

KINETICS AND THERMODYNAMICS STUDY OF MALACHITE GREEN DYE ONTO ACTIVATED CARBON OBTAINED FROM THE GLORIOSA SUPERBA STEM

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ABSTRACT

The present work deals with adsorption of Malachite Green (MG) dyes carried out in the presence of Activated GloriosaSuperba stem Carbon (AGSC). Various parameters such like the dose of adsorbent, temperature and pH have been studied. The result reveals when the amount of adsorbent increases, the percentage removal of dye also increases. The applicability of pseudo first order and pseudo second order studies were also studied. The thermodynamics parameter such as ΔG^0 , ΔH^0 and ΔS^0 is calculated. The adsorption capacities of Activated GloriosaSuperba stem Carbon (AGSC) is being calculated by using batch process.

Keywords: Adsorption, Thermodynamics, Malachite Green (MG).

1. INTRODUCTION

Dyes can causes allergic, dermatitis, skin irritation, cancer, mutation, etc. In general dyes are unsuccessfully biodegradable and some of the dyes produce aromatic amine which is highly carcinogenic in nature^{1,2}. Many researchers have studied the feasibility of using inexpensive alternative materials like peral millet husk, date pits, saw dust, buffing dust of leather industries, coir pith, crude oil, residue, tropical grass, olive stone, almond shell, pine bark, wool waste, coconut shell etc^{3,4}. The present study tries to evaluate the efficiency of an activated gloriosasuperba adsorbent in the removal of malachite green dyes from dye solution.

2. Experimental methods

2.1 Adsorbent

Gloriosasuperbastemis collected from the nearby Trichy district has carbonized with concentrated sulphuric acid and washed with water and activated around 1000°C in a muffle furnace for 6 hrs then it has been taken out and stored in a vacuum desiccators.

2.2 Adsorbate

The stock solution of malachite green concentration 1000 mg/L is prepared by dissolving 1 g of malachite green in 1000 ml of double distilled water. Different concentration of dye solutions which begin from the range of (50 to 250 mg/L) have been prepared from the stock solution by appropriate dilution.

2.3 Batch adsorption experiments

Batch adsorption is being tested by adding 25 mg of AGSC to 50 ml of the MG dye solution of different initial concentration (50 to 250 mg/L) at a particular pH. The experiment has been carried out by using a wrist action shaker for a period of 180 min and 120 rpm using 250 ml stopper glass flasks at (30°C to 60°C). The residual concentration of dyes in each sample after adsorption at different time intervals have determined by UV-Visible spectrophotometer. The equilibrium q_e (mg/g) is calculated by the following mass balance principle.

$$q_e = (C_0 - C_e) V/M \dots\dots\dots (1)$$

Where C_0 and C_e are the initial and equilibrium concentrations (mg/L) of dyes, V is the volume (L), M is the weight (g) of the adsorbent. The removal efficiency of the adsorbents on dyes is being calculated by using the following expression.

$$\%R = (C_0 - C_t) \times 100/C_0 \dots\dots\dots (2)$$

2.4 Kinetic Experiments

The batch kinetic⁵ experiments are basically similar to those used in testing the adsorption equilibrium method. The dyes samples have taken at specific time intervals and the concentration of dyes is also similarly measured. The all kinetic experiments have carried out at 30, 40, 50 and 60°C with initial dye concentration (50, 100, 150 200 and 250 mg/ L) at the amount of adsorption at time t. The q_t (mg/g) is calculated by.

$$q_t = (C_0 - C_t)V/M \dots\dots\dots (3)$$

Where C_0 (mg/L) is the liquid phase concentration of dye occur at any time.

3. RESULTS AND DISCUSSION

3.1 Effect of adsorbent dosages

The effect of the AGSC doses datas were given in table 1 and it was have studied at 30°C by varying the amount of adsorbent dose 50-250 mg for the initial concentration of 50 mg/L. Fig.1 reveals that the increase in percentage removal of MG dye with increases in dose of adsorbent due to the increase in adsorbent surface area and the availability of more adsorption sites.

