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Removal of malachite green from aqueous solution using pulverized teak leaf litter: equilibrium, kinetic and thermodynamic studies

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Abstract

The removal of malachite green (MG) from aqueous solution using teak leaf litter powder (TLLP) was investigated. The process was influenced by initial concentration, pH and temperature of dye solution as well as TLLP dosage. Optimum removal of MG per gram of TLLP occurred at 2 g/L and at pH 6–8. Dubinin–Radushkevich and Freundlich isotherm models fit the batch adsorption data better than Langmuir isotherm. The monolayer capacity of TLLP was 333.33 mg/g at 293–313 K. The mean free energy of 7.07 kJ/mol implied physical adsorption. The pseudo-second order model fit the kinetic data better than the pseudo-first order model. Both intraparticle diffusion and film diffusion mechanisms jointly influenced the adsorption process but the latter was the rate-controlling step. Thermodynamic data indicated that the process was endothermic, spontaneous and feasible. Therefore, TLLP could be an important low-cost adsorbent for removal of MG from aqueous solution.

Keywords: Adsorption, Malachite green, Teak leaf litter, Isotherm, Kinetics, Thermodynamics

Introduction

Malachite green (MG) is a synthetic triarymethane dye mainly employed for dyeing wool, silk, acrylic, leather, wood and paper [1]. It is also used in aquaculture as an ectoparasiticide and a fungicide because of its efficacy and low cost. The application of MG has been curtailed by some countries in recent years due to a number of toxicological concerns which are well documented. The dye is a possible carcinogen, tends to persist in the environment, and is toxic to aquatic and terrestrial organisms [2–4].

A number of methods are available for treating dye-impacted wastewater. However, adsorption method using activated carbon is popular due to its simplicity and efficacy [5]. The main impediment to unfettered employment of the method is the high cost of commercial activated carbon and the extra cost incurred

in regenerating it. These have stimulated the interest of researchers to study non-conventional materials as cheaper and reliable substitutes for commercial activated carbon.

Forest plantations are established in Ghana mainly for production of fuel wood, electric poles, timber, environmental protection and reduction of rural poverty through employment generation. Teak, *Tectona grandis*, is among the most popular species of trees for reforestation in the country [6]. Plants contribute to nutrient cycling through litter fall. The factors that control litter production include: climate, age, size and species of trees; spacing of trees, type of forest, location and human activities [7, 8].

Rapid decomposition of litter assists to maintain soil fertility in tropical forest ecosystems [9]. The determinants of quality of any litter include: the specific weight and levels of carbon, nitrogen, lignin and polyphenols. Torreta and Takeda [10] indicated that, litter with C:N ratio greater than 30–40 may significantly reduce microbial activity leading to immobilization of nitrogen and impeded decomposition. Teak leaf litter (TLL) decomposes slowly due to a combination of its high C:N ratio,

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which is normally greater than 50; and high specific weight.

A comparison of the quantities of litter fall under monoculture teak plantation forests in Nigeria revealed that between 3774 and 6043 kg/ha litter was produced per annum [8]. Leaf litter accounts for at least 70% of the total litter fall [9]. It is estimated that an average of at least 3000 kg/ha of teak leaf litter is expected annually in Ghana. This important biomass is abundantly available and inexpensive [11] but currently either left unused or burnt. This research focused on the feasibility of employing pulverized TLL to remove MG dye from aqueous solution. The impacts of equilibrium adsorption, kinetic and thermodynamic parameters on the overall adsorption process were investigated to shed light on the nature of the adsorption process.

Experimental

Materials

TLL was collected from a monoculture teak plantation at Navrongo, north-eastern Ghana. The sample was washed continuously with large volume of tap water until the wash water was colorless and finally rinsed with distilled water. It was then air-dried for 10 days and crushed using a clean blender. The pulverized sample was washed repeatedly with distilled water until the wash water was colorless. The TLL sample was filtered, dried overnight in an oven at 105 °C. The cooled dry sample was then ground with a blender and sieved to obtain particles lesser than 210 µm. The sample was transferred into a glass bottle, tightly corked and labeled teak leaf litter powder (TLLP).

The MG (oxalate) dye used for the study was manufactured by Surechem Products Limited, Suffolk, England. The dye was used as supplied without any purification. A stock solution containing 1000 mg/L MG was prepared and dilute working solutions were prepared from the stock solution as appropriate. The maximum wavelength (λ_{\max}) of dilute MG solution was found to be 620 nm using UV/visible spectrophotometer (Jenway, model 6305). Concentrated hydrochloric acid and sodium hydroxide pellets used were manufactured by Panreac Quimica S.A., Barcelona, Spain. Distilled water was used for the preparation of all reagents.

