

Removal of malachite green from aqueous solution using activated carbon prepared from teak leaf litter

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Abstract

Teak leaf litter (TLL) was impregnated with phosphoric acid and activated at 400 °C for 1 h to produce teak leaf litter activated carbon (TLLAC). Equilibrium adsorption, kinetics and thermodynamics study was then used to assess the removal of malachite green (MG) from aqueous solution by the novel adsorbent. Temperature, pH and initial concentration of dye solution as well as dosage and contact time influenced the adsorption process. The optimum TLLAC dosage for adsorption of MG was 0.5 g/L. Removal of MG from aqueous solutions increased up to pH 10. The adsorption process was best described using Langmuir isotherm with 91.74 mg/g as the monolayer capacity of TLLAC. Pseudo-second order kinetic model best fit the adsorbent-dye interactions. The mechanism of uptake of MG by TLLAC was jointly influenced by both liquid film and intraparticle diffusion but neither was the rate controlling step. The exothermic process was spontaneous below 313 K. The value of ΔH° (-83.82 kJ/mol) implies possibility of influence of chemical adsorption in the system. The study revealed that TLLAC exhibited potentials to remove MG from aqueous solutions.

Keywords: Activated Carbon, Isotherm, Kinetics, Malachite Green, Teak Leaf Litter, Thermodynamics

1. Introduction

Water is invaluable for the sustenance of living organisms. However, fresh water suitable for the use of man is much less than 0.05% of all the global water bodies[1]. Furthermore, climate change, industrialisation, unsustainable use of agrochemicals, increasing population and urbanisation contribute immensely to water pollution. Therefore, the need to ensure adequate availability of safe potable water is a pressing challenge for governments and researchers worldwide. Malachite green (MG) or C.I. Basic Green 4 is a triarylmethane dye used extensively as parasiticide, fungicide and antiprotozoan in aquaculture. It is equally used in healthcare, textile, food and some other applications[2]. However, use of the dye at certain concentrations and low temperatures as well as possible risk to consumers of MG-treated aquaculture products has led to restrictions on its use. The toxicological effects of malachite green have been reviewed extensively [2, 3]. A number of technologies are employed for water and wastewater treatment [4]. Each of these methods has its own benefits and limitations. Adsorption process using activated carbon is a popular treatment technology for dye-impacted wastewaters. The benefits of adopting this technology were earlier discussed in other works [5, 6]. However, activated carbon is expensive and the need to regenerate it before it can be reused may further exacerbate the cost implications of this effective treatment technology. Many researchers are devoted to producing low-cost activated carbon and other adsorbents as alternatives to expensive commercial activated carbon. Teak, *Tectonagrandis*, is the most prevalent species of trees for reforestation in many countries in Asia and Africa[7]. Ojo and his co-workers [8] studied the quantities of litter fall under monoculture teak plantation forests in Nigeria and revealed that between 3774 and 9020 kg/ha litter was produced per annum. However, litter quantity is influenced by factors such as: age, climate, size, species, spacing, human activities and type of forest. Thakur and Thakur [9] who worked in India estimated that leaf litter accounts for 70% or more of total teak litter fall. This enormous biomass is often left unused and considered a nuisance. This work investigated the prospect of employing low-cost teak leaf litter activated carbon (TLLAC) prepared from teak leaf litter (TLL) to remove malachite green from aqueous solution. The study includes: equilibrium adsorption, kinetics and thermodynamics studies.

2. Materials and Methods

2.1. Materials

All chemicals used were of analytical grade and used as supplied without further purification. MG oxalate dye (C.I. 42000) was manufactured by Surechem Products Limited, Suffolk, England. 85% (w/w) concentrated ortho-phosphoric acid was manufactured by Merck Darmstadt, Germany, 35.4% (w/w) concentrated hydrochloric acid was manufactured by BDH Chemicals, Poole, England, 99.0% sodium hydroxide pellets was manufactured by VWR Chemicals, Leuven, Belgium. Distilled water was used for the preparation of all reagents.

