mg/g) at equilibrium of MG dye, Ce 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. 7) and presented in Table 1.

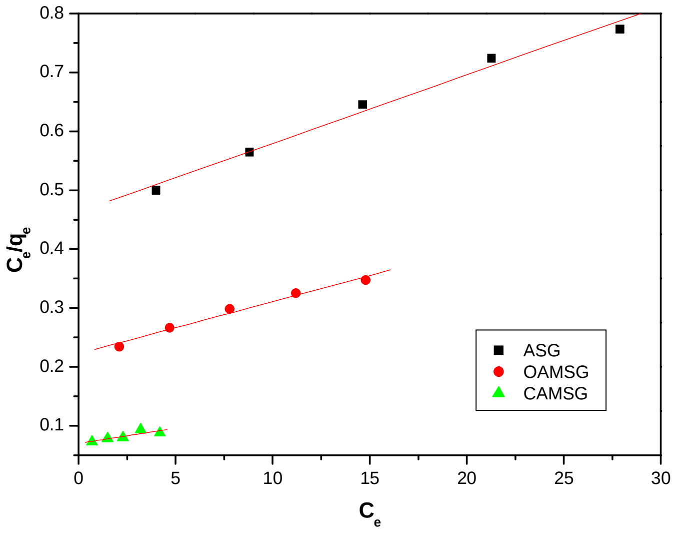


Fig. 7 The Langmuir plots for the adsorption of MG on ASG, OAMSG and CAMSG.

Linear plots of C_e/q_e vs. C_e show that the adsorption isotherm of MG on ASG, OAMSG and CAMSG follows the Langmuir isotherm model. Table 1 show higher Q_m value for adsorbent CAMSG, indicates higher monolayer adsorption capacity for MG than ASG and OAMSG.

Freundlich isotherm model

Freundlich isotherm can be expressed as follows [21]

$$q_e = K_f C_e^{1/n} \qquad (5)$$

The linearized forms of Eq. 5 can be written as follows:

$$\ln q_e = \ln K_f + (1/n) \ln C_e \qquad (6)$$

where K_f and n are Freundlich constants related to sorption capacity [mg g^{-1} (mg $L^{-1})^{-1/n}$] and sorption 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. 8) and the results are presented in Table 1. Linear plots of ln q_e vs. ln C_e show that the adsorption isotherm of MG on ASG, OAMSG and CAMSG also fitted well in the Freundlich isotherm model. The values of $n > 1$ indicate favourable adsorption conditions [22, 23].

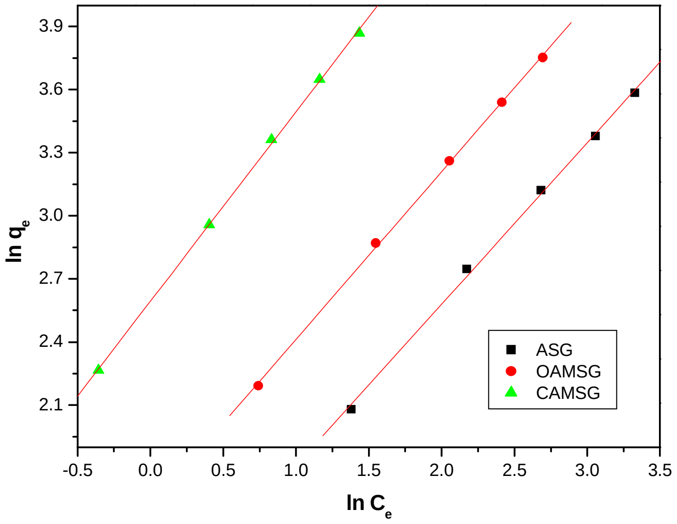


Fig. 8 The Frendlich plots for the adsorption of MG on ASG, OAMSG and CAMSG.

Table 1 Isotherm parameters for MG adsorption on ASG, OAMSG and CAMSG

Adsorbents	Langmuir isotherm parameters			Freundlich isotherm parameters		
	Q_{max}	b	R^2	K_f	n	R^2
ASG	90.9	0.0238	0.987	2.83	1.303	0.998
OAMSG	125	0.036	0.981	5.02	1.25	0.999
CAMSG	200	0.072	0.756	13.36	1.109	0.999

Sorption kinetics

Sorption kinetics were studied for adsorption of MG of initial concentration 60 mg/L. Fig. 9 shows that the rate of sorption decreases with increase of time and after 30 min, equilibrium was achieved.