Adsorption equilibrium

Adsorption equilibrium tests were conducted for the removal of MG in aqueous solution using TLLP. Very dilute concentrations of the dye were first used to prepare a standard calibration plot use for the determination of the concentration of the dye samples. The effects of contact time, TLLP dose, pH of aqueous dye solution, temperature and concentration of MG dye were

studied. For each test, a known mass of TLLP was weighed into a 250 mL stoppered Erlenmeyer flask, and a predetermined volume of MG solution of known concentration was added. The flask, with its content, was then shaken at 120 rpm and dye samples withdrawn at regular time intervals or after equilibrium as appropriate. The withdrawn sample was centrifuged at 5000 rpm for 5 min and the residual dye in the supernatant was determined by measuring its absorbance at 620 nm using UV/visible spectrophotometer (Jenway, model 6305). The quantity of MG, q_e (mg/g), removed from aqueous solution by TLLP was calculated from the following relationships:

$$q_e = \frac{(C_0 - C_e)V}{w} \quad (1)$$

and

$$R = \frac{(C_0 - C_e) \times 100}{C_0} \quad (2)$$

where, C_0 and C_e (mg/L) are the initial and equilibrium concentration of MG, respectively; V (L) is the volume of the dye, w (g) is the mass of TLLP used; q_e (mg/g) and R (%) is the quantity of MG removed from aqueous solution. All experiments were conducted at room temperature except for the study of the effect of temperature on the adsorption process. Each experiment was conducted in triplicate and the average values reported.

The effects of contact time and initial concentration of MG solution were studied together by adding 100 mL of dye solution to 1 g of TLLP in 250 mL Erlenmeyer flask. The initial concentration of the dye solution ranged between 50 and 200 mg/L. The impact of the dose of TLLP on removal of MG dye from aqueous solution was studied by fixing the initial concentration and volume of dye at 100 mg/L and 100 mL, respectively. The mass of TLLP was then varied from 0.05 to 1.00 g. The effect of pH of MG solution was examined by fixing the initial concentration of MG and mass of TLLP at 200 mg/L and 0.20 g, respectively. The pH of the dye solution was adjusted using 0.1 M HCl and 0.1 M NaOH solution. The initial volume of the dye used was 50 mL and the range of pH studied was 2–8 pH. The dye solution was partially decolorized and unstable at higher pH values. Calibrated pH meter (Crison, model Basic C20, Crison Instruments S.A., Barcelona, Spain) was used to take the readings. The effect of temperature of dye solution on its adsorption by TLLP was conducted by fixing initial concentration and volume of MG at 200 mg/L and 100 mL, respectively. The dye solution was initially fixed at pH 6 and the range of temperature studied was 20–40 °C.

Adsorption kinetics

The adsorption kinetics experiments were conducted using initial MG concentrations of 200, 400 and 800 mg/L. The TLLP mass, temperature and initial pH of dye solution and volume of dye solution were kept constant at 1 g, 40 °C, 6.5 and 100 mL; respectively. The experiments were similar to those of batch equilibrium adsorption tests but dye samples were taken at regular intervals until the process reached equilibrium. The concentration of MG removed from aqueous solution by the adsorbent was determined using the equation below.

$$q_t = \frac{(C_0 - C_t)V}{w} \quad (3)$$

where q_t (mg/g) is the quantity of MG solution at any time, C_0 (mg/L) is the initial concentration of the aqueous solution of MG, C_t (mg/L) is the concentration of MG remaining in aqueous solution at any time, w is the mass of TLLP and V (L) is the volume of MG solution.

Adsorption thermodynamics

The thermodynamics experiments were similar to the kinetic tests except that the temperature of dye solution was varied between 20 and 40 °C. The initial concentration and volume of the dye solution were fixed at 100 mg/L and 100 mL, respectively; the initial pH of dye solution was adjusted to 6.5 while the mass of TLLP used was fixed at 0.2 g. The concentration of the residual MG in solution was determined using Eq. (1).

Results and discussion

Effect of contact time and initial concentration of MG

The plot of the effect of contact time and initial concentration of MG is presented in Fig. 1. The removal of MG from aqueous solution by TLLP was very rapid within the first 5 min before slowing down, and gradually became constant on attaining equilibrium. The rapid uptake of the dye during the first stage could be attributed to the availability of large number of sites on the surface of the adsorbent to facilitate the adsorption process. There was a marked reduction in the speed of adsorption during the second stage because of significant decrease in the number of vacant surface sites available for adsorption. There was equally repulsion between dye molecules already adsorbed on the surface of the adsorbent and dye molecules in the aqueous phase. Similar results have been reported by other researchers who studied the removal of MG from aqueous solution by adsorbents [1, 12].