2.2. Preparation of Activated Carbon

Activated carbon was prepared from TLL by adopting the chemical activation method [10] with slight modifications. 500 g pulverised air-dried TLL was mixed with 40% (w/w) ortho-phosphoric acid to achieve an impregnation ratio of 1:1 and left for 24 h. Excess acid was removed and acid-impregnated TLL dried at 105 °C for 6 h in an oven. The carbon obtained was left to cool in the oven, weighed and transferred into a muffle furnace. The furnace was heated at average rate of about 4 °C/min until it reached 400 °C where it remained unchanged for 1 h. The activated carbon produced was then allowed to cool in the furnace before washing it repeatedly with distilled water until the pH of wash water was neutral. It was later dried overnight in an oven at 105 °C, cooled in a desiccator and its yield calculated[11]. The final product was ground, sieved to produce average particle size below 210 µm, transferred into a clean glass bottle, corked tightly and labeled TLLAC.

2.3.Characterisation of TLLAC

Proximate analysis of TLLAC comprising determination of moisture content, volatile matter, ash and fixed carbon (by difference) was carried out as described by [12]. Surface area (m^2/g) was assessed using the method of Sears, Jr. [13]. pH was determined using properly calibrated pH meter [14]. The pH of point of zero charge (pH_{pzc}) for was determined using the method described by [15]. Iodine number was determined as described by Babatunde and his co-workers [16]. The bulk density was estimated using 50-ml capacity measuring cylinder [17]. The values of matter soluble in water and matter soluble in acid were equally determined [18]. Every parameter was determined in triplicates and the mean values reported.

2.4.Preparation of MG Solutions

Stock solution of MG was prepared by dissolving 1 g of the dye in 1 L volumetric flask and topping it up to the mark with distilled water to produce 1000 mg/L MG solution. The working solutions were prepared from the stock solution as needed. Furthermore, a linear calibration plot of MG was prepared using dilute dye solutions.

2.5.Equilibrium Adsorption and Isotherm

Equilibrium adsorption experiments were conducted at room temperature (except for the effect of temperature) using 250 mL stoppered Erlenmeyer flasks agitated on mechanical shaker at 120 rpm. Portions of residual dye samples were removed from the flasks periodically and centrifuged at 2000 rpm for 5 min. The residual dye was then analysed at 617 nm using uv/visible spectrophotometer. The quantity of dye, q_e (mg/g) or R (%), adsorbed was calculated from the equations below.

$$q_e = \frac{C_o - C_e}{w}, \quad (1)$$

$$R = \frac{C_o - C_e}{C_o} \quad (2)$$

where, C_o (mg/L) is the initial concentration of dye, C_e (mg/l) is the final concentration of dye, V (l) is the volume of dye solution and w (g) is the mass of TLLAC. Every experiment was repeated thrice and the average value recorded. Any individual value that deviated from the average value by more than 5% was repeated. The experiment on effects of contact time and initial concentration of MG solution were conducted using 1 g of TLLAC and 100 mL of MG solution. The initial concentrations of MG studied were: 50, 100, 150 and 200 mg/L. The impact of adsorbent dosage on adsorption was studied by fixing initial concentration and volume of MG at 100 mg/L and 100 mL, respectively. The mass of TLLAC was varied from 0.05 g to 1 g. The impact of pH of dye solution on adsorption was investigated by fixing the mass of TLLAC, volume and initial concentration of MG at 0.2 g, 50 mL and 200 mg/L, respectively. The effect of temperature was studied at 5 K intervals from 303 to 318 K. The mass of adsorbent, initial concentration, volume and pH of MG were fixed at 0.2 g, 100 mg/L, 100 mL and 6.5, respectively. Data used for describing the isotherm was obtained by fixing the mass of TLLAC, temperature, volume and pH of MG at 1 g, 303 K, 100 mL and pH 10, respectively. However, the initial concentration of the dye solution was varied from 100 to 900 mg/L.

