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Batch adsorption of malachite green dye from aqueous solution using sawdust of *Swietenia macrophylla* (mahogany wood)

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ABSTRACT

Sawdust of *Swietenia macrophylla* waste was used as a bio-sorbent for the removal malachite green from aqueous solutions in this study. Various parameters' effect such as contact time, pH, initial dye concentration, temperature and adsorbent dosage were studied on the bio-sorbent. Spectrophotometric technique was implemented for the measurement of dye concentration before and after adsorption. The study indicated that the quantity of dye adsorbed increased steadily with increase in the dye's initial concentration and contact time because as the concentration increases the dye molecules available for adsorption also increases. There was a sharp rise in the quantity of dye adsorbed as the pH increases from pH 2 to pH 7, equilibrium was obtained at pH 10 after which the quantity of dye adsorbed decreased with an increased to pH 12. As the temperature increases the quantity of dye adsorbed decreased, this can be attributed to an increase in solubility as the temperature increases. The experimental data were fitted to the Langmuir and Freundlich adsorption isotherms with Langmuir isotherm showing a better fit than Freundlich isotherm model, this shows that the adsorption follows a homogenous coverage signifying saturated monolayer coverage of the solute molecules on the adsorbent surface. The adsorption kinetics data were fitted to pseudo-first and pseudo-second order kinetic model with pseudo-second order kinetic model showing a better fit than pseudo-first order kinetic model, indicating that more than one process affects the adsorption of malachite green dye onto *Swietenia macrophylla*. In terms of thermodynamic parameters, negative values were obtained for Gibbs free energy ΔG^{o}, indicating a spontaneous adsorption process; also the enthalpy change $\Delta H°$ was negative signifying the adsorption is exothermic in nature. Similarly, entropy $\Delta S°$ values were negative indicating that the degree of disorderliness of malachite green reduced as it got adsorbed onto the surface of the adsorbent.

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***Keywords*:** Adsorption, Aqueous solution, Malachite Green, Isotherm, *Swietenia macrophylla*, Thermodynamic parameters

1. INTRODUCTION

Over the past few decades, society has become increasingly sensitive towards the protection of the environment; resulting to a global concern about the potential adverse effects of the chemical industry on the environment. The response in some parts of the world has been much faster and more intensive than others in this regard. The colour manufacturing industry represents relatively small part of the overall chemical industry. People have used natural colourants since prehistoric times for painting their surrounding and dyeing skin and clothes [1]. This practice continued till mid-19th century in which all colourants used were of natural origin. Inorganic colouring pigments like soot, hematite, manganese oxide and ochre were utilized earlier. Even the organic natural colourants, especially textile dyes are aromatic in nature and originated from plants (that is the red dye alizarin from madder and indigo from wood), insects, fungi and lichens [1].

Colourants include both dyes and pigments. Pigments are insoluble materials which are applied on substrates such as paints whereas dyes are applied to various substrates such as textile materials from liquid in which they are completely or at least partly insoluble. Dyes just like pigments are highly visible materials. Thus, even there minor release into the environment may cause the appearance of colour, for example in open waters, which may attract critical attention of the public and local authorities. Therefore, the industries are required to minimize the release of these colourants into the environment, even in cases where a small but visible release might be considered as toxicologically rather innocuous [2].

Synthetic dyes are widely employed in a variety of sectors, including textiles, leather, and food processing, dyeing, cosmetics, paper, and dye production. In recent years, the release of numerous toxic dyes into the environment by these sectors has gotten a lot of attention across the world. Dyes in water sources, as is widely known, can reduce light penetration, photosynthetic activity, and gas solubility, as well as generate visual pollution. Many dyes, as well as their degradation products, are extremely poisonous and cancer-causing. For a healthier ecology, these toxic colours must be removed from polluted water [3, 4]. Previous research efforts have focused on adsorption technology for dye remediation from wastewater. This has been recognized as one of the most versatile processes used in developing countries for the removal of organic pollutants as well as heavy metals from aqueous media [31]. This method can handle to an extent large flow rates, resulting in a high quality effluent that devoid of the formation of hazardous, harmful and toxic substances.

There is growing demand for activated carbon which has given rise to its increasing cost. Hence, there is need for research on substances with promising biosorbent tendencies like agricultural and biological waste materials for effective dye removal and treatment of industrial wastewater [30]. The objectives of the study include determination of the capacity of *Swietenia macrophylla* dust in the removal of Malachite green dye from aqueous. To establish the effect of factors such as contact time, pH, temperature, initial dye concentration and adsorbent dose for the adsorptive capability of Malachite green dye from aqueous solution using *Swietenia macrophylla* (mahogany wood) sawdust as adsorbent.

Finally the determination of thermodynamic parameters of malachite green dye from aqueous solution using *Swietenia macrophylla (*mahogany wood) sawdust as the adsorbent. The importance of the study owns to fact that biosorption techniques for dye removal and industrial wastewater treatment are viewed as a good alternative [32].

This is because most physical, chemical and biological techniques for industrial wastewater treatment have certain drawbacks such as complexity of operational designs and techniques, high cost of operation and maintenance. This is in addition to insensitivity to toxic substances, coupled with sludge production and other by products which are environmentally unfriendly and have the tendency to damage the ecosystem. This technique will help in reducing the discharge of toxic substances from industries and reduce environmental threat to human life and damage to the ecosystem at a very low cost. The study evaluated the contact time and initial dye concentration, against the adsorption of malachite green dye from aqueous solution onto sawdust of *Swietenia macrophylla*. Additionally, variables like pH and temperature as a function of the adsorption of malachite green dye from aqueous solution onto sawdust of *Swietenia macrophylla* will be evaluated. Therefore five factors having five levels will give 25 experimental units. If each unit is replicated 5 times, then these are 25 × 5 experimental observations. Therefore 125 experiments will be required to prove the objectives wrong or right.

2. MATERIALS AND METHODS

Adsorbent

The sawdust of *Swietenia macrophylla* used in the present studied was collected from timber market located at Aba Port Harcourt Road, Aba, Abia State, Nigeria. It was washed severally with distilled water and sun dried for 2 days and later oven dried at a temperature of 70 °C for 8 hours [5, 6]. The dried sample was sieved to obtain a particle size range of between 1.0 mm – 2.0 mm (standard mesh sizes: 10 and 18), with no further physical or chemical treatment the sample was stored in plastic bottles and used in the present study.

Adsorbate

Analytical grade malachite green (MG) dye was used in the present investigation, a basic (cationic) dye with chemical formula $C_{23}H_{25}N_2Cl$, C.I. = 42,000B, nature is basic green; melting point of 112–114 °C, molar mass: 364.911 g/mol (supplied by Trust chemical Laboratories) CAS No.:2437-29-8, UN No.: NR, TARIFF: 3204 13 16. The dye concentration in supernatant solution was determined at characteristic wavelength (λmax = 620 nm) by UV-visible spectrophotometer (Shimadzu-752 M/s Shimadzu, China).

Preparation of aqueous silution

A stock solution (1000 mg/L) of MG was prepared by dissolving the appropriate amount of dye in distilled water, which was diluted to desired concentrations of 50, 100, 150, 200 and 250 mg/L obtained from this stock solution by serial dilution [7].

Adsorption process

Batch adsorption research was carried out to investigate the effect of contact time, pH, temperature, initial dye concentration and adsorbent dose on the adsorption of malachite green dye from aqueous solution onto *Swietenia macrophylla*. This was achieved by varying the parameters under study and keeping other parameters constant. In each experiment pre-weighed amount of adsorbent was added to an appropriate volume of dye's aqueous solution and shaken constantly in a water bath shaker at constant temperature and 180 rpm [16].

This was shaken for a time period of 180 minutes and aqueous samples were taken from the shaker, and the concentrations were analyzed at 620 nm by a double beam UV/VIS spectrophotometer. The effect of varying temperatures on the adsorptions process were carried out at 303 K, 313 K and 323 K. The pH was adjusted using 0.1M NaOH and 0.1M HCl. The percentage removal of dye and amount of dye adsorbed on *Swietenia macrophylla* was calculated using equation (1 & 2) respectively.

$$\% \, Removal = \frac{100(C_O - C_e)}{C_e} \tag{1}$$

$$(q_e) = \frac{(C_O - C_e)V}{W} \tag{2}$$

where q_e is the quantity of dye adsorbed on the adsorbent at the time of equilibrium (mg/g), C_o and C_e are the initial and equilibrium concentrations (mg/L) of the dye in solution respectively; V is the volume (L) of solution and W is the weight of adsorbent (g). All adsorption experimental processes were carried out thrice and their mean values were used in data analysis [8, 9, 10].

3. RESULTS AND DISCUSSION

Effect of contact time and initial dye concentration

The initial concentration of dye increased from 50 mg/L to 250 mg/L based on the fact that at lower concentration the ratio of the initial quantity of dye molecules available on the surface area of the adsorbent is low and its fractional adsorption does not depend of the initial concentration.