The contact time required for the process to attain equilibrium was dependent on the initial concentration of MG in aqueous solution. For the initial MG

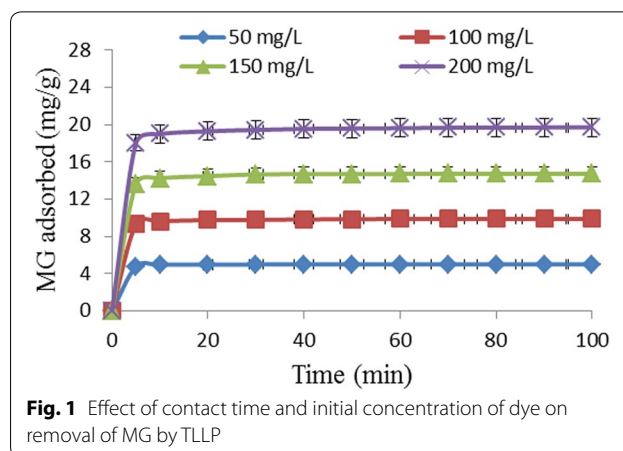


Fig. 1 Effect of contact time and initial concentration of dye on removal of MG by TLLP

concentration of 50, 100, 150, and 200 mg/L, the contact times required for the adsorption to attain equilibrium were: 30, 60, 70, and 90 min, respectively. The variation in the contact time required for adsorption to attain equilibrium could be explained on the basis of the boundary layer film the dye molecules must overcome to move from aqueous solution onto the surface of TLLP. Moreover, the dye molecules had to diffuse from the surface into the pores of the adsorbent. The more concentrated the dye solution, the more time it will take for dye molecules to move from the bulk solution into the pores of the adsorbent [13].

The adsorption capacity of TLLP was dependent on the initial concentration of the MG solution. The capacity of the adsorbent to remove dye molecules from solution increased from 4.99 to 19.70 mg/g when the initial concentration of MG solution was increased from 50 to 200 mg/L. These results could be interpreted in terms of concentration gradient. This provided the driving force to overcome resistances to mass transfer of dye molecules from the solution, toward the surface of the adsorbent [14, 15].

Effect of TLLP dosage

The impact of TLLP dosage on the removal of MG from aqueous solution is shown in Fig. 2. The uptake of dye molecules increased from 33.76 to 98.19% as adsorbent dose was increased from 1 to 10 g/L. However, although the adsorption capacity increased marginally from 33.76 to 34.07 mg/g when the adsorbent dose was raised from 1 to 2 g/L, increase in dosage beyond 2 g/L led to continuous decrease in the adsorption capacity of the adsorbent. The observation could be attributed to rapid superficial adsorption onto the surface of the adsorbent as TLLP to MG concentration ratio increased. The superficial adsorption did not favor optimum uptake of

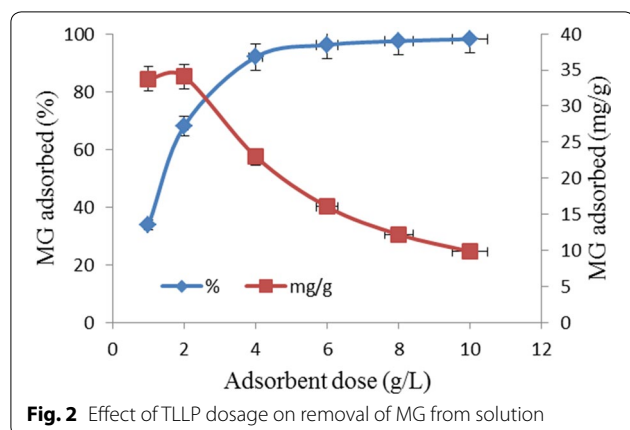


Fig. 2 Effect of TLLP dosage on removal of MG from solution

the dye molecules by the adsorbent. This was responsible for the decrease in adsorption capacity of TLLP as dosage increased. Other researchers who observed similar phenomenon include Hamdaoui et al. [14], Sun et al. [15] and Oyelude et al. [16].

Effect of pH of MG solution

pH plays important role in adsorption. The effect of pH of MG solution on adsorption is presented in Fig. 3. The uptake of MG by TLLP decreased sharply below pH 6 but remained approximately constant from pH 6 to 8. The reduced uptake of the dye below pH 6 was due to electrostatic repulsion between positively charged surface of the adsorbent and the positively charged cationic MG dye. The number of positively charged sites on the adsorbent increased as the pH reduced. Hence the adsorption of the dye molecules to the surface of the adsorbent reduced as pH was lowered [1, 17, 18].

Adsorption isotherms

An adsorbate may not interact with different adsorbents in the same way. Isotherms are plots used to express the distribution of adsorbate molecules between two phases

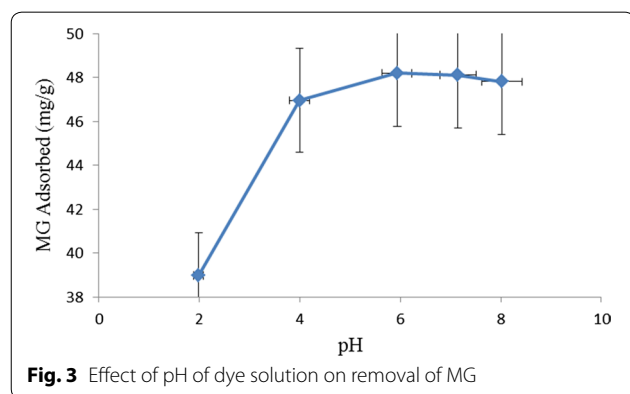


Fig. 3 Effect of pH of dye solution on removal of MG

with respect to time. The removal of MG from aqueous solution by TLLP was studied using isotherm models of Langmuir [19], Freundlich [20] and Dubinin–Radushkevich [21].