2.6.Adsorption Kinetics

The kinetics experiments were conducted by varying the initial concentration of MG solution from 200 to 800 mg/L. However, mass of TLLAC, volume, temperature and pH of dye solution were fixed at 1 g, 100 mL, 313 K and pH 10, respectively. The rate of uptake of dye by the adsorbent was monitored at predetermined uniform time intervals until it attained equilibrium.

2.7. Adsorption Thermodynamics

The thermodynamic experiments were similar to the experiments on the effects of temperature described earlier. The experiment was conducted by placing the flask containing the adsorbent-dye mixture in a water bath earlier set at a predetermined temperature. The rate of removal of the dye by the adsorbent was monitored until it reached equilibrium.

Table 1. Characteristics of TLLAC used to remove MG from aqueous solution

S/N	Property	TLLAC
1	pH	6.91±0.02
2	pH _{pzc}	6.45±0.01
3	Moisture (%)	1.24±0.01
4	Volatile matter (%)	6.21±0.12
5	Ash (%)	2.40±0.02
6	Fixed carbon (%)	90.15±0.17
7	Surface area (m ² /g)	469.13±1.85
8	Matter soluble in water (%)	1.66±0.03
9	Matter soluble in acid (%)	3.54±0.02
10	Bulk density (g/cm ³)	0.34±0.01
11	Iodine number (mg/g)	230.33±3.78

3. Results and Discussion

3.1. Characterisation of TLLAC

The mean yield of TLLAC prepared was 40.60%. The values obtained for the characterisation of TLLAC are summarised in Table 1. The adsorbent was acidic with appreciable fixed carbon content. However, its surface area and iodine number values are below the minimum value of 500 m²/g and 500 mg/g, respectively, recommended for commercial activated carbons. The quality might probably be better if the activation process were carried out in an inert environment and the preparation conditions optimised.

3.2. Effects of Contact Time and Initial Concentration of MG

The changes in the initial concentration of MG, shown in Figure 1(a), influenced the quantity of dye removed and the time required for equilibrium to be attained. Only 40 min was required for the initial MG concentration of 50 mg/L to reach equilibrium. However, it took 160 min for 200 mg/L dye solution to reach equilibrium. Similarly, MG adsorbed at equilibrium increased from 9.75 to 73.36 mg/g as the initial dye concentration was increased from 50 to 200 mg/L. This observation is attributable to the fact that the higher the dye concentration the easier it is for MG molecules to overcome the resistance at the MG-TLLAC surface interface [19]. Removal of MG was rapid within the first 10 min and then slowed down. The rapid removal of the dye from aqueous solution by the adsorbent at the initial stage is attributable to the presence of large number of free binding sites on the surface of TLLAC. The rate of uptake of dye by the adsorbent was slow in the second stage because of significant reduction in the number of vacant sites. There was equally a possibility of repulsion between dye molecules at the liquid-solid interface. This observation is similar to earlier reports [20, 21] for activated carbon prepared from rubber seed coat and coconut shell, respectively as adsorbents.

3.3. Effect of TLLAC Dosage

The influence of TLLAC dosage on the removal of MG is shown in Figure 1(b). The removal of dye from solution rose from 41.24% to 95.84% as the adsorbent dosage was increased from 0.5 to 10 g/L. Every increment in TLLAC dosage without corresponding change in the concentration of the MG solution led to the availability of more binding sites leading to removal of larger quantity of the dye [22].

