



Removal of Malachite Green from Aqueous Solution by Activated Carbon Developed from Cocoa (*Theobroma cacao*) Shell: Kinetic and Equilibrium Studies

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ABSTRACT

The removal of Malachite Green (MG) by Cocoa (*Theobroma cacao*) Shell Activated Carbon (CSAC) was investigated in present study. Adsorption studies were performed by batch experiments as a function of process parameters such as initial pH, contact time, initial concentration and adsorbent dose. A comparison of kinetic models applied to the adsorption of MG on CSAC was evaluated for the pseudo-first order and pseudo-second order kinetic models. Results showed that the pseudo-second order kinetic model was found to correlate the experimental data well. The experimental equilibrium adsorption data was represented with Langmuir, Freundlich, Tempkin, Dubinin-Radushkevich and Flory-Huggins isotherms. The experimental data obtained in the present study indicated that activated carbon developed from cocoa shell can be attractive options for dye removal from waste water.

Key words: Adsorption, Malachite Green, Cocoa shell, Kinetics, Isotherm.

INTRODUCTION

Dyeing industries are the largest sector of chemical industries in India. Over 7×10^5 tons and approximately 10000 different types of dyes and pigments are produced worldwide annually¹. Dyes used as colouring materials are toxic to aquatic organisms when unspent substances are discharged into the environment. It is estimated that 10% of the dye is lost in the effluent during the dyeing process². The treatment process for removing dyes from waste water comprises ozonation³, coagulation⁴, ultrafiltration⁵, oxidation⁶,

photocatalytic degradation⁷ and adsorption⁸. Adsorption has been found highly efficient for removal of color from wastewater in terms of initial cost, ease of operation and simplicity of design⁹. Adsorption using activated carbon is the most widely used technique because of excellent adsorption efficiency for organic compounds¹⁰. Activated carbon is a highly porous material; therefore it has an extremely high surface area for contaminant adsorption. The equivalent surface area of 1 pound of activated carbon ranges from 60 to 150 acres¹¹. In recent years due to high cost of activated carbon, attention has prompted interest in the production

of carbon based adsorbents from agricultural waste products¹². The production of activated carbon from wastes saves the non renewable natural resources and producing a valuable product with potential applications in pollution control¹³.

In the present study it was proposed to evaluate the capacity of cocoa shell, an agricultural waste as a precursor for the preparation of activated carbon material. This adsorbent was successfully used to remove Malachite Green (MG) dye from aqueous solution. Batch studies were carried out involving processes such as initial dye concentration, contact time, pH and adsorbent dosage. Equilibrium and kinetic data analysis were conducted to understand sorption process and optimization of various parameters in dye recovery was investigated.

EXPERIMENTAL

Preparation of adsorbent

Cocoa shell collected from local agricultural field was air -dried and carbonized with concentrated sulphuric acid in the weight ratio of 1:1(w/v). The resulting black product was kept in muffle furnace maintained at 550°C for 7 hours. The carbon obtained was washed with distilled water until it became free from excess acid and dried at 110°C for overnight in a hot air oven. The carbonized material was taken out, grounded to fine powder and sieved to 150µm size and stored in a vacuum dessicator.

Preparation of dye solution

Stock solution of Malachite Green (Chemical formula: $C_{23}H_{25}N_2Cl$, M.W.:364.92, C.I. 42000, CAS no.:569-64-2) was prepared by dissolving 1g of dye in 1L of distilled water to give concentration of 1000 mg/L. The serial dilutions say 20, 40, 60, 80 mgL⁻¹ were made by diluting the dye stock solution in accurate proportions. The pH of dye solutions were adjusted with 0.1M NaOH or 0.1M HCl using a pH meter.

Batch Adsorption experiments

Adsorption experiments were carried out in temperature controlled orbital shaker at a constant speed of 125 rpm at 35°C using 250ml conical flasks containing 100mg of CSAC with 50ml of dye

solutions. All the experiments (except the study of pH effect) were carried out at pH of 7.0. After agitating the flasks for predetermined time intervals samples were withdrawn from the flasks. The adsorbents were separated from the solution by centrifugation (REMI make) at 2000rpm for 10 minutes¹⁴. The absorbance of the supernatant solution was estimated to determine the residual dye concentration¹⁵, measured at $\lambda_{max} = 617nm$ spectrophotometrically using Elico make UV-Visible spectrophotometer.