Moreover at higher concentration the sites available of adsorption become fewer, therefore the percentage removal of dye is dependent upon initial concentrations. The effect of initial dye concentration on the malachite green dye adsorbed on *Swietenia macrophylla* saw dust was investigated in the range of 50-250 mg/L. The adsorbent mass, particle size, and agitation speed were fixed at 1g, 1.0 – 2.0 mm and 180 rpm respectively, at varying contact time ranging from 0 minutes to 180 minutes. The experimental processes were carried out at room temperature.

Results shown in Figure 1 and Figure 2 describes the effect of initial dye concentration and contact time on the rate of adsorption by *Swietenia macrophylla* sawdust during experiments. These plots showed the amount of dye adsorbed at various intervals of time and indicate that the removal of dye initially increase steadily from 0.263 mg/g for 50 mg/L to 20.468 mg/g for 250 mg/L within a time frame of 0 minutes to 180 minutes in which equilibrium was attained at about 120 min.

Adsorption of the total amount of dye increases relates linearly to the dye concentration in the solution. There was a corresponding increase in dye concentration, indicating that removal of dye was dependent upon the concentration of dye in the solution [11-13].

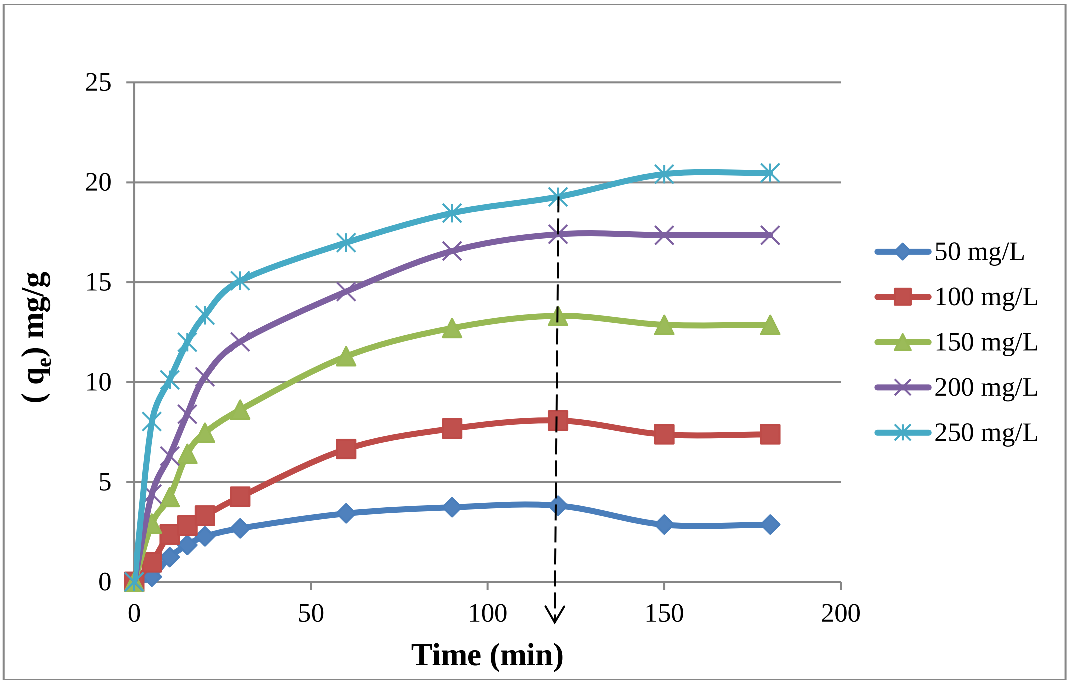

Figure 1. Effect of Contact Time and initial concentration on the adsorption of Malachite Green Dye from aqueous solution onto *Swietenia macrophylla*

Effect of pH

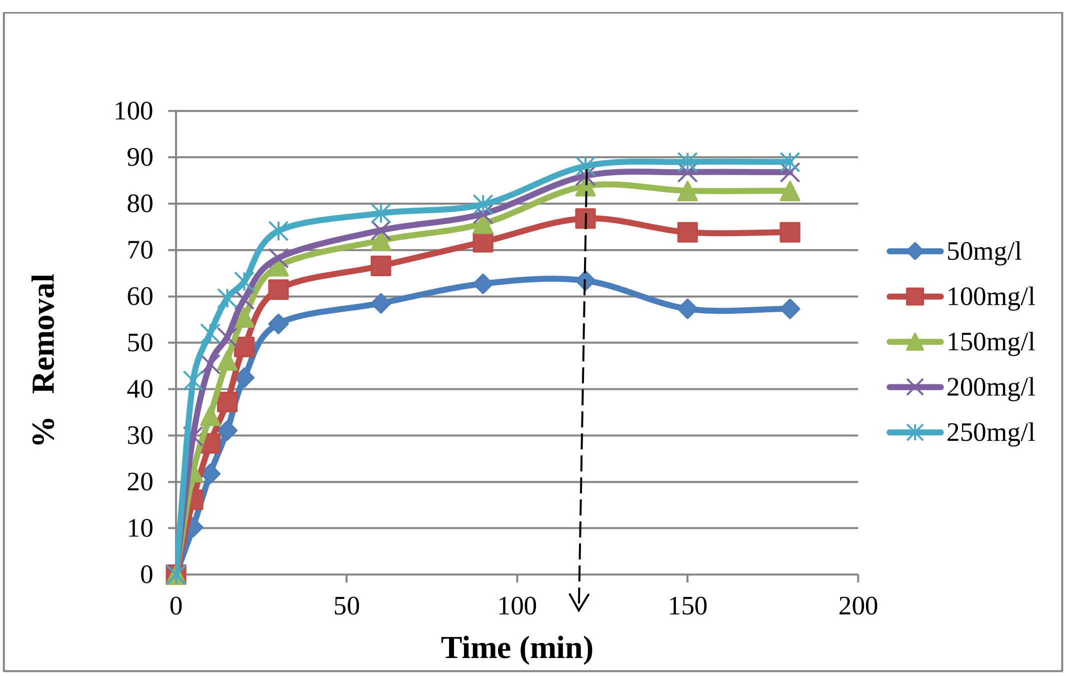

Figure 2. Effect of contact time and initial concentration on the removal of malachite green dye from aqueous solution on *Swietenia macrophylla*

In this work, the effect of pH on the adsorption of malachite green dye from aqueous solution on *Swietenia macrophylla* was studied in the range of 2.0-12.0. The initial dye concentration, adsorbent dosage, contact time, particle size and agitation speed were fixed at 100 mg/L, 0.5g, between 30 to 180 min, 1.0 to 2.0 mm and 180 rpm respectively, at room temperature. pH is viewed as one of the most vital parameters that affects any adsorption process. Hence the effect of pH on the removal efficiency of malachite green was studied at different pH ranging from 2.0 to 12.0. The maximum adsorption of malachite green occurred between pH 10 and 12. The sharp increase in dye removal capacity at pH range of 2 to 4 may also be attributed to the reduction of H^+ ions as the acidity reduces.

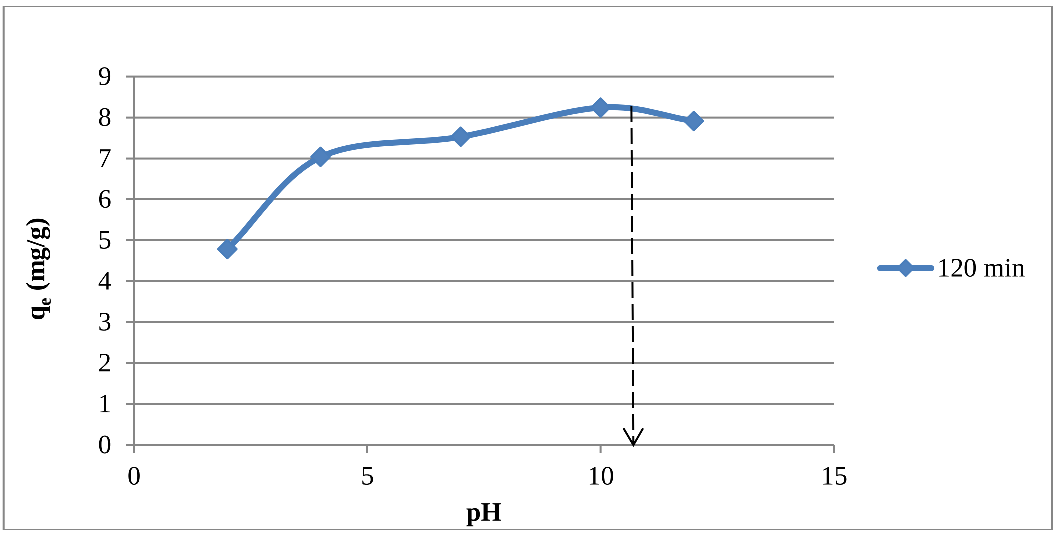

Figure 3a. Effect of pH on the adsorption of 100 mg/L malachite green dye from aqueous solution on *Swietenia macrophylla*