Several kinetic models have been proposed to clarify the mechanism of a solute sorption from aqueous solution on to an adsorbent. The rate constant of adsorption was determined from the pseudo-first order rate expression (Eq.7) [24] given by Lagergren:

$$\ln (q_e - q_t) = \ln q_e - k_{ad}t \qquad (7)$$

where q_e and q_t are the amount of MG adsorbed at equilibrium and at time t (mg/g) respectively and k_{ad} (min^{-1}) is rate constant of adsorption.

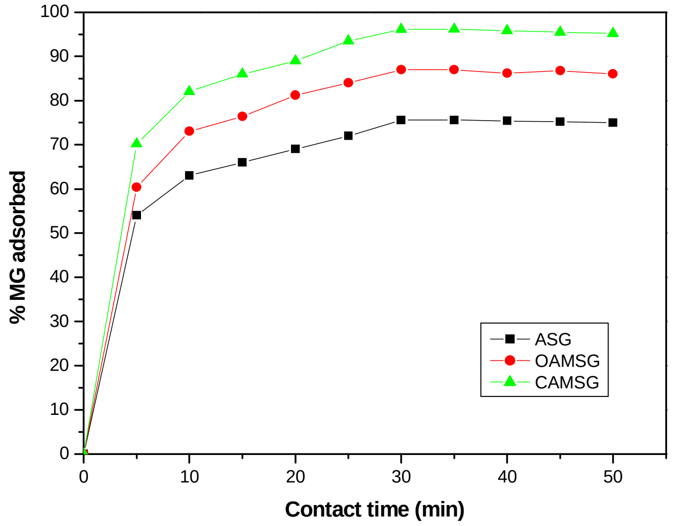


Fig. 9 Sorption kinetics of MG on ASG, OAMSG and CAMSG (adsorbent dose: 2 g/L; pH: 7; Temperature: 303 K).

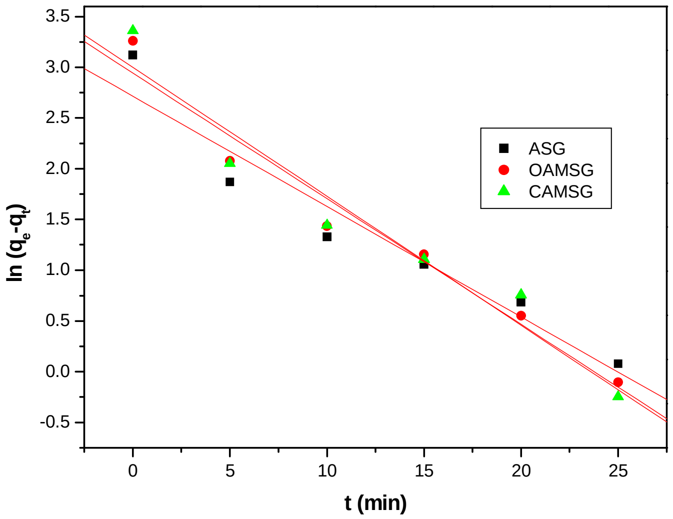


Fig. 10 Pseudo-first order kinetics plots for adsorption of MG on ASG, OAMSG and CAMSG (adsorbent dose: 2 g/L; pH: 7; Temperature: 303 K).

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 (Fig.10) respectively and reported in Table 2. Table 2 shows that there is a large difference in the values of q_e^{cal} and q_e^{exp} and the regression correlation coefficients (R^2) are not close to unity for all the three adsorbents. This concluded that the pseudo-first order model was not suitable to describe the kinetic profile of the adsorption.