The adsorption isotherms were specified at pH 7 for adsorption of MG onto CSAC at 35°C. Adsorption data obtained from the effect of initial concentration and contact time were employed in testing the applicability of isotherm and kinetic equations, respectively.

RESULTS AND DISCUSSION

Effect of agitation time and initial concentration

To study the effect of dyes initial concentration and contact time on adsorption uptake, MG solution with initial concentrations 20-80 mgL⁻¹ were agitated with 100mg of CSAC. The experimental results of sorption of MG on to CSAC at various initial concentrations are shown in Figure 1. The adsorption at different dye concentrations was rapid at the initial stages and then gradually decreases with the progress of adsorption until the equilibrium was reached. The rapid adsorption at the initial contact time can be attributed to the availability of the positively charged surface of activated carbon. As shown in Fig. 1, the contact time needed for MG solution to reach equilibrium was 120min. The results indicated that there was no change in the sorption capacity after 120mins, therefore 180mins was fixed as the agitation time for isotherm studies. The adsorption capacity at equilibrium (q_e) increased from 9.09 to 50.00 mgg⁻¹ with an increase in the initial concentrations from 20 – 80 mgL⁻¹.

Effect of adsorbent dosage

In order to investigate the effect of adsorbent mass on the adsorption, a series of adsorption experiments was carried out with different adsorbent dosages at initial concentration of 40mg/l without changing the volume of dye

solution (50ml) with constant speed of 125rpm for 3 hours (Fig. 2). Similarly the pH (7.0) and temperature (35°C) was kept constant. The results follow the expected pattern, in which the percentage sorption increased with increased adsorbent dosage. The increase in carbon dosage is due to adsorbent dosage or due to conglomeration of carbons at higher doses¹⁶.

Effect of pH

The pH is one of the most important factor for controlling the adsorption of dye on to the adsorbent. The pH of the system exerts influence on the adsorptive uptake of adsorbate molecules. The effect of solution pH was studied between 2 to 10, initial pH controlled by the addition of 0.1M HCl or 0.1M NaOH and agitated with 100mg of adsorbent for 3 hours. The effect of initial pH of dye

solution on the adsorption of MG for initial dye concentration of 40 mg/L was illustrated in Fig. 3. As the pH increases from 2 to 7, the percent adsorption increases from 33.33 to 86.67% and from pH 7 to 10 the percent adsorption decreases from 86.67 to 40.00%. The maximum uptake of MG by CSAC was obtained at pH 7.0. So, pH 7.0 was chosen for the study on adsorption isotherm.

Adsorption Isotherms

The five most common adsorption isotherm models were used to fit the equilibrium adsorption data. These are Langmuir, Freundlich, Tempkin, Dubinin-Radushkevich and Flory-Huggins model.

Langmuir isotherm

Langmuir adsorption isotherm model was

Table 1: Results of various isotherm plots for the adsorption of MG onto CSAC

Models	Isotherm constants			
	Q_m (mg/g)	b (10^{-3} L mg $^{-1}$)	R^2	
Langmuir	37.03	12.4	0.989	
Freundlich	k_f (mgg $^{-1}$)	$1/n$	R^2	
	1.9817	0.504	0.982	
Tempkin	α (L mol $^{-1}$)	β	b	R^2
	0.36	20.87	122.7	0.988
Dubinin-Radushkevich	q_m (mgg $^{-1}$)	K_{DR} (10^{-7} mol 2 J $^{-2}$)	E (kJmol $^{-1}$)	R^2
	1	3.161	0.4	0.947
Flory-Huggins	K_{FH} (10^3 L g $^{-1}$)	n	ΔG° %(kJmol $^{-1}$)	R^2
	40.95	11.35	-10.62	0.953

Table 2: Calculated kinetic parameters for the adsorption of MG onto CSAC

Concentration (mg/L)	20	40	60	80
Pseudo-first order kinetics				
$k_1 \times 10^{-2}$ (min $^{-1}$)	2.07	2.53	2.07	2.53
$q_{e(cal)}$ (mg/g)	6.95	12.33	17.86	24.71
$q_{e(exp)}$ (mg/g)	9.09	16.00	23.68	30.00
R^2	0.994	0.988	0.963	0.990
Pseudo-second order kinetics				
$k_2 \times 10^{-3}$ (g/mg min)	2.5	1.8	1.73	1.03
$q_{e(cal)}$ (mg/g)	11.62	20.00	25.00	35.7
h	0.34	0.7	1.08	1.3
R^2	0.996	0.998	0.999	0.999