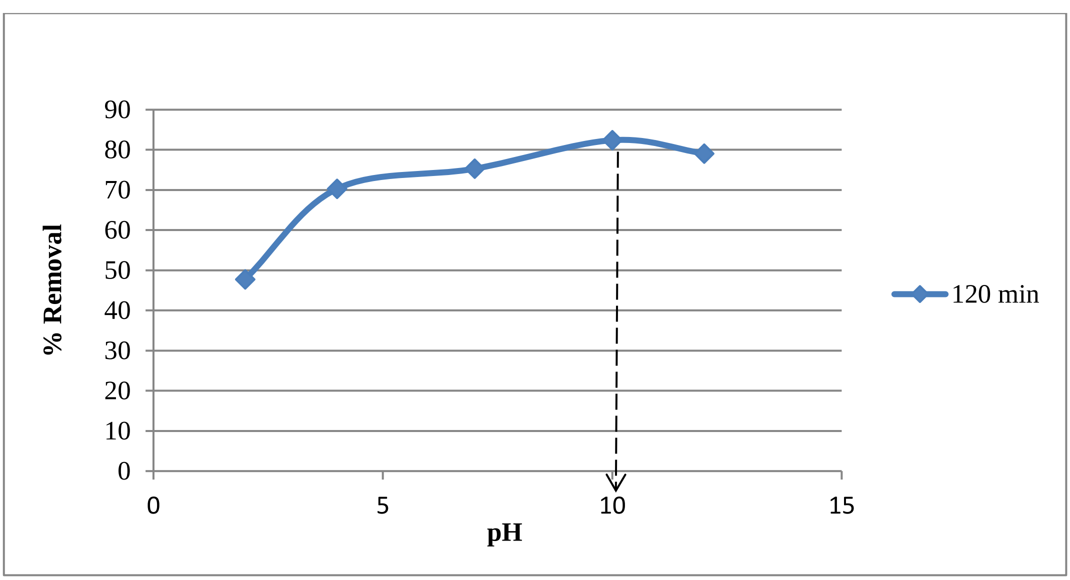

Figure 3b. Effect of pH on the removal of 100 mg/L Malachite Green dye from aqueous solution on *Swietenia macrophylla*

Figure 3a showed the effect of pH on the adsorption of 100 mg/L malachite green dye from aqueous solution on *Swietenia macrophylla* while Figure 3b showed the effect of pH on the removal of 100 mg/L malachite green dye from aqueous solution on *Swietenia macrophylla* [14, 15]. It was observed that there was a sharp rise on the amount of dye adsorbed at almost all the pH levels for about 60 minutes, followed by a decrease in the amount of dye adsorbed. The decrease in the adsorption may be attributed to two reasons. As pH of the system increased, the number of negatively charged adsorbent sites increased and the number of positively charged surface sites decreased, which did not favour the adsorption of positively charged dye cations as a result of electrostatic repulsion. Secondly adsorption of malachite green dye at acidic range pH can be attributed to the presence of excess H^+ ions competing with dye cations for the adsorption sites of the adsorbent [16, 17].

Effect of temperature

The temperature dependence of the adsorption process is a complex phenomenon. Thermodynamic parameters, such as the heat of adsorption and the energy of activation play an important role in predicting the adsorption behaviour and both are strongly dependent on temperature. Temperature rises affects the solubility of molecular interaction and chemical potential of the adsorbate, the latter being a controlling factor for adsorption [20, 21]. It has been reported that if the solubility of the adsorbate increases with an increase in temperature then the chemical potential decreases. The two effects work in the same direction leading to a decrease in adsorption process. On the other hand, if temperature has the reverse effect on the solubility then the effects will act in the opposite direction and adsorption may increase or decrease depending upon the predominant factor.

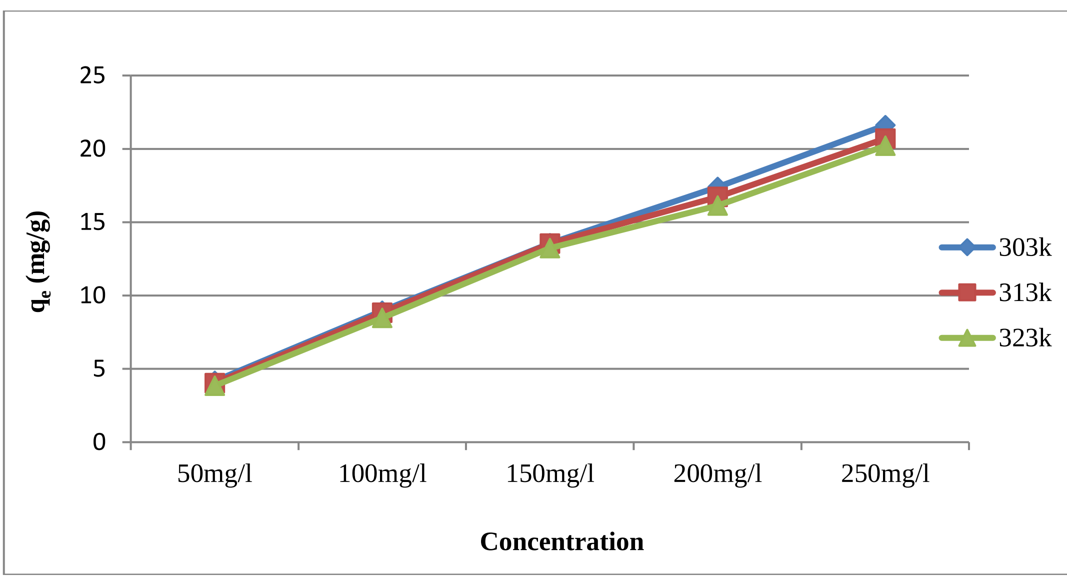

Figure 4. Effect of temperature on the adsorption of malachite green dye from aqueous solution onto *Swietenia macrophylla*

In the present experiments the adsorption rates at three different temperatures (303 K, 313 K and 323 K) have been analyzed as shown in Figure 4 and Figure 5. The rate of dye uptake increased with an increase in concentration 50 mg/L to 100 mg/L from 83.24 % to 86.4 % at 30 °C and from 76.88 % to 80.8 % at 50 °C, but decreases with increase in temperature, this may be due to the tendency of dye molecules to escape from the solid phase to bulk phase with an increase in the temperature of the solution. Also there was decrease in the % removal at all temperatures. The comparative removal studies were done at different temperatures. The highest percentage removal of malachite green was 90.39 % at 313 K.

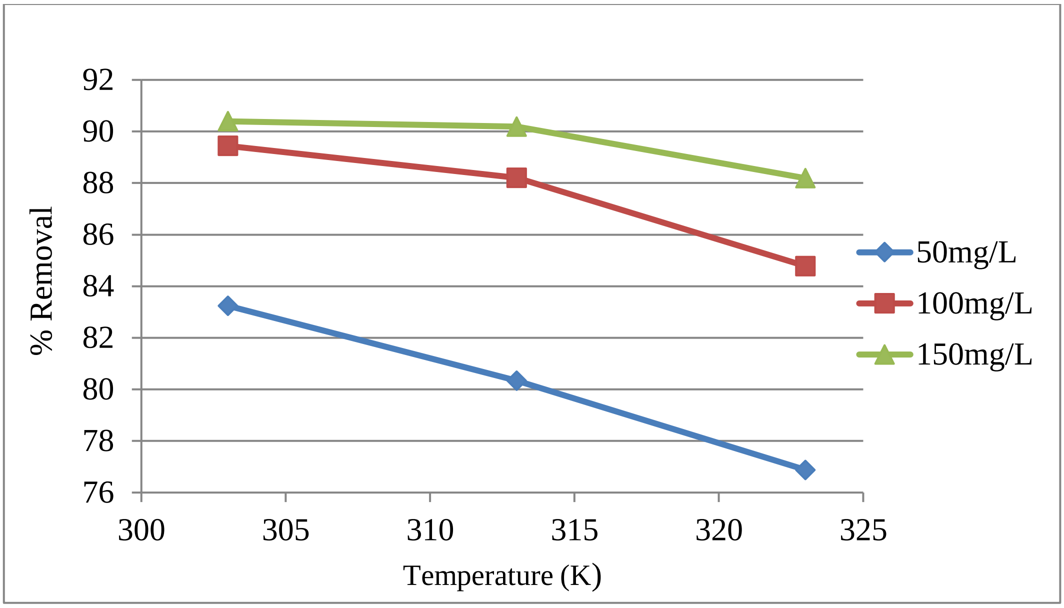

Figure 5. Effect of temperature on the removal of malachite green dye from aqueous solution on *Swietenia macrophylla*

Effect of adsorbent dose

The effects of sawdust mass on aqueous dye solution are presented in Figures 6 and 7. The result revealed that there was a decrease in dye concentration adsorbed as the adsorbent mass is increased with a corresponding increase in percentage removal as the adsorbent mass increases. An equilibrium percentage removal of 61.08 %, 72.9 %, 74.88 %, 77.34 % and 79.31 % were achieved with 2 mg/L, 4 mg/L, 6 mg/L, 8 mg/L and 10 mg/L respectively at 120 minutes. Maximum percentage of dye removal was found to be rapid in the first 90 minutes which later slowed as equilibrium was attained.