Langmuir isotherm assumes constant adsorption energy and monolayer adsorption of adsorbate onto the surface of the adsorbent [19]. The linear form of the equation for the model is:

$$\frac{C_e}{q_e} = \frac{1}{q_m} C_e + \frac{1}{q_m K_L} \quad (4)$$

where C_e (mg/L) is the concentration of MG adsorbed at equilibrium, q_e (mg/g) is the mass of MG adsorbed at equilibrium per unit mass of TLLP, q_m (mg/g) is a constant related to the monolayer adsorption capacity of the adsorbent, and K_L (L/mg) is the Langmuir constant related to the rate of adsorption. A straight-line plot of C_e/q_e versus C_e where slope equal to C_e/q_e and intercept equals $(1/q_m)(1/K_L)$ is presented in Fig. 4. The values of K_L , q_m , R_L and the linear correlation coefficient, R^2 , are presented in Table 1.

A dimensionless constant called separation factor, R_L , can be used to explain the essential characteristics of Langmuir equation. R_L is defined as:

$$R_L = \frac{1}{1 + K_L C_o} \quad (5)$$

where K_L is the Langmuir adsorption constant (L/mg) and C_o (mg/L) is the highest initial concentration of MG. The adsorption process is only favorable if $0 < R_L < 1$, unfavorable if $R_L > 1$, linear if $R_L = 1$ and irreversible if $R_L = 0$. The value of R_L for this present study was 0.0332 which indicates that the process was favorable.

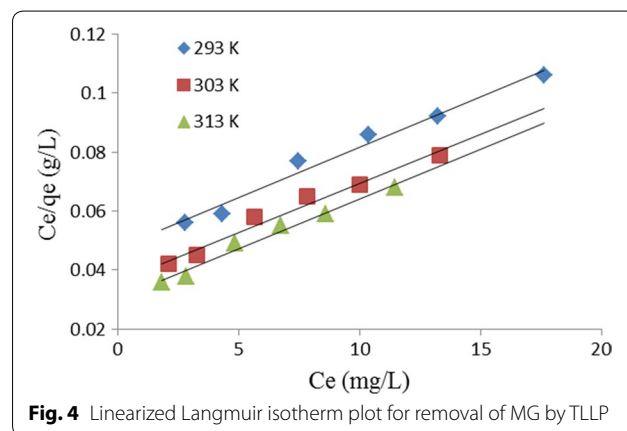


Fig. 4 Linearized Langmuir isotherm plot for removal of MG by TLLP

Table 1 Isotherm constants for the adsorption of MG onto TLLP at pH 6.5

Temperature (K)	K_L (L/mg)	q_m (mg/g)	R_L	R^2
Langmuir isotherm				
293	0.0638	333.33	0.0429	0.978
303	0.0833	333.33	0.0332	0.975
313	0.1000	333.33	0.0278	0.981
Temperature (K)	K_F (mg/g)	n	R^2	
Freundlich isotherm				
293	26.1216	1.5267	0.994	
303	31.4051	1.5198	0.994	
313	35.2371	1.5314	0.993	
Temperature (K)	B (mol ² /J ²)	q_{DR} (mg/g)	E (kJ/mol)	R^2
Dubinin–Radushkevich isotherm				
293	1.0×10^{-8}	348.50	7.07	0.996
303	1.0×10^{-8}	418.91	7.07	0.993
313	1.0×10^{-8}	435.57	7.07	0.997

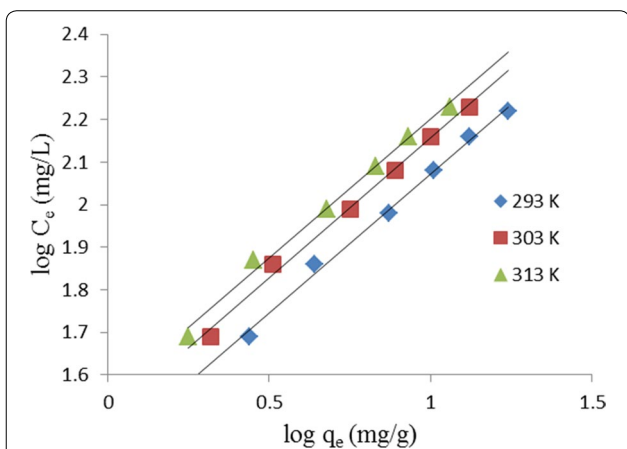


Fig. 5 Linearized Freundlich isotherm plot for removal of MG by TLLP

Freundlich isotherm assumes adsorption from bulk solution onto an adsorbent with heterogeneous surface [20]. The linear form of the equation for the model is:

$$\log q_e = \frac{1}{n} \log C_e + \log K_F \tag{6}$$

where q_e and C_e are as earlier defined, K_F (mg/g)(L/mg)^{1/n} is a constant representing the adsorbent capacity and 1/n is a constant the heterogeneity factor. The numerical value of 1/n must be lesser than one for the adsorption to be favorable. A linear plot of $\log q_e$ against $\log C_e$ is shown in Fig. 5.

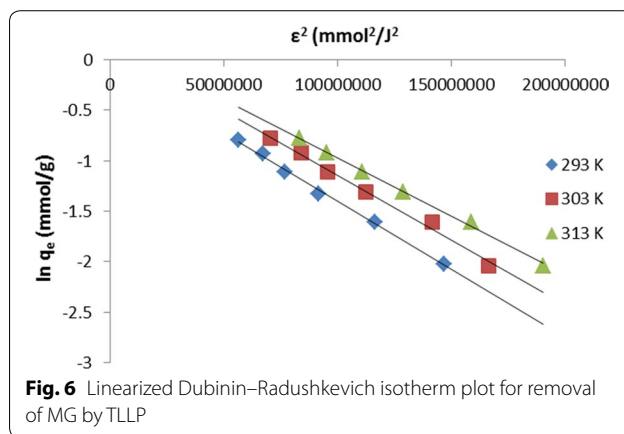


Fig. 6 Linearized Dubinin–Radushkevich isotherm plot for removal of MG by TLLP

The Dubinin–Radushkevich isotherm model [21] is used to determine the characteristic porosity of adsorbent and the mean free energy of adsorption. The isotherm assists to determine whether an adsorption is either physical or chemical in nature. The linear form of Dubinin–Radushkevich equation is:

$$\ln q_e = \ln q_{DR} - \beta \epsilon^2 \tag{7}$$

where q_{DR} (mg/g) is the Dubinin–Radushkevich maximum monolayer adsorption capacity, β (mol²/J²) is a constant related to mean adsorption energy, and ϵ is the Polanyi potential which is calculated using the following relationship:

$$\epsilon = RT \ln \left(1 + \frac{1}{C_e} \right). \tag{8}$$

A plot of $\ln q_e$ against ε^2 is presented in Fig. 6. The values of β and q_{DR} were calculated from the slope and intercept of the plot, respectively. The mean free energy of adsorption is estimated from the value of β using the equation below.

$$E = \frac{1}{\sqrt{2\beta}}. \quad (9)$$

The value of E provides valuable information about the mechanisms of adsorption process. If E is lesser than 8 kJ/mol, the adsorption is regarded as physical in nature. However, if the value of E lies between 8 and 16 kJ/mol, the adsorption is regarded as chemical or ion exchange in nature [22]. The mean adsorption free energy, E , was calculated as 7.07 kJ/mol for this present study. This implies that the adsorption mechanism was physical in nature.

The summary of the isotherm constants and correlation coefficient, R^2 , for the three isotherm models applied for this study is presented in Table 1. On the basis of correlation coefficient alone, all the isotherm models fit the adsorption data well. However, Dubinin–Radushkevich isotherm fits best followed by Freundlich and Langmuir isotherms in that order.

The reported monolayer adsorption capacities of selected low-cost adsorbents for MG are presented in Table 2. TLLP is a good adsorbent for MG based on the basis of its adsorption capacity which was estimated to be 333.33 mg/g. It is worthy of note that temperature is one of the most important parameters that influence the uptake of dye molecules in aqueous solution. For this study, the uptake of MG from aqueous solution increased as temperature of dye solution increased irrespective of the initial concentration of the dye solution. This suggests that the adsorption process is endothermic in nature. This observation is attributed to the driving

force of concentration gradient and increase in temperature which favored the endothermic process [23].

Adsorption kinetics

The kinetic of MG removal from aqueous solution were studied using pseudo-first order, pseudo-second order and intraparticle diffusion models. The equation for the pseudo-first order kinetic model [28] is:

$$\log(q_e - q_t) = \log q_e - \frac{k_1 t}{2.303} \quad (10)$$

where q_e (mg/g) and q_t (mg/g) are the quantity of dye adsorbed at equilibrium and time, t (min), respectively; and k_1 (1/min) is the pseudo-first order rate constant. Figure 7 is a plot of $\log(q_e - q_t)$ against t . The values of k_1 and q_e were determined from the slope ($k_1/2.303$) and intercept ($\log q_e$), respectively. The R^2 values obtained from the plot ranged from 0.970 to 0.983 which implies that the pseudo-first order kinetic model had good fit for the adsorption process. The values of k_1 , q_e and R^2 are shown in Table 3.