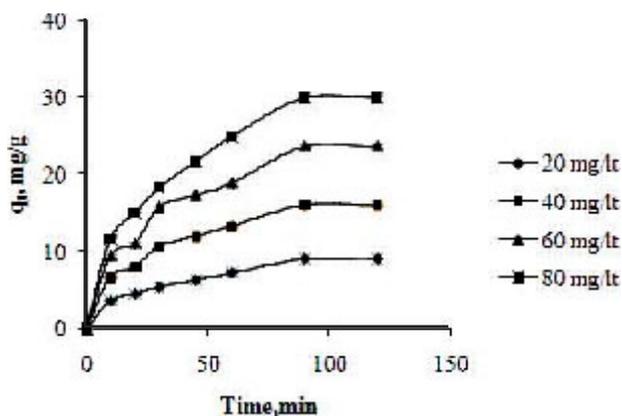


Fig. 1: Effect of agitation time on adsorption: Initial concentration variation (Temp = 308K, Initial pH = 7, Adsorbent dosage = 100mg/50ml)

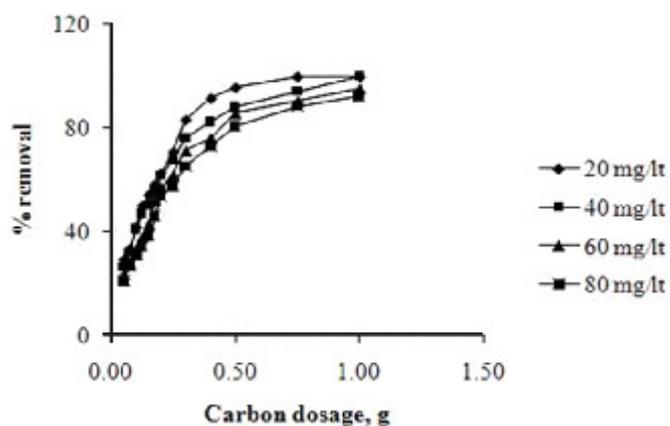


Fig. 2: Effect of adsorbent dose on the removal on MG onto CSAC (Temp = 308K, Initial pH = 7, Agitation time = 3 hrs)

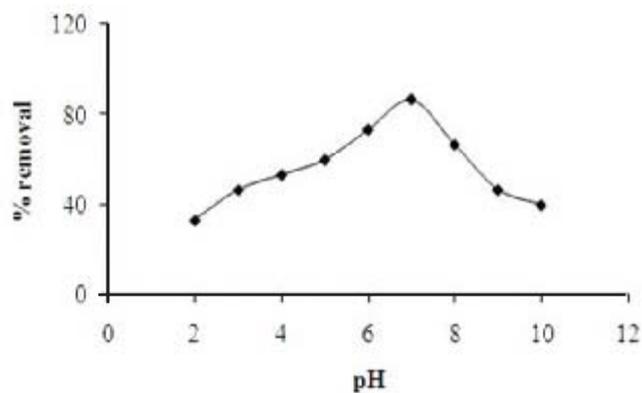


Fig. 3: Effect of pH on the removal of MG by CSAC (Temp: 308K, Initial pH = 7, Agitation time: 3 hrs, Concentration: 40mg/lt.)

usually adopted for homogenous adsorption and it is used successfully in monomolecular adsorption processes¹⁷. Linear form of Langmuir model was expressed by

$$\frac{C_e}{q_e} = \frac{1}{b} Q_0 + \frac{C_e}{Q_0} \quad \dots(1)$$

where, C_e is equilibrium constant of dye (mg/L), q_e is amount of dye adsorbed at equilibrium (mg/g), Q_0 is Langmuir constant related to adsorption capacity (mg/g), b is Langmuir constant related to energy of adsorption capacity (L/mg). The linear plot of C_e/q_e versus C_e is shown in Fig. 4(a). The constants Q_0 and b can be calculated from slope and intercept of the plot and the values are tabulated in Table 1. The shape of the Langmuir isotherm was investigated by the dimensionless constant separation term (R_L) to determine high affinity adsorption. R_L is calculated as follows

$$R_L = \frac{1}{1 + bC_0} \quad \dots(2)$$

where, C_0 is the initial dye concentration (mg/L). R_L indicates the type of isotherm to be irreversible ($R_L = 0$), favorable ($0 < R_L < 1$), linear ($R_L = 1$) (or) unfavorable ($R_L > 1$)¹⁸. In the present investigation, the R_L values were less than one which shows the adsorption process was favorable.