The initial rise in adsorption with adsorbent or adsorbate mass was probably due to a stronger driving force and larger surface area. A larger surface area of the adsorbent and smaller size of adsorbate favour adsorption. The rate of adsorption was higher in the beginning as more sites were available and the unimolecular layer increases. Adsorption and desorption occur together and the rates become equal at a stage called adsorption equilibrium when isotherms were applied.

The subsequent slow rise in the curves is due to adsorption and intra-particle diffusion taking place simultaneously with the dominance of adsorption. With a rise in adsorbent dose there was a less proportionate increase in adsorption resulting from lower adsorptive capacity utilization of adsorbent [15, 16].

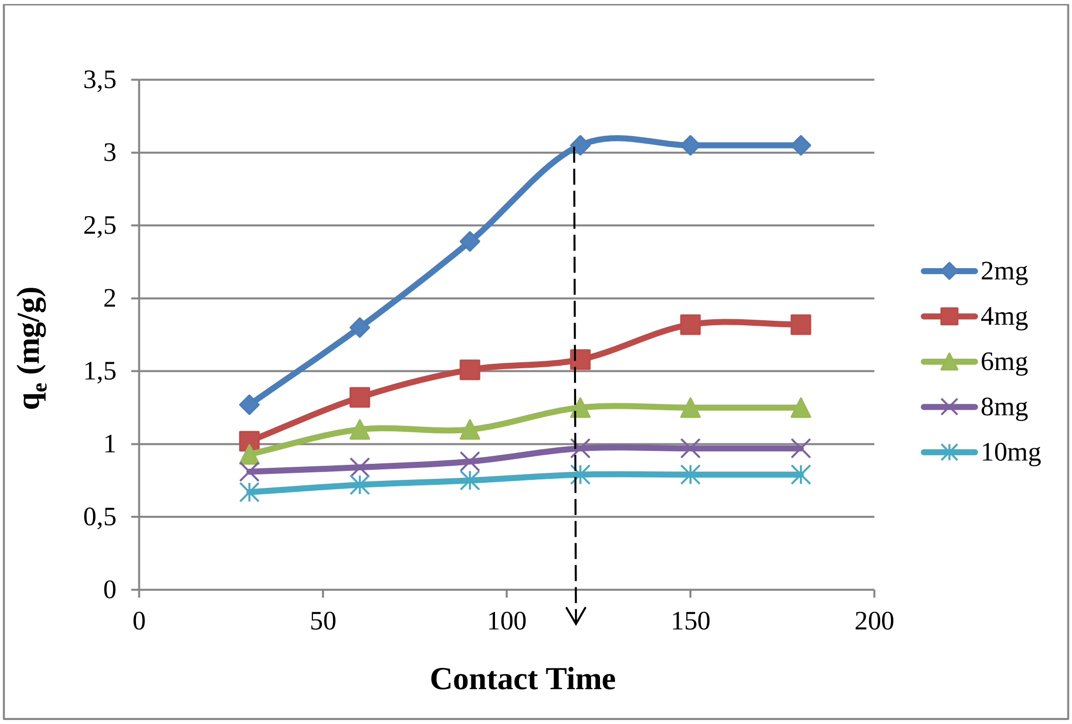

Figure 6. Effect of adsorbent dose on the adsorption of 100 mg/l malachite green dye from aqueous solution on *Swietenia macrophylla*

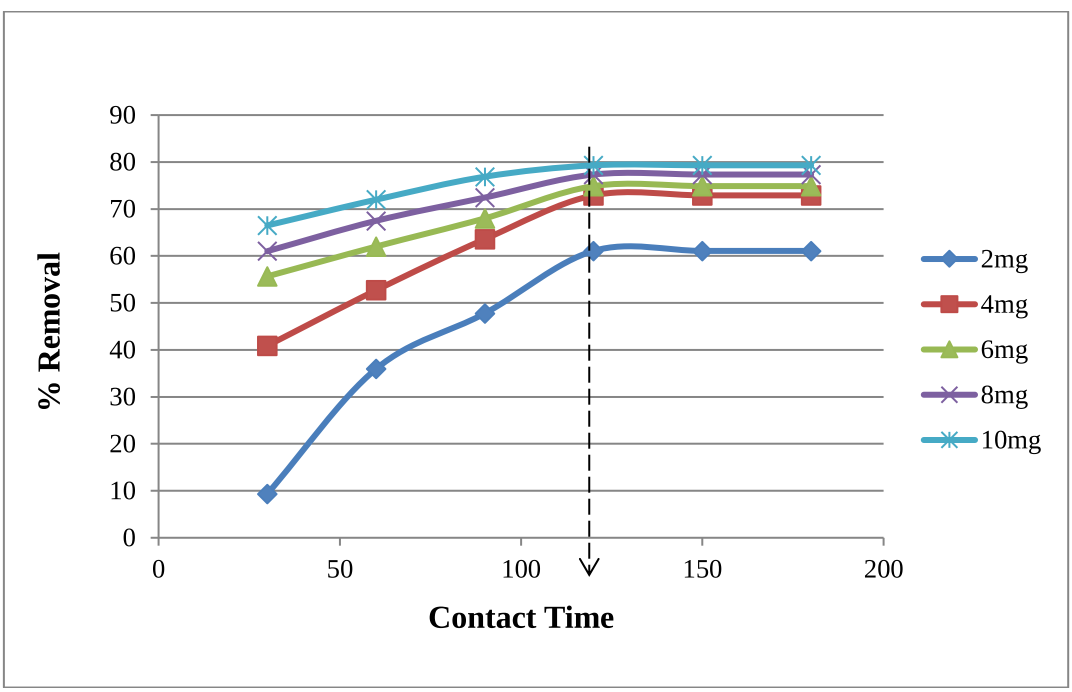

Figure 7. Effect of adsorbent dose on the removal of 100 mg/l malachite green dye from aqueous solution on *Swietenia macrophylla*

Adsorption Isotherm

In order to optimize the design of an adsorption system to remove the dye, it is important to establish the most appropriate correlations of the equilibrium data of each system. Equilibrium isotherm equations are used to describe the experimental adsorption data. The parameters obtained from the different models provide important information on the adsorption mechanisms and the surface properties and affinities of the adsorbent. The most widely recognized surface adsorption models for single-solute systems are the Langmuir and Freundlich models. The correlation with the amount of adsorption and the liquid phase concentration was tested with them. Linear regression was used to determine the best-fitting isotherm, and the applicability of isotherm equations is compared by judging the correlation coefficient [17].

Langmuir Isotherm

The theoretical Langmuir isotherm is valid for adsorption of a solute from a liquid solution as monolayer adsorption on a surface containing a finite number of identical sites. Langmuir isotherm model assumes the same energies of adsorption onto the surface without the migration of adsorbate in the plane of the surface. Therefore, the Langmuir isotherm model was chosen for the estimation of the maximum adsorption capacity corresponding to complete monolayer coverage on the adsorbent surface. The Langmuir equation is commonly expressed as follows:

$$\frac{Ce}{qe} = \left(\frac{1}{K_L q_m}\right) + \left(\frac{1}{q_m}\right) C_e \tag{3}$$

where q_m is monolayer adsorption capacity (mg/g), K_L is Langmuir isotherm constant related to the affinity of the binding sites and energy of adsorption (L/mg). The values of qm and K_L can be calculated by plotting C_e/q_e versus C_e [18, 19].

Table 1. C_e and q_e of initial concentration of 100 mg/L after adsorption of Malachite Green dye from aqueous solution onto *Swietenia macrophylla*

C_e at initial concentration 100 mg/L	q_e at initial concentration 100 mg/L	C_e/q_e
28.49	7.151	3.984058
24.42	7.558	3.231013
23.26	7.674	3.031014
19.19	8.081	2.374706
26.16	7.384	3.542795
26.16	7.384	3.542795

Figure 8 shows the plot of C_e/q_e versus C_e for the adsorption of Malachite Green dye from aqueous solution onto *Swietenia macrophylla* an initial concentration of 100 mg/L at constant temperature according to the linear forms of Langmuir isotherm.