Table.1. Percentage removal of MG with adsorbent dosages

Adsorbent dose	% Removal
25	52
50	76
75	79
100	83.5
150	87
200	89.5
250	90.5

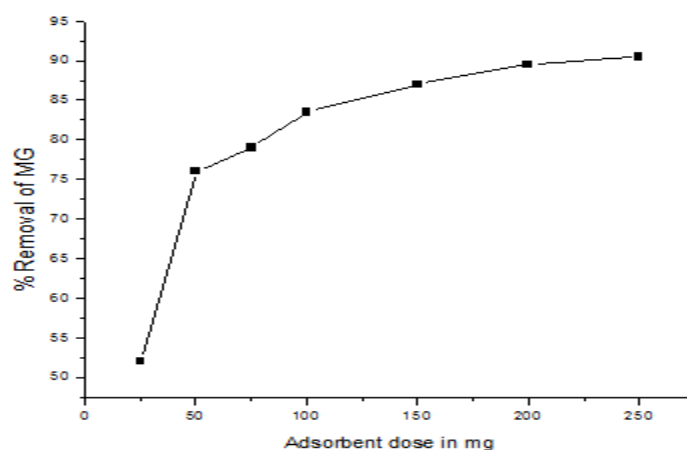


Fig. 1: Effect of adsorbent dose on the removal of MG dye

[MG]=50mg/L; Temp:30°C; Contact time=50 min.

3.3 Effect of pH

The solution pH is one of the most important factors which control the adsorption of MG dye. To examine the effect of pH on the % removal of MG dye, the pH of initial solution is used that varied from 2.0 to 10.0 by the addition of sodium hydroxide or hydrochloric acid into them. When the % of removal increases, the pH also increases up to 6.5. There after the % of removal decreases. The optimum % of removal takes place at pH 6.5. So the remaining experiment has carried out at pH 6.5. The experiment's result is shown in table 2 and fig 2.

Table 2: Percentage removal of MG with different pH

pH	Removal %
2	71
3	76
4	81
5	85
6	88
6.5	90.5
7	86
8	48
9	42
10	40

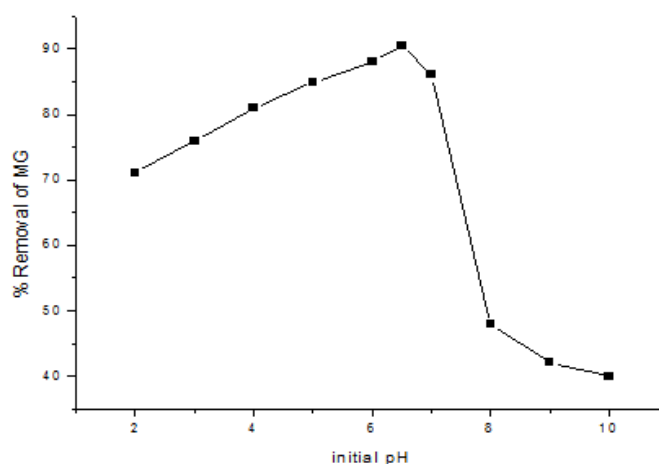


Fig. 2: Effect of initial pH on the removal of MG dye
[MG]=50mg/L; Temp:30°C; Contact time=50 min. Adsorbent dose = 25mg/ml

Pseudo – first order model

The pseudo –first order rate model equation given by Lagergren in 1898

$$\frac{dq}{dt} = k_1(q_e - q) \text{ -----(4)}$$

Where q_e is the amount of solute adsorbed at equilibrium per unit weight of adsorbent (mg/g), q The amount of solute adsorbed at any time (mg/g) and k_1 is the adsorption constant. The above Equation is integrated for the boundary conditions $t = 0$ to $>$ ($q = 0$ to >0) and then rearranged to Obtain the following linear time dependence function

$$\text{Log } (q_e - q) = \text{log } (q_e) - (k_1 / 2.303) t$$

This is the most popular form of pseudo-first order kinetic model equation. Fig 3. Shows an example for these plots. The correlation coefficients in this model have very poor correlation coefficients for best fit data. Therefore, it can be calculated that this model has satisfactory value to be predicated as

a suitable model constant k_1 and correlated coefficients for all possible changes have been calculated and summarized in table 3.

Pseudo- second order model

The rate constant for the adsorption of dye on to was determined by Lagergren equation this equation is modified by Ho and McKay and the differential equation for this reaction is

$$Dq/dt = k_2 (q_e - q)^2 \text{ -----5}$$

Integrating eq for the boundary conditions $t = 0$ to > 0 and recharging to obtain the linearized From which is shown as follows

$$t / q = (1/k_2 q_e^2) + (1/q_e) t$$

From this equation slope and intercept can be calculated. Fig 3. Shows an example for these plots Therefore, it can be calculated that this model has no satisfactory value to be predicated as a suitable model constant k_1 and correlated coefficients compare with pseudo first order summarized in table 3

Table 3: Pseudo –first and second order model for the adsorption of Malachite Green on to AGSC