Freundlich isotherm

The Freundlich isotherm model was chosen to estimate the adsorption intensity of the adsorbate on the adsorbent surface¹⁹. Linear form of Freundlich model is expressed by

$$\log C_e = \log k_f + \frac{1}{n} \log C_e \quad \dots(3)$$

where, q_e is dye concentration in solid at equilibrium (mg/g), C_e is dye concentration in solution at equilibrium (mg/L), K_f (L/mg) and $1/n$ are adsorption capacity at unit concentration and adsorption intensity, respectively. $1/n$ values indicate the type of isotherm to be irreversible ($1/n = 0$),

favorable ($0 < 1/n < 1$), unfavorable ($1/n > 1$). The linear plot of $\log q_e$ versus $\log C_e$ is shown in Fig. 4(b). The values of $1/n$ and k_f can be calculated from the slope and intercept respectively and the results are given in Table 1. The value of $1/n$ was less than one indicating the favorable adsorption²⁰.

Dubinin-Raduskevich (D-R) isotherm

The D-R isotherm was used to determine the characteristic porosity and the apparent free energy of adsorption²¹. The linear form can be represented as

$$\log q_e = \log q_m - K_{DR} \varepsilon^2 \quad \dots(4)$$

where, K_{DR} is a constant related to the mean free energy of adsorption ($\text{mol}^2 \text{J}^{-2}$), q_m is the theoretical saturation capacity (mol g^{-1}), ε is the polyani potential (Jmol^{-1}), which is related to the equilibrium concentration (C_e , gL^{-1}) as follows

$$\varepsilon = RT \ln \left(1 + \frac{1}{C_e} \right) \quad \dots(5)$$

The slope of the plot of $\ln q_e$ versus ε^2 gives K ($\text{mol}^2 \text{J}^{-2}$) and the intercept yields the adsorption capacity, q_m (mgg^{-1}). Fig. 4(c) shows D-R plot and the results are given in Table 1. The mean free energy of adsorption (E) (KJmol^{-1}) is calculated from the equation²²

$$E = \frac{1}{\sqrt{2K_{DR}}} \quad \dots(6)$$

Tempkin isotherm

The Tempkin isotherm model predicts a uniform distribution of binding energies over the population of surface binding adsorption²³. The model was chosen to determine the adsorption potentials of the adsorbent for adsorbates.

The Tempkin isotherm is applied in the following form

$$q_e = \frac{RT}{b} \ln AC_e \quad \dots(7)$$

The linear form of Tempkin equation is

$$q_e = \beta \ln \alpha + \beta \ln C_e \quad \dots(8)$$

where,

$$\beta = \frac{RT}{b} \quad \dots(9)$$

T is the absolute temperature in Kelvin, R is the universal gas constant, $8.314 \text{ J (mol K)}^{-1}$, b is the Tempkin constant related to heat of sorption (J/mg). The Tempkin constants α and b are calculated from the slope and intercept of q_e versus $\ln C_e$ (Fig. 4(d)) and parameters are given in the Table 1.

Flory-Huggins model

The Flory-Huggins model was used to determine for the degree of surface coverage characteristics of the adsorbate on the adsorbent²⁴. The linear form of the Flory-Huggins equation is expressed as

$$\ln\left(\frac{\theta}{C_0}\right) = \ln K_{FH} + n \ln(1-\theta) \quad \dots(10)$$

where, $\theta = (1-C_e/C_0)$ is the degree of surface coverage, n is the number of dye occupying adsorption sites, K_{FH} is the equilibrium constant (L mol^{-1}). K_{FH} and n can be determined by plotting $\ln(\theta/C_0)$ versus $\ln(1-\theta)$ (figure not shown) and the