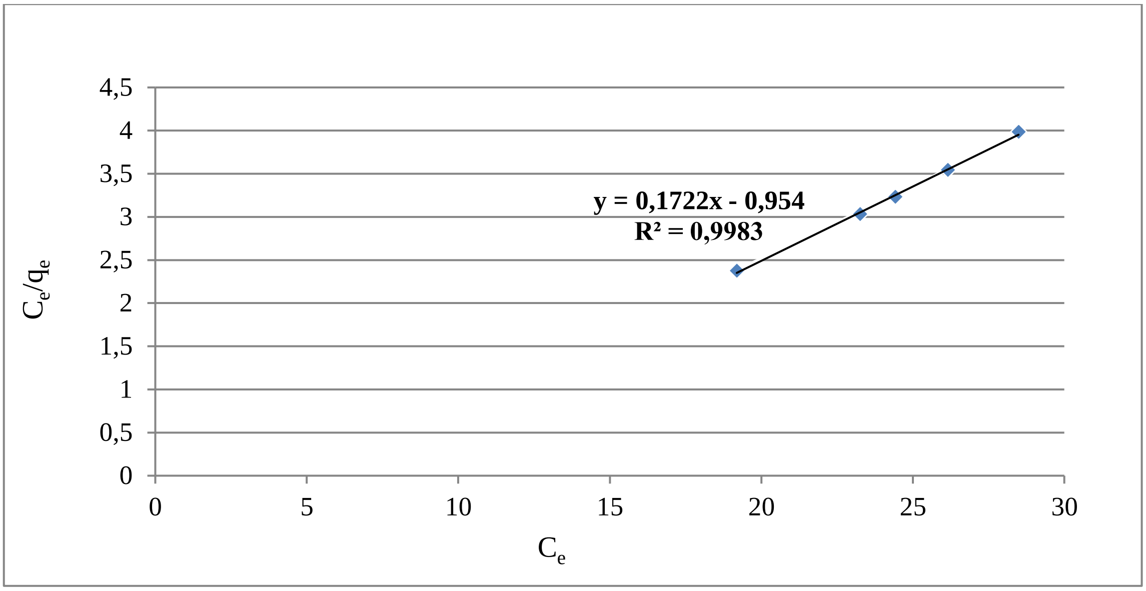

Figure 8. Langmuir isotherm Plot for adsorption of 100 mg/L of Malachite Green dye from aqueous solution onto *Swietenia macrophylla*

Slope = 0.1772	Intercept = -0.954
Slope = $1/Q^o$	$1/b\, Q^o$ = Intercept
Q^o = 5.64	b = -0.186
R^2 = 0.9983	

$$q_e = \frac{Q^o . bC_e}{1+b.C_e}$$

Table 2. Langmuir constants for the adsorption of Malachite Green dye from aqueous solution on *Swietenia macrophylla* at 100 mg/L

Initial Conc.	Q^o	b	R^2
100mg/L	5.64	0.186	0.9983

Freundlich Isotherm

The Freundlich equation was employed for the adsorption of malachite green dye on the adsorbent. The Freundlich isotherm was represented by the equation below

$$logqe = logk_F + \frac{1}{nlogCe} \tag{4}$$

where qe is the amount of malachite green dye adsorbed (mg/g), C_e is the equilibrium concentration of dye in solution (mg/L), and K_F and n are constants incorporating the factors affecting the adsorption capacity and intensity of adsorption, respectively.

Table 3. C_e and q_e at initial concentration of 150 mg/L after adsorption of malachite green dye from aqueous solution on *Swietenia macrophylla* at 100 mg/L

C_e at initial concentration of 150 mg/L	q_e at initial concentration of 150 mg/L	log C_e	log q_e
47.13	10.29	1.673297	0.223573
25.41	12.46	1.405005	0.147678
22.95	12.71	1.360783	0.133789
16.8	13.32	1.225309	0.088246
21.31	12.87	1.328583	0.123389
21.31	12.87	1.328583	0.123389

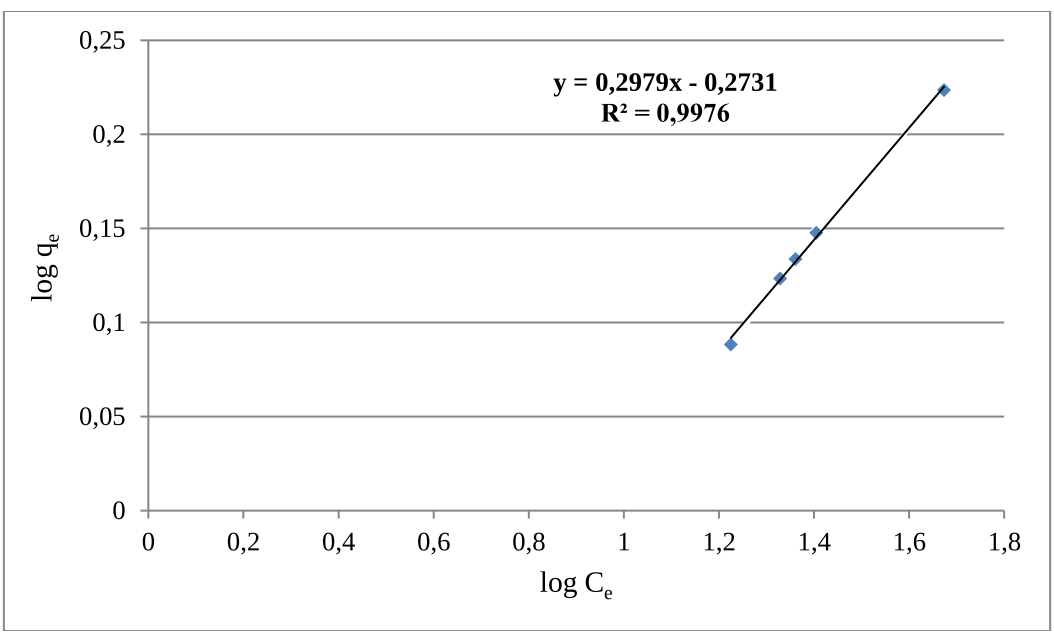

Figure 9. Freundlich Isotherm pot for adsorption of 150 mg/L of malachite green dye solution on *Swietenia macrophylla*

Slope = 0.298
Slope = 1/n
n =3.36

Intercept = -0.273
Log K_F = Intercept
K_F = 0.533

R^2 = 0.9976
$q_e = K_F C_e^{(1/n)}$

Linear plots of log q_e versus log C_e (Figure 9) shows that the adsorption of malachite green dye obeys the Freundlich adsorption isotherm. The values of K_F and n given in Table 4 show that the rise in negative charges on the adsorbent surface makes electrostatic force like van der Waals force between the surface and dye. The molecular weight as well as the size either limit or increase the chances of the adsorption of the dye on the adsorbent. Moreover, the values clearly reveal the dominance of adsorption capacity. The intensity of adsorption is a pointer of the bond energies that exist between dye and adsorbent, as well as possibility of slight chemical adsorptions rather than physical adsorption [19]. The results indicate that there is fitting of both Langmuir isotherm and Freundlich isotherm (Table 2 and 4)

Table 4. Freundlich Isotherm constants for the adsorption of Malachite Green dye from aqueous solution on *Swietenia macrophylla* at 150mg/L

K_F	n	R^2
0.533	3.36	0.9976

Thermodynamic Parameters

The adsorption process is temperature dependent. For temperature study the concentration was varied between 50 mg/L to 250 mg/L and all other conditions like volume of solution (100 mL), contact time (120 min), adsorbent dose (1g) were kept constant. As the temperature rises the capacity of the adsorbent enhances. In the present experiment the temperature study was done from 303K to 323K with variation of 10K. The amount of adsorption increased from 4.017mg/g to 20.2 mg/g with the highest amount of dye adsorbed at a concentration of 250 mg/L with respect to all the temperature while the highest % removal was obtained at a concentration of 150 mg/L [28, 29]. The temperature is useful to determining the thermodynamic parameters such as standard Gibbs free energy change ΔG°, standard enthalpy change ΔH° and standard entropy change ΔS°. The Gibbs free energy change for sorption of malachite green on *Swietenia macrophylla* is estimated by using equilibrium constant K_c as shown in equation (5)

$$G^o = -RTInK_c \tag{5}$$

Standard enthalpy change ΔH° and standard entropy change ΔS° of adsorption were calculated from the slope and intercept of the linear variation of InK_c with the reciprocal of temperature (1/T) in Van't Hoff equation as shown in equation (6)

$$InK_c = \Delta\frac{S^o}{R} - \Delta\frac{H^o}{RT} \tag{6}$$

where K_c is equilibrium constant for sorption, R gas constant, T temperature (K). The value of ΔH° and ΔS were calculated from the slope and intercept of the linear regression of $\ln K_c$ versus 1/T (Figure 10). The K_c value was determined by the relation in equation (7)

$$K_c = \frac{C_O - C_e}{C_e} \tag{7}$$

Table 5. Values of K_c at different temperatures after adsorption of malachite green dye from aqueous solution on *Swietenia macrophylla*

K_c					
T (K)	50 mg/L	100 mg/L	150 mg/L	200 mg/L	250 mg/L
303k	4.967	8.47	9.409	6.686	6.353
313k	4.087	7.475	9.19	5.088	4.814
323k	3.325	5.57	7.465	4.168	4.208

Table 6. Values of ln K_c at different temperatures after adsorption of malachite green dye from aqueous solution on *Swietenia macrophylla*