Type of adsorbent	Concentration of MG in ppm	Pseudo first order		Pseudo second order	
		Rate constant (min^{-1})	r^2	Rate constant (mg/g/ min)	r^2
AGSC	50	0.044	0.9859	0.0068	0.9574
	100	0.0370	0.9886	0.0041	0.9368
	150	0.0402	0.9638	0.0031	0.8608
	200	0.0379	0.9752	0.0039	0.8656
	250	0.0395	0.9752	0.0033	0.8948
	300	0.0390	0.9416	0.0035	0.9178

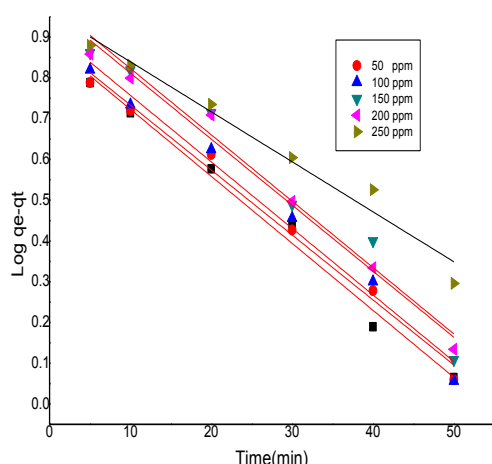


Fig. 3:

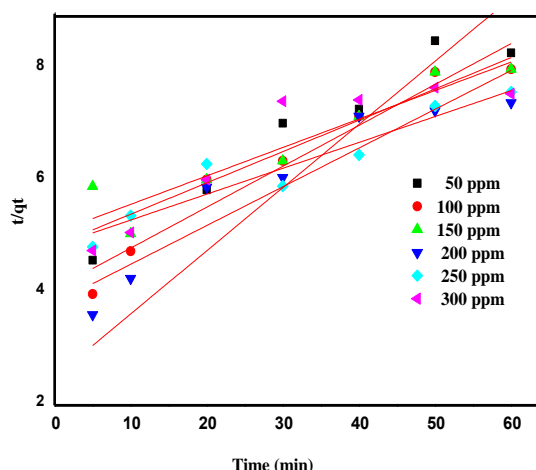


Fig. 4:

Figs.3, 4:Pseudo- First- Order and Pseudo second order kinetic plots for the adsorption of Malachite Green onto AGSC

The high correlations and coefficients of the pseudo – first order kinetic model over the other model rendered it best in adsorption of MG on AGSC⁶. This confirms that the sorption data are well represented by the pseudo – first order kinetics for the entire sorption period.

Thermodynamic study

Thermodynamic parameter such as change in free energy (ΔG^0) (KJ/mol), Enthalpy (ΔH^0) (KJ/mol) and entropy (ΔS^0) (JK/mol) has been calculated by using the following equation (7,8) and (9)

$$K_0 = C_{\text{solid}} / C_{\text{liquid}} \text{ ----- (4)}$$

$$\Delta G^0 = -RT \ln K_0 \text{ ----- (5)}$$

$$\log K_0 = \frac{\Delta S^0}{2.303R} - \frac{\Delta H^0}{2.303RT} \text{ ----- (6)}$$

Where K_o is the equilibrium constant, C_{Solid} is the solid phase concentration at equilibrium (mg/L). C_{liquid} is the liquid phase concentration at equilibrium (mg/L). T is temperature in Kelvin and R is the gas constant ($8.314 \text{ J mol}^{-1} \text{ K}^{-1}$). A graph has drawn between $\ln K_o$ vs $1/T$ and shown the following figures from 5 to 9. The ΔH^0 and ΔS^0 values obtained from the slope and intercept of Van't Hoff plots. These values are given in Table.3. The negative ΔG^0 indicates the adsorption is spontaneous in nature and also the magnitude of ΔG^0 indicates the adsorption is physical adsorption (ie, less than 70 KJ/mol). The value of ΔH^0 is negative; this indicates the adsorption is exothermic process. The positive ΔS^0 indicates an increased randomness during the adsorption. This also support the adsorption is a physical adsorption⁶.