Ho and McKay [29] expressed the equation for the pseudo-second order kinetic as follows:

$$\frac{t}{q_e} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (11)$$

where k_2 (g/mg min) is the rate constant. The plot of t/q_e against t is presented in Fig. 8 from which q_e and k_2 are determined from the slope and the intercept, respectively. The initial rate of adsorption, h (mg/g min), is calculated from the following equation:

$$h = k_2 q_e^2. \quad (12)$$

Table 2 Comparison of the reported maximum monolayer adsorption capacities of selected adsorbents for MG

Adsorbent	q_m (mg/g)	References
Teak leaf litter powder	333.33	This study
Commercial powder activated carbon	222.22	[24]
Dead leaves of plane tree	97.09	[14]
Chitosan beads	93.5	[25]
Bivalve shell- <i>Zea mays</i> L husk leaf	81.5	[18]
Rattan sawdust	62.71	[12]
Degreased coffee bean	55.3	[26]
Pineapple leaf powder	54.64	[27]

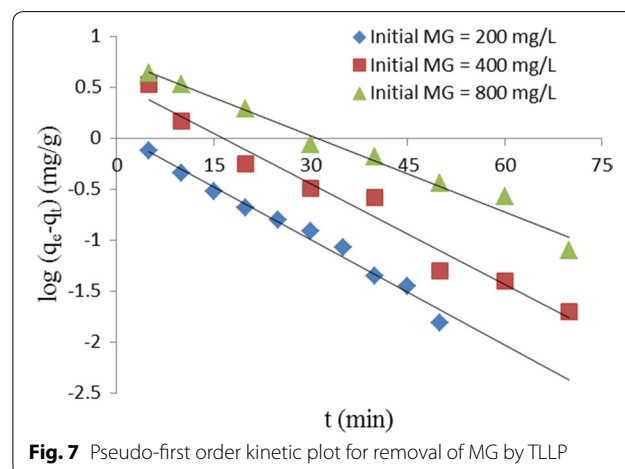
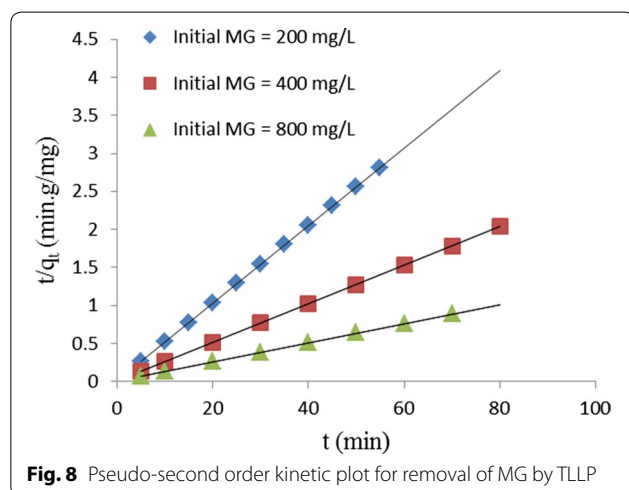


Fig. 7 Pseudo-first order kinetic plot for removal of MG by TLLP

Table 3 Kinetic constants for removal of MG from aqueous solution by TLLP at different temperatures

Kinetic models	Co (mg/L)		
	200	400	800
Pseudo-first order			
q_e , mg/g	1.102	3.524	5.929
k_1 , 1/min	0.015	0.014	0.010
R^2	0.983	0.970	0.979
Pseudo-second order			
q_e , mg/g	19.608	40.000	83.333
k_2 , g/mg min	0.260	0.089	0.029
h , mg/g min	99.963	142.880	199.999
R^2	1.000	1.000	0.999
Intraparticle diffusion			
k_{int} , mg/g min ^{1/2}	0.120	0.407	0.649
C , mg/g	18.730	36.190	73.570
R^2	0.856	0.708	0.899

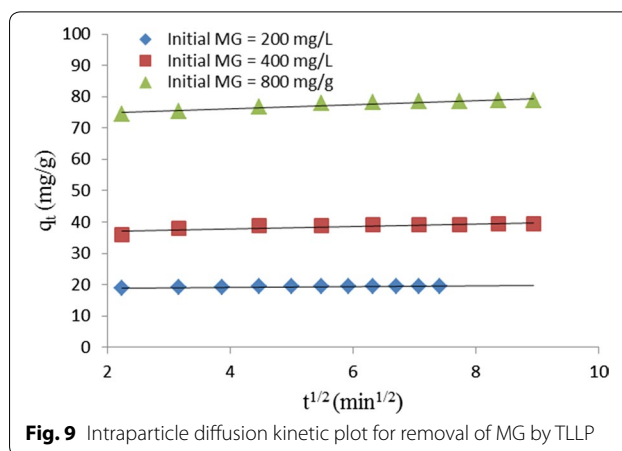
**Fig. 8** Pseudo-second order kinetic plot for removal of MG by TLLP

The values of R^2 ranged between 0.999 and 1.000, which indicates that the adsorption of MG by TLLP perfectly fit the pseudo-second order kinetic model. The values of k_2 , q_e , h and R^2 are presented in Table 3.