$\ln K_c$					
T (K)	50 mg/L	100 mg/L	150 mg/L	200 mg/L	250 mg/L
303	1.408	2.012	2.218	1.627	1.572
313	1.201	1.717	2.010	1.427	1.437
323	1.608	2.137	2.242	1.900	1.849

Table 7. Values of $\ln K_c$ at different temperatures after adsorption of MG dye from aqueous solution on *Swietenia macrophylla* and values of 1/T

T (K)	1/T	ln K_c at 100 mg/L
303	0.00330	2.1365
313	0.00319	2.0116
323	0.00310	1.7174

$- \Delta H°/R = 2041.1$
$- \Delta H° = 2032.6 \times 8.314$
$- \Delta H° = 16972.1996 J/mol$
$- \Delta H° = 16.9721996 kJ/mol$
$\Delta H° = - 16.9722 kJ/mol$
$\Delta S°/R = - 4.5713$
$\Delta S° = - 4.5713 \times 8.314$
$\Delta S° = - 38.0057883 J/mol$
$\Delta S° = - 0.038 kJ/mol$

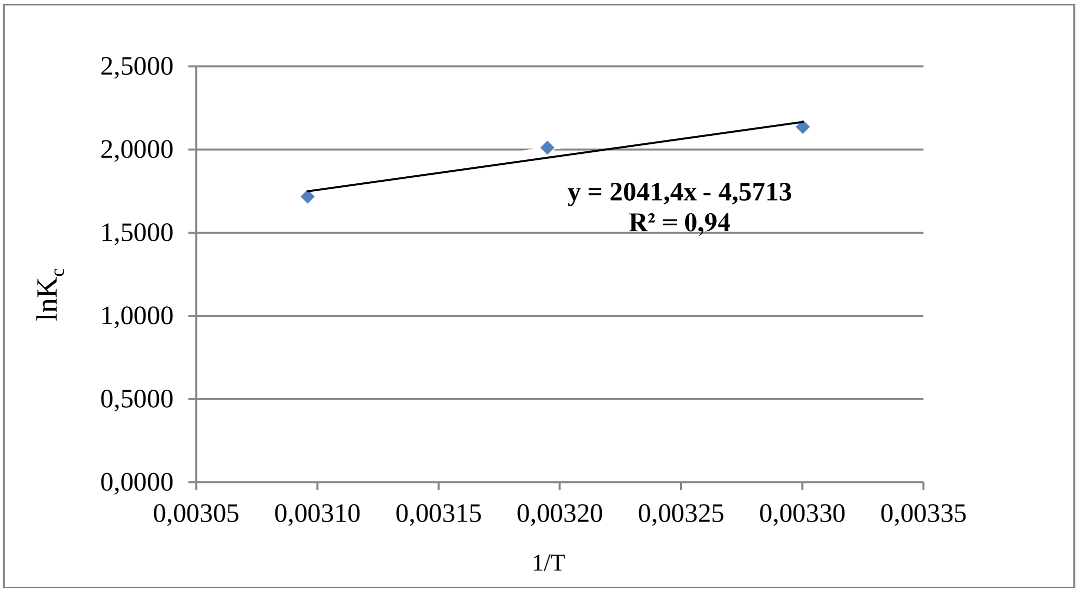

Figure 10. Plot of ln Kc vs 1/T for the estimation of Thermodynamics Parameter for the adsorption of MG dye from aqueous solution onto *Swietenia macrophylla*

Slope = 2041.4
Intercept = - 4.5713
R^2 = 0.94

Table 8 illustrates the thermodynamic parameters that were calculated by equations 11, 12 and 13. The absolute magnitude of ΔG° gives an idea about the type of adsorption. The spontaneous nature of sorption appears due to negative values of ΔG° with average value of -4.933 kJ/mol. This suggests that *Swietenia macrophylla* has strong affinity for Malachite Green dye. The negative ΔH° values could lead to exothermic nature of the interaction between Malachite Green dye and *Swietenia macrophylla* adsorbent. Standard entropy determines the disorderliness of the adsorption at solid–liquid interface [20, 21]. The thermodynamic studies play important role in understanding the nature of adsorption. The thermodynamics parameters related to the adsorption of dyes such as free energy change (ΔG°), enthalpy change (ΔH°), and entropy change (ΔS°) evaluated in this study are shown in Table 8.

Table 8. Thermodynamic parameters for adsorption of Malachite Green dye from aqueous solution onto *Swietenia macrophylla*

T (K)	K_c 100 mg/L	lnK_c 100 mg/L	ΔGo = $-RTlnK_c$ (J/mol)	ΔGo = $-RTlnK_c$ (kJ/mol)	ΔS° (kJ/Kmol)	ΔH° (kJ/Kmol)
303	8.47	2.137	-21337.13	-21.337		
313	7.475	2.012	-19452.05	-19.452	- 0.038	- 16.972
323	5.57	1.717	-14957.80	-14.958		

The negative ΔG° values confirm the spontaneous nature of adsorption of malachite green on *Swietenia macrophylla* sawdust. The lesser values of ΔG° suggest that adsorption is physical process. The enthalpy change (ΔH) of the adsorption process was found to be -16.972 kJ/mol, the negative sign indicates that the adsorption was exothermic i.e., the adsorption takes place with the release of energy. On the other hand, the value of the entropy change (ΔS) was - 0.038 kJ/Kmol. The negative value of the entropy change indicates that the degree of disorderliness of Malachite Green reduced as they got adsorbed on the surface of the adsorbent. The high regression coefficient (R^2) value of 0.94 shows that the thermodynamic equation was suitable for describing the adsorption process [21, 22].

Kinetic Studies

The kinetic model is one of the most important factor in predicting the rate at which sorption takes place for a given system and also very essential in understanding sorbent design, with sorbate residence time and reactor dimensions [22]. The sorption kinetics shows a large dependence on the physical and chemical characteristics of the sorbent material which influences the sorption process and its mechanism. The rate constants for the adsorption of Malachite Green on *Swietenia macrophylla* were obtained using the pseudo-first order (Lagergren), pseudo-second order kinetic models and Intraparticle diffusion models.

Pseudo-First Order Kinetic Model

The kinetic of sorption described by the pseudo-first order expression given by Lagergren was adopted. When the adsorption is preceded by diffusion through a boundary, the kinetics in most cases follows the pseudo-first order rate equation. The differential rate equation is of the form of equation (8)

$$\frac{dq_t}{dt} = K_1(q_e - q_t) \tag{8}$$

where q_t and q_e are the amounts of dye adsorbed at time t (mg/g) and at equilibrium (mg/g), respectively and k_1 is the pseudo-first order rate constant (min^{-1}). Integrating the above equation using the boundary condition, $q_t = 0$ at $t = 0$ leads to equation (9) [22, 26, 27].

$$\log(q_e - q_t) = log q_e - \left(\frac{k_1}{2.303}\right) t \tag{9}$$

Table 9. Values of log ($q_e - q_t$) of various concentrations at different time after adsorption of Malachite Green dye from aqueous solution on *Swietenia macrophylla*

	log($q_e - q_t$)				
Time	50 mg/L	100 mg/L	150 mg/L	200 mg/L	250 mg/L
0 min	0.4573	0.8683	1.1096	1.2395	1.3111
5 min	0.4155	0.8613	0.9520	1.1024	1.1605
10 min	0.0527	0.7443	0.8820	0.9569	1.0555

15 min	-0.0899	0.6686	0.7366	0.9271	0.9765
20 min	-0.4067	0.6401	0.7163	0.7845	0.8528
30 min	-0.7399	0.4947	0.6875	0.7105	0.7853