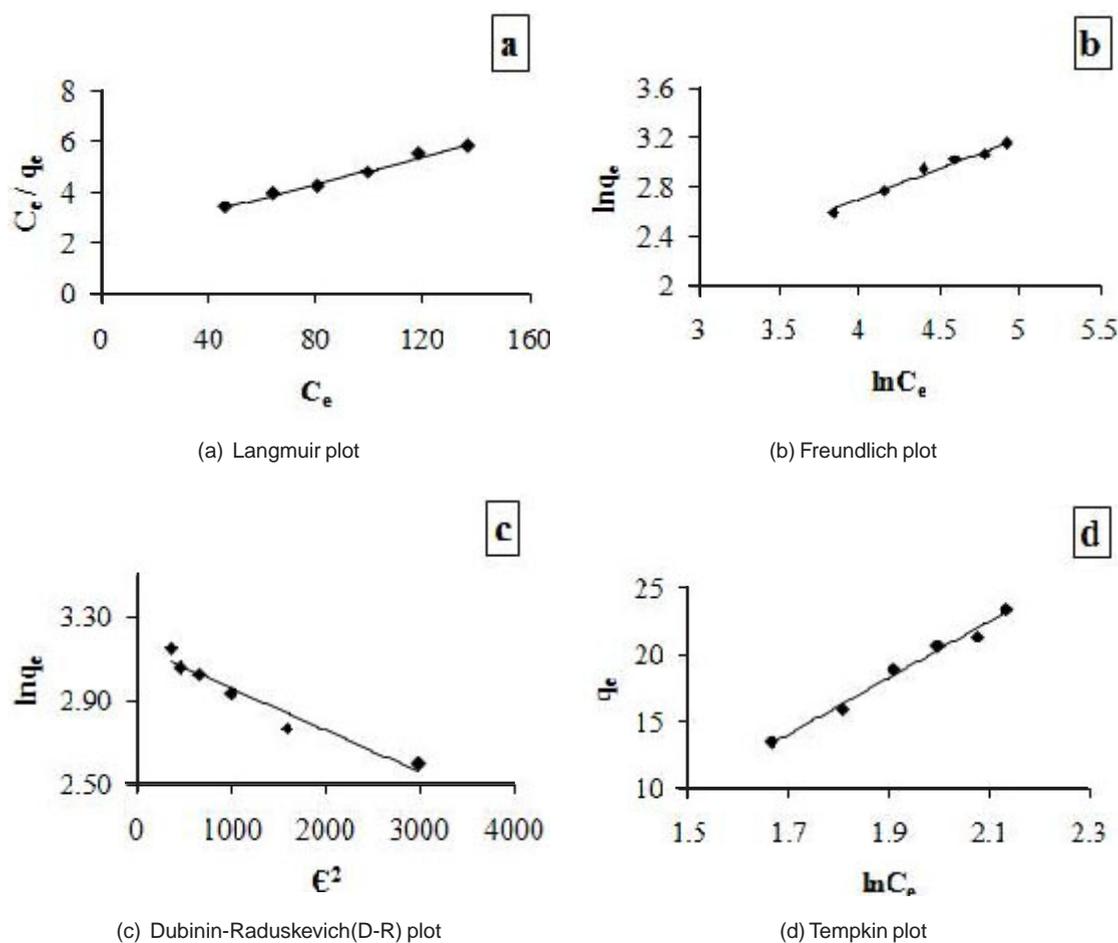


Fig. 4: Adsorption isotherm plots for MG onto CSAC
(Temp. = 308K, Initial pH = 7, Agitation time = 3 hrs, Adsorbent dosage = 100mg/50ml)

parameters are given in Table1. K_{FH} and ΔG° are related as follows

$$K_{FH} = \exp\left(\frac{-\Delta G^\circ}{RT}\right) \quad \dots(11)$$

where, ΔG° is the standard free energy change, R is the universal gas constant and equal to $8.314 \text{ Jmol}^{-1}\text{K}^{-1}$ and T is the absolute temperature. The values of ΔG° calculated was negative which shows that the adsorption process is spontaneous in nature and supports an exothermic nature.

Adsorption kinetics

Kinetic studies are necessary to optimize different operation condition for the sorption of dyes. The kinetics of MG onto CSAC was analyzed using pseudo- first order and pseudo- second order kinetic models.

Pseudo – first order kinetic model

It is based on the fact that the change in dye concentration with respect to time is proportional to the power one²⁵. The differential equation is described as follows:

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \quad \dots(12)$$

where, q_e and q_t are the adsorption capacity(mg/g) at equilibrium and time t , respectively and k_1 is the rate constant (min^{-1}) of pseudo first order kinetic model.