Intraparticle diffusion equation [30] is another important kinetic model commonly used to study adsorption kinetics. The intraparticle diffusion equation is:

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

where k_{id} (mg/g min^{1/2}) is the intraparticle diffusion rate constant, q_t (mg/g) is the quantity of dye adsorbed at time t (min), and C (mg/g) is the boundary layer thickness. The plot of q_t against $t^{1/2}$ shown in Fig. 9 is linear for every initial concentration of MG implying that the

**Fig. 9** Intraparticle diffusion kinetic plot for removal of MG by TLLP

adsorption process followed the intraparticle diffusion model. However, none of the plots passed through the origin indicating influence of boundary layer or film diffusion. The plot shows that the thickness of the boundary layer is proportional to the initial concentration of MG in aqueous solution. The values of k_{id} , C and R^2 determined from the plots are shown in Table 3.

Adsorption mechanism

The mechanism for removal of dye molecules from aqueous solution may involve up to four steps. These steps include: bulk diffusion of molecules from solution to the surface of the adsorbent, boundary layer or film diffusion of molecules to the surface of the adsorbent, movement of molecules from the surface into the pores of the adsorbent or intraparticle diffusion and adsorption of dye molecules on active sites on the adsorbent through ion exchange, chelation and/or complexation [31].

It is clear from Fig. 9 that both intraparticle diffusion and film diffusion mechanisms take place at the same time in the uptake of MB by TLLP. The uptake of the dye by the adsorbent was very rapid within the first 5 min before slowing down, and gradually became constant on attaining equilibrium. Boyd model was used to further assess the kinetic data as to the rate-controlling step between intraparticle diffusion and film diffusion. The Boyd equation [32] is:

$$F = 1 - \frac{6}{\pi} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp(-n^2 Bt) \quad (14)$$

and

$$F = \frac{q_t}{q_e} \quad (15)$$

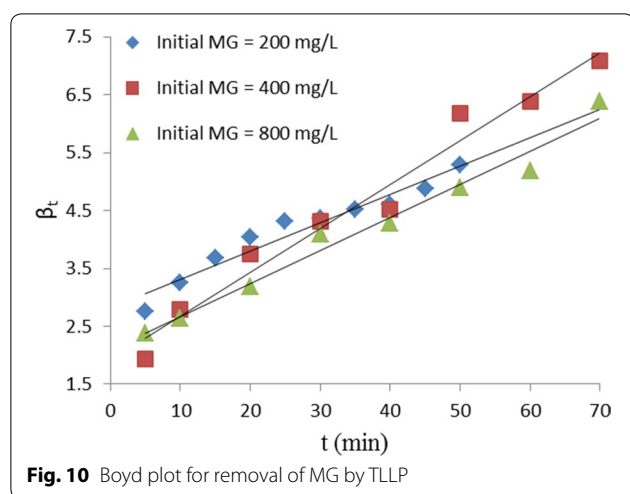


Fig. 10 Boyd plot for removal of MG by TLLP

where F equals the fractional attainment of equilibrium at time, t (min), n is the Freundlich constant, Bt is a function of F , and q_t (mg/g) and q_e (mg/g) represent quantity of dye adsorbed at time, t , and at equilibrium, respectively.

Reichenberg [33] proposed a simpler equation for calculating the values of Bt for each values of $F > 0.85$.

$$Bt = -0.4977 - \ln(1 - F). \quad (16)$$

The plot of Bt versus t used to predict the mechanism of the adsorption process is presented in Fig. 10. The linear plot did not pass through the origin for every initial concentration of the dye in aqueous solution. This confirms that film diffusion was the rate-controlling step in the uptake of MG in aqueous solution by TLLP.

Adsorption thermodynamics

Standard enthalpy (ΔH° , kJ/mol), standard entropy (ΔS° , J/mol K), and standard free energy (ΔG° , kJ/mol), are vital thermodynamics parameters that must be considered for proper assessment of any adsorption process. The following equations were employed to estimate their values for the studied temperature ranging between 293 and 313 K.