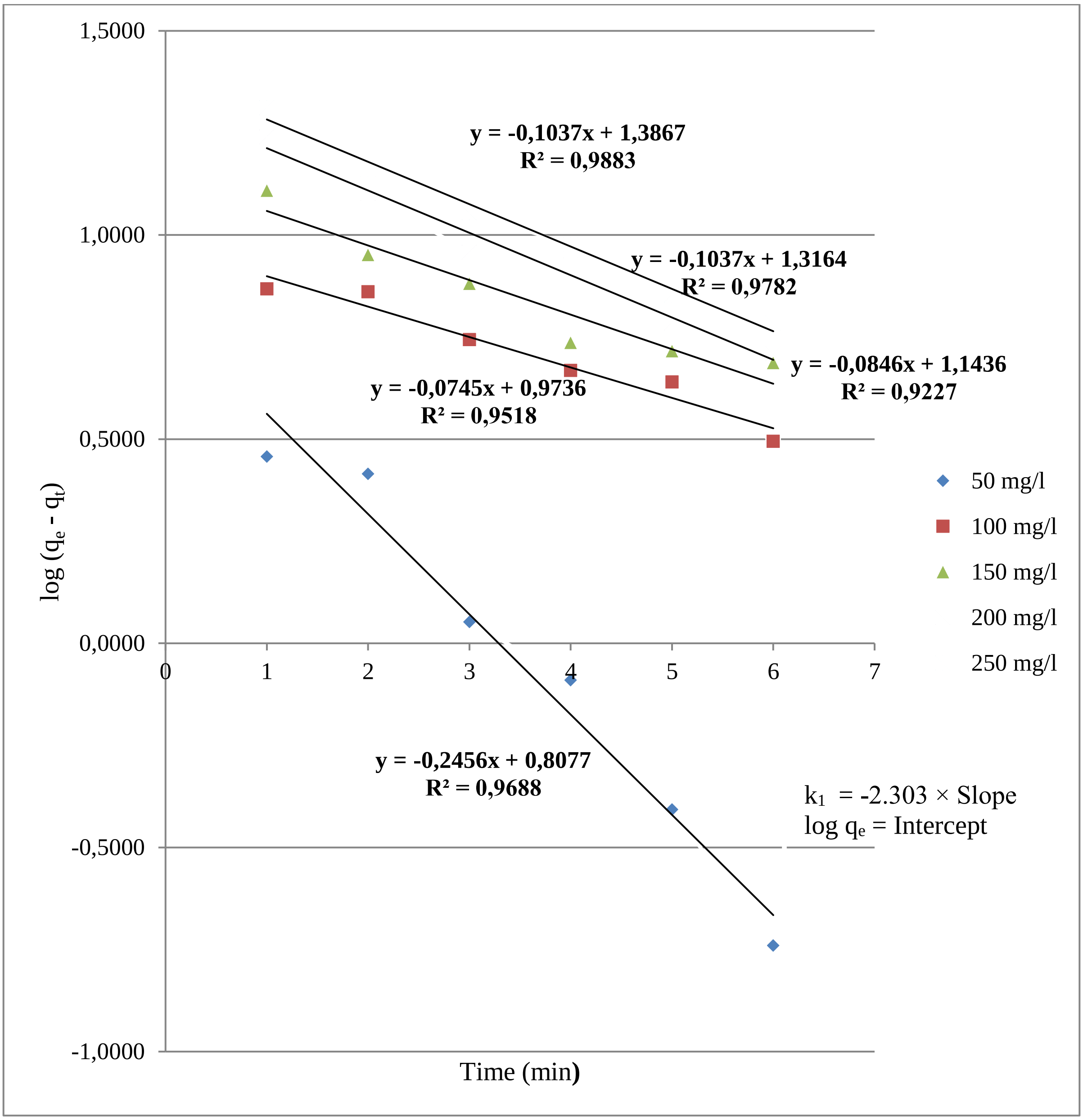

Figure 11. Pseudo-First Order curve for the adsorption of Malachite Green dye from aqueous solution on *Swietenia macrophylla.*

Pseudo-Second Order Kinetic Model

This model is based on the assumption that adsorption follows a second order mechanism, so the rate at which the adsorption site is occupied is proportional to the square of the number of unoccupied site. The linear form of the equation is given by equation (10)

$$\frac{t}{q_t} = \frac{1}{h_o} + \frac{t}{q_e} \tag{10}$$

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \tag{11}$$

The pseudo-second order kinetic model is presented according to equation (11) where qt and qe are the amount of dye adsorbed at time t (mg/g) and at equilibrium (mg/g), respectively and k_2 is the pseudo-second order rate constant (g/mg min). Integrating the above equation using the boundary condition, qt = 0 at t = 0 leads to equation (12)

$$\frac{t}{q_t} = \frac{1}{k_2 {q_e}^2} + \frac{t}{q_e} \tag{12}$$

The values of k_2 and q_e were calculated from intercepts and slopes of the linear plots of t/qt vs. t. (Figure 11). The values of correlation coefficients (R^2) are closer to unity confirms that adsorption of Malachite Green on *Swietenia macrophylla* follows pseudo-second order kinetics [19-21].

The rate constants and correlation coefficients (R^2) of the models considered in this study are listed in Table 13 as well as the q_e, k_1, k_2, k_p and C values. A better fit of pseudo-second-order kinetic model in comparison with pseudo-first-order kinetic model of the experimental data was observed with the pseudo-second-order model (R^2 = 0.992). Since pseudo-second-order kinetic model fitted better with this system than the pseudo first-order kinetic model values it can be suggested that the adsorption was controlled by chemisorption. It can also implies that more than one process affects the adsorption of Malachite Green onto the surfaces of the *Swietenia macrophylla* adsorbent particles, hence this process may involve valence forces through exchange of electrons between adsorbate and adsorbent [25].

Table 10. t/qt Values of various concentrations at different time after adsorption of Malachite Green dye from aqueous solution on *Swietenia macrophylla*

Time (min)	50 mg/L	100 mg/L	150 mg/L	200 mg/L	250 mg/L
0	0.0	0.0	0.0	0.0	0.0
5	1.011	2.373	1.276	1.064	0.833
10	5.757	5.453	1.905	1.204	1.098
15	7.306	5.511	2.022	1.684	1.364
20	8.084	6.627	2.609	1.774	1.499
30	11.177	7.042	3.750	2.454	2.088

60	20.499	9.023	6.457	4.433	3.754
90	25.445	11.728	7.084	5.434	5.154
120	32.267	14.850	9.009	6.897	6.226
150	52.338	20.314	11.656	8.642	7.350
180	62.805	24.377	13.987	10.370	8.794

It was observed that the R^2 values for the pseudo-second-order kinetic curves are higher than that of pseudo first-order kinetic curves and Intra-particle diffusion model curves, this implies that the experimental results follow the pseudo-second-order kinetic best.

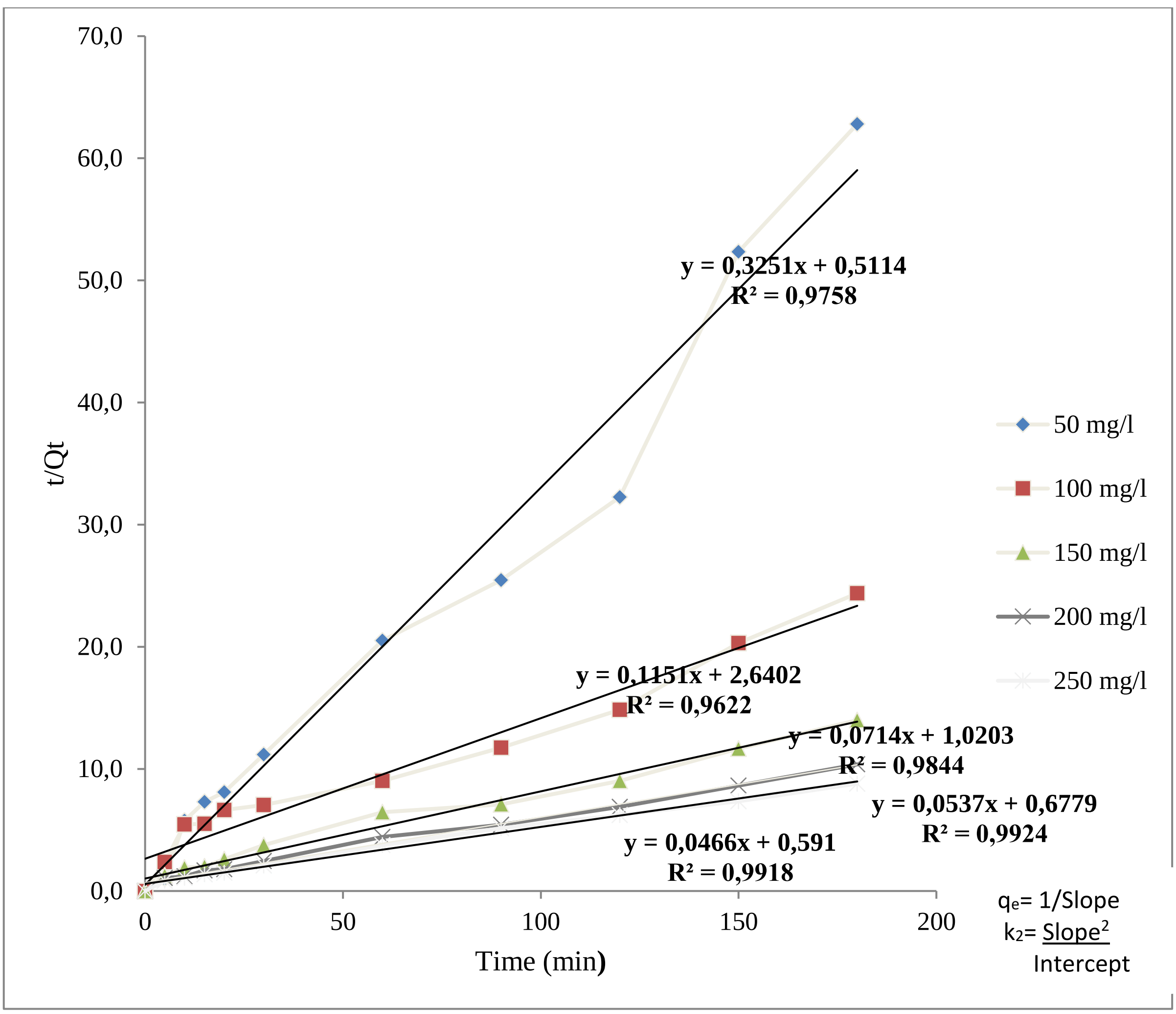

Figure 12. Pseudo-Second Order curve for the adsorption of Malachite Green dye from aqueous solution onto *Swietenia macrophylla*