The integrated linear form of the model is as follows:

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303}t \quad \dots(13)$$

A plot of $\log(q_e - q_t)$ versus t gives a linear line(Fig. 5(a)) from which the values of k_1 and q_e can be determined from the slope and intercept respectively and presented in Table 2. This value showed that the q_e calculated was not equal to q_e experimental, although the values of R^2 are satisfactory. This shows that the kinetics for the entire process did not follow the pseudo-first order model.

Pseudo – second order kinetic model

The adsorption mechanism over a complete range of the contact time is explained by the pseudo – second order kinetic model²⁶. The differential equation is described as follows:

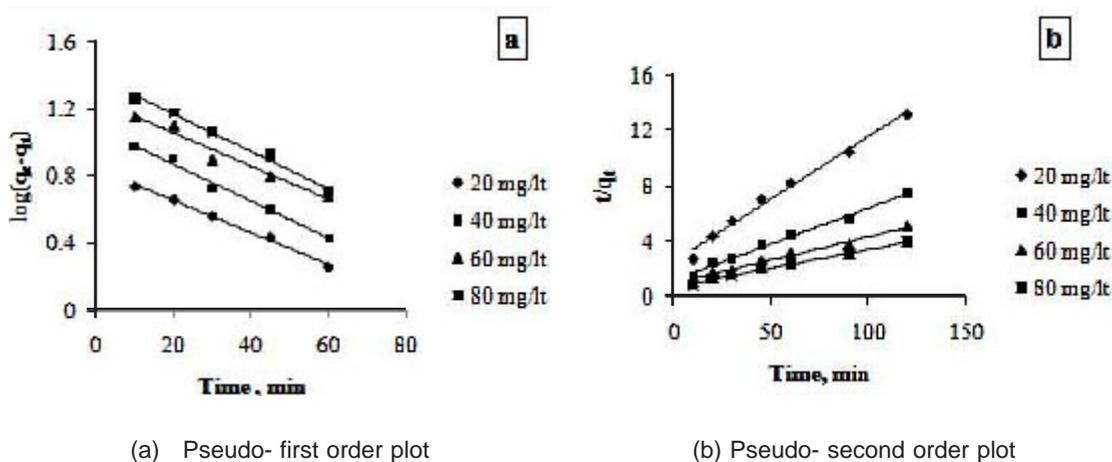


Fig. 5: Kinetic plots for the adsorption of MG onto CSAC (Temp. = 308K, Initial pH = 7, Adsorbent dosage = 100mg/50ml)

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \quad \dots(14)$$

where, q_e and q_t are the adsorption capacity(mg/g) at equilibrium and time t , respectively and k_2 is the rate constant of pseudo second order adsorption (g/mg min).

The linearised form of the above model is

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad \dots(15)$$

The initial adsorption rate, h (mg/g min), as $t \rightarrow 0$ can be defined as

$$h = k_2 q_e^2 \quad \dots(16)$$

A plot of t/q_t versus t gives a linear relationship (Fig. 5(b)), from which q_e and k_2 can be determined from the slope and intercept of the plot respectively and presented in Table 2. The values of q_e calculated show good agreement with experimental data. The correlation coefficient R^2 was

close to unity. Thus the sorption of MG by CSAC could be approximated more appropriately by the pseudo - second order model²⁷, supporting the assumption of chemisorptions as the rate-limiting mechanism through sharing or exchange of electrons between sorbent and sorbate²⁸.

CONCLUSION

The present study shows that the agricultural waste material, cocoa shell, can be effectively used as an adsorbent for the removable of malachite green from aqueous solution. The adsorption characteristics have been examined by initial pH, contact time, initial concentration and adsorbent dose. The equilibrium data were evaluated by Langmuir, Freundlich, Tempkin, Dubinin-Radushkevich and Flory-Huggins isotherms. Kinetic studies showed that the adsorption process followed the pseudo-second order model and pseudo-second order rate constant, k_2 , decreases from 2.5×10^{-3} to 1.03×10^{-3} g/mg min with increase in initial dye concentration for CSAC. Based on the data of present study, it could be employed that CSAC is an effective adsorbent for the removal of MG from aqueous solution.

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