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (17)$$

$$\Delta G^\circ = -RT \ln K_d \quad (18)$$

where R is the gas constant (8.314 J/mol K), T (K) is temperature and

$$K_d = q_e/C_e \quad (19)$$

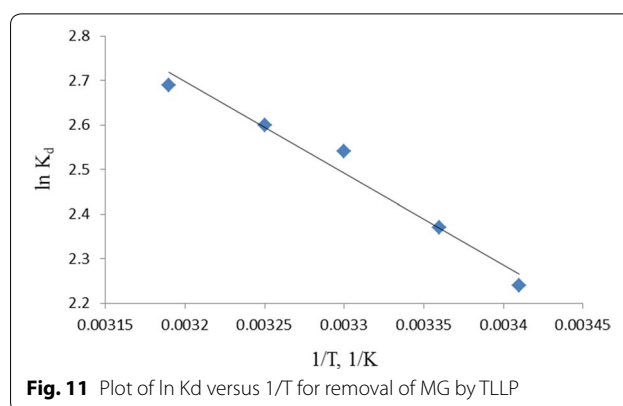


Fig. 11 Plot of $\ln K_d$ versus $1/T$ for removal of MG by TLLP

where K_d is the distribution coefficient, q_e (mg/g) is the quantity of MG adsorbed at equilibrium and C_e (mg/L) is the quantity of MG remaining in solution at equilibrium. Equation (18) was used to estimate the values of ΔG° at various temperatures. The equalization of Eqs. (17) and (18) produce:

$$\ln K_d = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT}. \quad (20)$$

The plot of $\ln K_d$ versus $1/T$ shown in Fig. 11 is used for the estimation of the magnitudes of ΔH° and ΔS° . The values of ΔH° , ΔS° and ΔG° are presented in Table 4. The values of ΔG° were negative at the range of temperature studied implying that the adsorption process was spontaneous and thermodynamically favorable. However, the positive value of ΔH° was positive indicating an endothermic process. The positive value of ΔS° was a reflection of the increased randomness at the TLLP/MG solution interface due to the affinity of the adsorbent for the dye.

Conclusion

The removal of MG from aqueous solution revealed that the process was influenced by initial concentration, pH and temperature of dye solution as well as TLLP dosage. Optimum uptake of the dye per gram of the adsorbent occurred at 2 g/L and at pH 6–10. Dubinin–Radushkevich and Freundlich isotherm models fit the batch adsorption data better than Langmuir isotherm. However, the monolayer capacity of TLLP for the removal of MG in aqueous solution was calculated to be 333.33 mg/g at 293–313 K. The adsorption process was physical in nature because the mean free energy was 7.07 kJ/mol.

Table 4 Thermodynamic parameters for the removal of MG from aqueous solution by TLLP

ΔH° (kJ/mol)	ΔS° (kJ/mol K)	ΔG° (kJ/mol)				
		293 K	298 K	303 K	308 K	313 K
17.069	0.077	-1.964	-2.138	-2.348	-2.447	-2.575

The pseudo-second order model fit the kinetic data much better than the pseudo-first order model. Intra-particle diffusion and film diffusion jointly influence the mechanism of adsorption. However, film diffusion was the rate-controlling step for the uptake of MG in aqueous solution by TLLP. Thermodynamic data indicated that the process was endothermic, spontaneous and feasible. Therefore, TLLP could be an important low-cost adsorbent for removal of MG from aqueous solution.

Abbreviations

MG: malachite green; TLL: teak leaf litter; TLLP: teak leaf litter powder; C:N: carbon to nitrogen ratio; q_e : mass of MG (mg) per gram of TLLP at equilibrium; q_t : mass of MG (mg) per gram of TLLP at any time; C_0 : initial concentration of MG (mg/L); C_e : concentration of MG remaining in aqueous solution at equilibrium (mg/L); C_t : concentration of MG remaining in aqueous solution at any time (mg/L); t: time (min); V: volume of aqueous solution of MG (L); R: proportion of MG removed from aqueous solution (%); T: temperature (Kelvin); q_m : Langmuir isotherm monolayer adsorption capacity of TLLP (mg/g); K_L : Langmuir isotherm constant; R_L : linear correlation coefficient (R^2); K_F : Freundlich isotherm constant; $1/n$: heterogeneity factor of Freundlich isotherm; q_{DR} : Dubinin–Radushkevich monolayer adsorption capacity of TLLP (mg/g); β : constant related to mean free energy of adsorption; ϵ : Polanyi potential; R: gas constant (8.314 J/mol K); E: mean free energy of adsorption; k_1 : pseudo-first order kinetic rate constant; k_2 : pseudo-second order kinetic rate constant; h: initial rate of adsorption (mg/g min); k_{id} : intraparticle diffusion rate constant; F: fractional attainment of equilibrium; Bt: function of F; ΔH° : change in standard enthalpy; ΔS° : change in standard entropy; ΔG° : change in standard free energy; K_d : distribution coefficient.

Authors' contributions

This work is part of the doctorate research of EOO jointly supervised by JAMA and SKT at Kwame Nkrumah University of Science and Technology, Kumasi, Ghana. EOO designed the study and conducted all analyses. JAMA and SKT approved the study design and provided guidance during laboratory analyses. EOO wrote the first draft of the manuscript and JAMA and SKT contributed to the subsequent revisions. All authors read and approved the final manuscript.

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The authors declare that they have no competing interests.

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