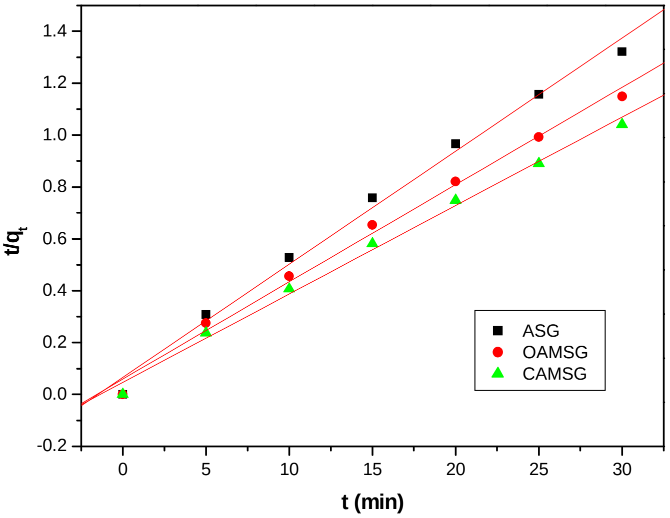


Fig. 11 Pseudo-second order kinetics plots for adsorption of MG on ASG, OAMSG and CAMSG (adsorbent dose: 2 g/L; pH: 7; Temperature: 303 K).

The pseudo-second order adsorption kinetics [24] may be written as follows:

$$t/q_t = 1/k_2 q_e^2 + t/q_e \qquad (8)$$

where k_2 is the rate constant of adsorption (g/mg/min), q_e and q_t are the amount of MG adsorbed at equilibrium and at time t (mg/g) respectively. The values of k_2 and q_e^{cal} were calculated from the intercepts ($1/k_2 q_e^2$) and the slopes ($1/q_e$) of the plots of t/q_t vs. t. (Fig.11) respectively, reported in Table 2. The results show that the values of q_e^{cal} and q_e^{exp} are almost equal and regression correlation coefficients (R^2) are closer to unity which confirm that adsorption of MG on to ASG, OAMSG and CAMSG follows pseudo-second order kinetic model.

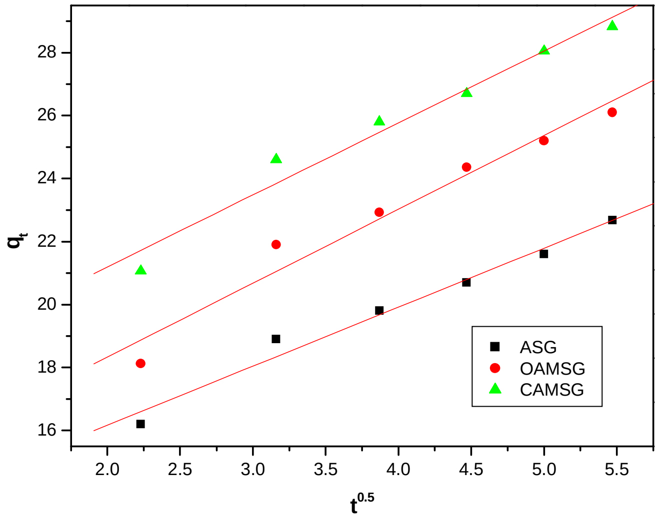


Fig. 12 Intraparticle diffusion plots for the removal of MG from aqueous solution on ASG, OAMSG and CAMSG (adsorbent dose: 2 g/L; pH: 7; Temperature: 303K).

The mechanism of adsorption can be explained by intraparticle diffusion model [25]. The equation for intraparticle diffusion can be expressed as follows:

$$q_t = k_i\, t^{0.5} + C \qquad (9)$$

where k_i is the intraparticle diffusion rate constant (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. $t^{0.5}$ (Fig.12) and presented in Table 2. Fig.12 shows that the lines of plots are not passing through the origin. Larger the value of C, greater is the contribution of the surface sorption in the rate-limiting step, confirms the presence of both surface adsorption and intraparticle diffusion [26].

Table 2 Kinetic parameters for MG adsorption on ASG, OAMSG and CAMSG

Adsorbents	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	I	R^2
ASG	22.68	15.10	0.108	0.932	23.2	0.028	0.992	1.87	12.42	0.979
OAMSG	26.1	18.97	0.123	0.964	27.0	0.023	0.992	2.34	13.64	0.962
CAMSG	28.85	20.10	0.127	0.945	29.4	0.025	0.994	2.28	16.62	0.968

Thermodynamic studies

To observe the effect of temperature on the adsorption of MG on ASG, OAMSG and CAMSG, experiments were conducted at three different temperatures 303, 313 and 323 K. It was observed that the adsorption increases with increasing temperature for all the three adsorbents, which indicates a high temperature favours MG removal by sorption onto the ASG, OAMSG and CAMSG sorbents.