Table 3: Thermodynamic parameter for the adsorption of MG dye onto AGSC

MG (mg / L)	Ko				ΔG^0				ΔH^0	ΔS^0
	30°C	40°C	50°C	60°C	30°C	40°C	50°C	60°C		
50	17.5797	20.3830	23.5459	26.0255	-7.2217	-7.8451	-8.4831	-9.0229	-11.1016	60.5184
100	6.8492	7.8920	9.8298	11.8346	-4.8471	-5.3759	-6.1373	-6.8411	-15.5729	67.2120
150	4.2624	4.9582	5.8250	6.8304	-3.6523	-4.1663	-4.7321	-5.3194	-13.2059	55.5765
200	2.6069	2.9040	3.1000	3.7176	-2.4137	-2.7742	-3.6175	-3.6353	-17.9865	67.9137
250	1.8893	2.0794	4.3425	2.5240	-1.6026	-1.9050	-3.9434	-2.5632	-13.7887	51.2350

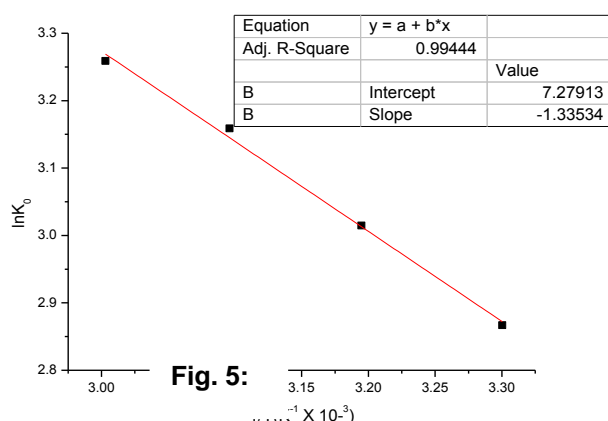


Fig. 5:

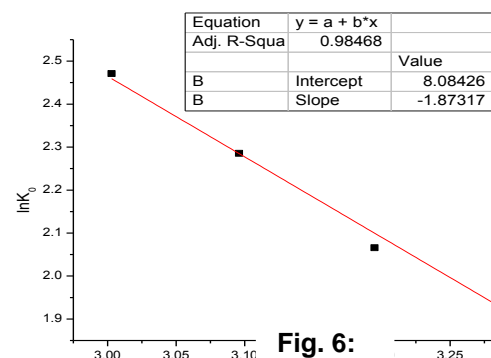


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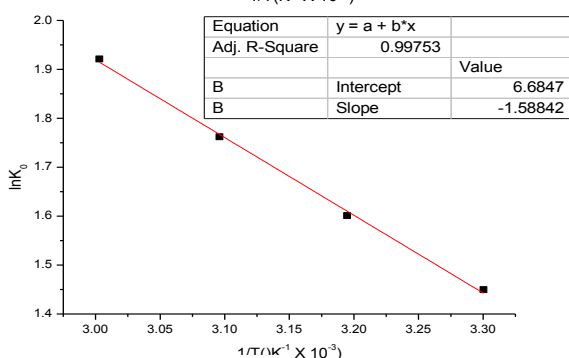


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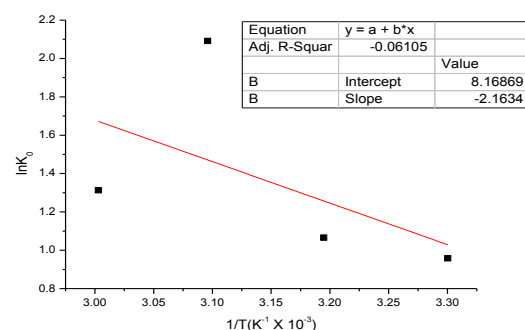


Fig. 8:

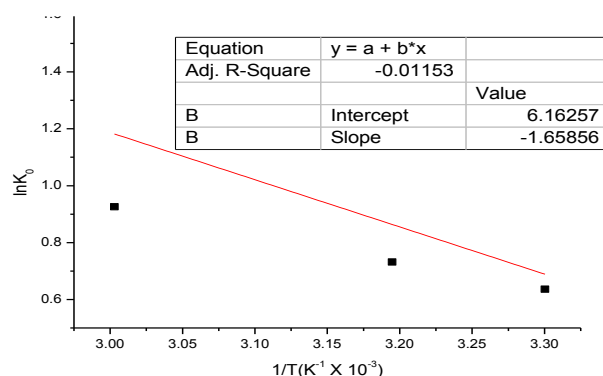


Fig. 9:

Figs. 5,6,7,8,9: Thermodynamic parameter for the adsorption of MG dye onto AGSC

CONCLUSION

The adsorption characteristics of MG dye onto Activated Gloriosa Superba are strongly affected by initial pH and the adsorbent dose. The pH 6.5 was favorable for the optimum adsorption of MG dye by AGSC. The thermodynamics parameter ΔG^0 , ΔH^0 values are negative so the reaction is spontaneous and exothermic and ΔS^0 values indicate the adsorption is physical adsorption.

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