Intra-particle diffusion model

The Intraparticle diffusion model used here refers to the theory proposed by Weber and Morris based on the equation (13) for the rate constant

$$q_t = k_{id} t^{1/2} + C \tag{13}$$

where k_{id} is the intraparticle diffusion rate constant (mg g^{-1} $min^{-1/2}$) and C is constant. If the rate limiting step is intraparticle diffusion, the graphical representation of adsorbed dye q_t (mgg^{-1}) depending on the square root of the contact time ($t^{1/2}$) should yield a straight line passing through the origin. The plot of q_t vs $t^{1/2}$ gives the value of the intraparticle diffusion rate constant (k_{id}) and correlation coefficient (R^2) can be determined from the slope respectively [23]. The intra-particle diffusion rate constant k_{id}, the correlation co-efficient (R^2) values are summarized in Table 13

Table 11. q_t values for various concentrations at different time after adsorption of Malachite Green dye from aqueous solution on *Swietenia macrophylla*

Time (min)	$t^{0.5}$	50 mg/L	100 mg/L	150 mg/L	200 mg/L	250 mg/L
0	0	0	0	0	0	0
5	2.236	0.263	0.118	3.917	4.700	6.000
10	3.162	1.737	1.834	5.250	8.304	9.106
15	3.873	2.053	2.722	7.417	8.905	10.996
20	4.472	2.474	3.018	7.667	11.272	13.344
30	5.477	2.684	4.260	8.000	12.226	14.371
60	7.746	2.927	6.650	9.292	13.534	15.983

Table 12. The intraparticle diffusion rate constant k_{id}, the correlation co-efficient

	50 mg/L	100 mg/L	150 mg/L	200 mg/L	250 mg/L
C	0.058	-0.891	1.227	1.337	1.641
kid	0.435	0.922	1.222	1.839	2.163
R^2	0.839	0.934	0.891	0.922	0.919

Figure 12 shows that all the lines are not passing through the origin and thus it can be concluded that the surface adsorption and intraparticle diffusion, both occur simultaneously. It seems that as the concentration of solution increases, linearity of the plot is lost because of intra-particle diffusion occurs at a faster rate than surface adsorption [24, 28, 29].

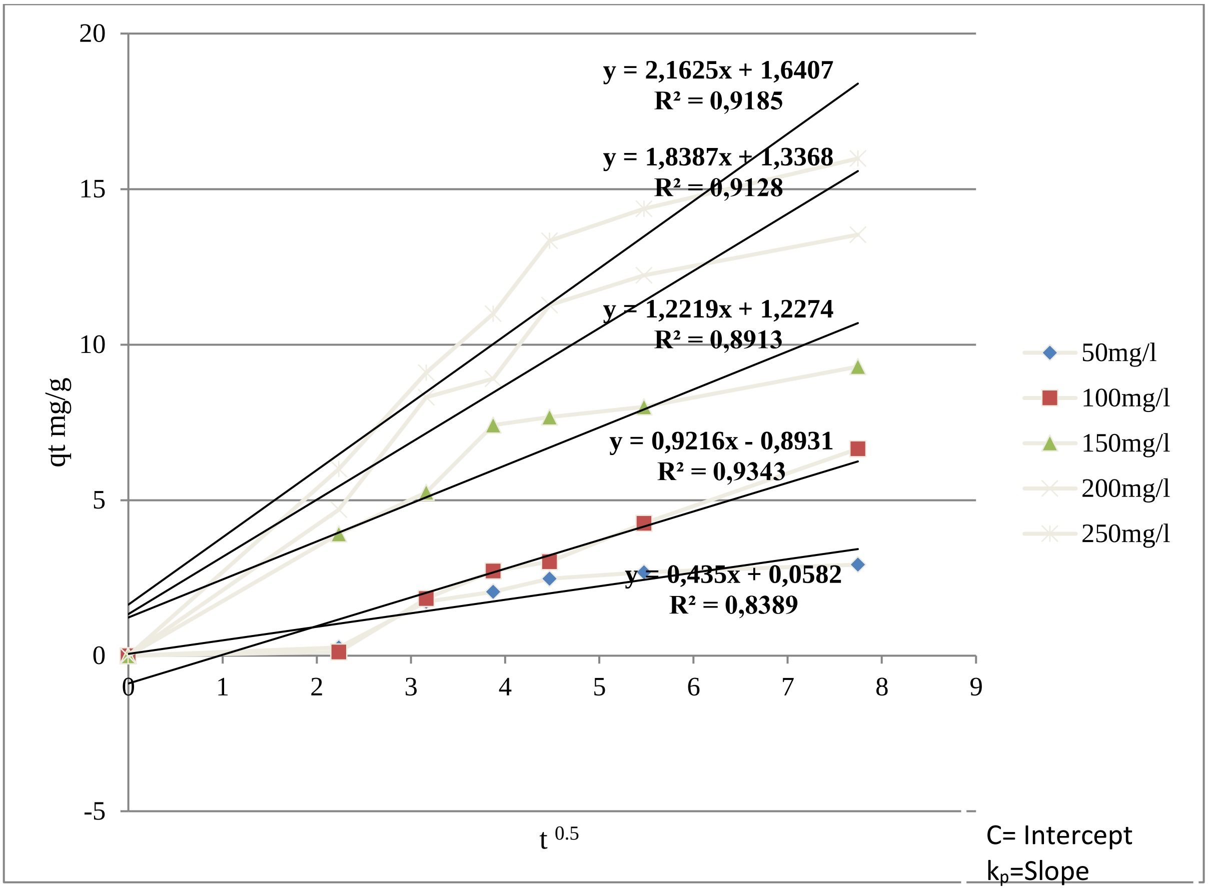

Figure 13. Intraparticle diffusion curve for the adsorption of MG dye from aqueous solution on *Swietenia macrophylla.*

Table 13. Kinetic models parameters for the adsorption of MG dye from aqueous solution on *Swietenia macrophylla.*

	Pseudo First Order			Pseudo Second Order			Intraparticle Diffusion		
Concentration	q_e	k_1	R^2	q_e	k_2	R^2	C	kp	R^2
50 mg/L	6.422	0.566	0.969	3.076	0.207	0.976	0.058	0.435	0.839
100 mg/L	9.410	0.172	0.952	8.688	0.005	0.962	-0.891	0.922	0.934
150 mg/L	13.919	0.195	0.923	14.006	0.005	0.984	1.227	1.222	0.891
200 mg/L	20.720	0.239	0.978	18.622	0.004	0.992	1.337	1.839	0.922
250 mg/L	24.361	0.239	0.988	21.459	0.004	0.992	1.641	2.163	0.919

4. CONCLUSIONS

Saw dust of *Swietenia macrophylla* (mahogany tree) wood waste, was successfully utilized as a low cost alternative adsorbent for the removal of hazardous dye Malachite Green. The following observations were made. Adsorption tends to increase with contact time. Initially the increase in adsorption was very rapid due to the availability of more free sites for adsorption to occur. Rate of adsorption slowly decreases till saturation occurred due to saturation of active site.

The optimum contact time for equilibrium was found to be around 120 minutes. There is increase in adsorption with increase in initial dye concentration until equilibrium was attained at about 120 minutes, this can be attributed to the high driving force for mass transfer as the concentration increases from 50 mg/L to 250 mg/L. The highest percentage removal of MG dye was found to be 90.39 % with concentration ranging from 50 mg/L to 25 0 mg/L at pH 2–12 in 3 hours by shaking at 180 rpm at room temperature and also altering the temperature between 303 – 323 K.

The experimental data correlated reasonably well with the Langmuir and Freundlich adsorption isotherms with Langmuir isotherm showing a better fit than Freundlich isotherm model. In terms of adsorption kinetics and base on the R^2 values and the comparison of the values of adsorption capacities (q_e) the Pseudo-second order kinetic model best described the kinetics of the adsorption. This implies that the experimental results tend to follow pseudo second-order kinetic model better.

Thermodynamic study demonstrates the spontaneous nature of biosorption process due to negative values of free energy change ($\Delta G°$) and negative value of entropy ($\Delta S°$) indicates that the degree of disorderliness of MG reduced as they got adsorbed on the surface of the adsorbent. Also the negative value of enthalpy change ($\Delta H°$) indicates the adsorption is exothermic hence the process is driven by temperature.

It can therefore be concluded that, sawdust of *Swietenia macrophylla* which is an agricultural waste material and is abundance in the country could be a good alternative for the effective removal of MG dye from aqueous solution.

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