Thermodynamic parameters such as change in enthalpy (ΔH°), entropy (ΔS°) and Gibb's free energy (ΔG°) were determined using Eq. 10 and 11 [27].

$$\ln (q_e m/C_e) = \Delta S°/R - \Delta H°/RT \qquad (10)$$
$$\Delta G° = \Delta H° - T\Delta S° \qquad (11)$$

where m is the adsorbent dose (mg/L), C_e is the equilibrium concentration (mg/L) of the MG in solution and q_em 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). ΔH°, ΔS° and ΔG° are changes in enthalpy (J/mol), entropy (J/mol/K) and Gibb's free energy (J/mol), respectively.

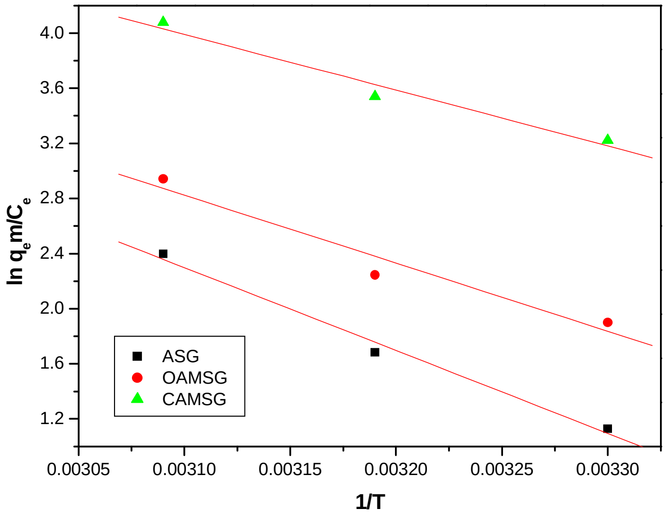


Fig. 13 The plots of ln $q_e m/C_e$ vs. 1/T for adsorption of MG on ASG, OAMSG and CAMSG (adsorbent dose: 2 g/L; pH: 7; Time 30 min).

The values of ΔH° and ΔS° were determined from the slopes (-ΔH°/R) and the intercepts (ΔS°/R) of the plots of ln ($q_e m/C_e$) vs. 1/T (Fig.13). The ΔG° values were calculated using Eq. (11). The values of thermodynamic parameters are presented in Table 3.

The negative values of ΔG° indicate that the adsorption process is feasible and spontaneous in nature. The positive values of ΔH° suggest the endothermic nature of adsorption and the positive values of ΔS° described the randomness at the adsorbent-solution interface increased during the sorption.

Table 3 Thermodynamic parameters for MG adsorption on ASG, OAMSG and CAMSG

Adsorbents	ΔH°	ΔS°	ΔG°		
			303 K	313 K	323 K
ASG	33.680	137.59	-8.009	-9.385	-10.761
OAMSG	41.079	150.81	-4.616	-6.124	-7.632
CAMSG	50.017	174.17	-2.756	-4.498	-6.239

CONCLUSION

The present study shows that the pH 7 was favourable for the adsorption study. The % removal of MG dye increased from 75 to 86 % after chemical modification of SG with OA and 75 to 96 % after chemical modification of SG with CA. Equilibrium studies show that the adsorption of MG on ASG, OAMSG and CAMSG are fitted well in Langmuir and Freundlich isotherm models. Kinetics studies shows that the rate of adsorption decreases with increase in time and equilibrium was achieved within 30 min. It was found that the pseudo-second order kinetic is better fitted than the pseudo-first order kinetics. Two mechanisms, intraparticle diffusion and surface adsorption were found to be involved in the rate determining step of the adsorption of the MG dye from solution. The thermodynamic study shows that the adsorption process was endothermic and spontaneous in nature for all the three adsorbents.

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