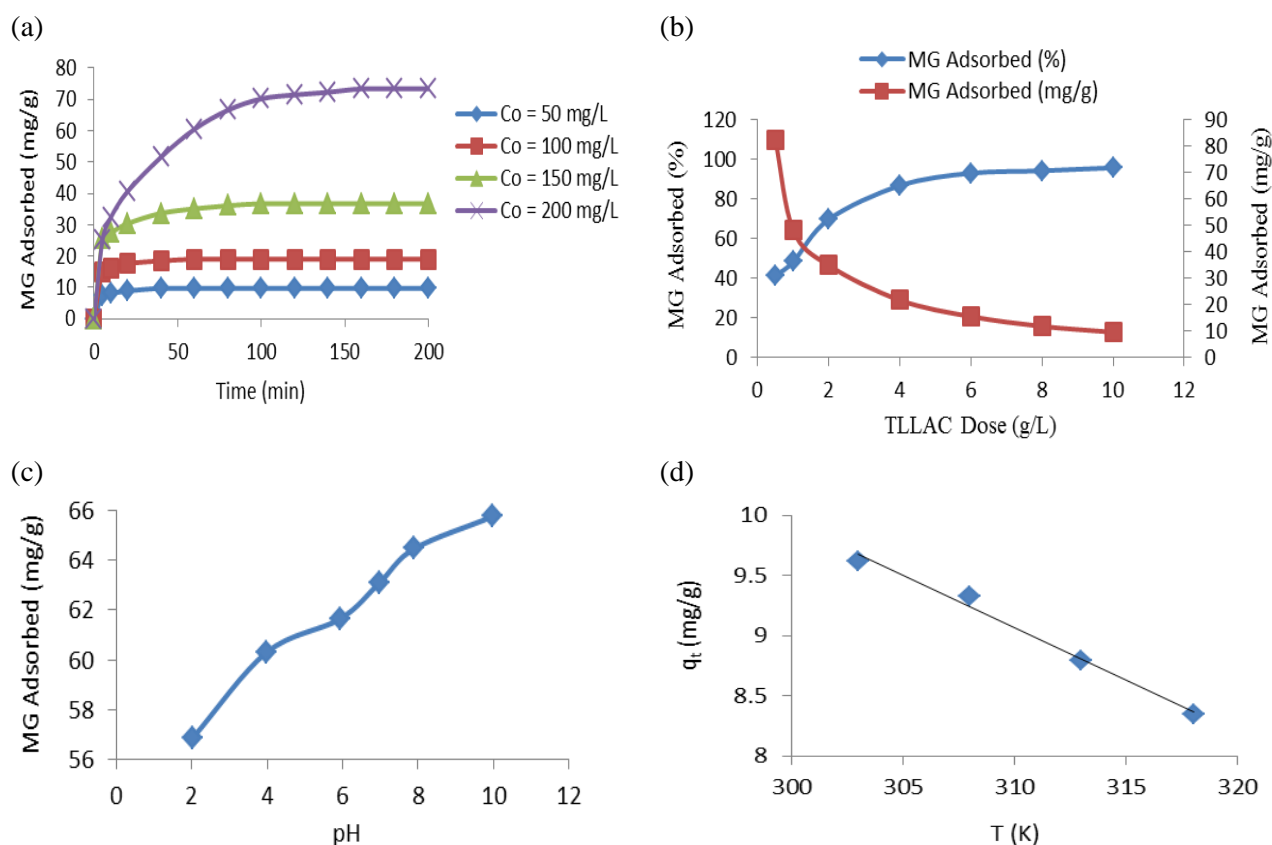


Figure 1. Effects of contact time and initial concentration of MG(a), TLLAC dosage (b), pH of MG solution (c) and temperature of MG solution (d) on removal of MG by TLLAC

The actual density of dye removed plunged from 82.48 to 9.58 mg/g. The observation was due to rapid superficial adsorption onto the surface of TLLAC as adsorbent to adsorbate concentration ratio increased and aggregation of particles of the adsorbent. Similar observation has been reported by other researchers who used dead leaves of plane tree [23] and activated carbon prepared from *Polygonum orientale* Linn [24].

3.4. Effect of pH of MG Solution

The uptake of MG by TLLAC, Figure 1(c), was influenced by the pH of the dye solution. The density of dye removed increased from 56.86 mg/g at pH 2 to 65.75 mg/g at pH 10. Electrostatic repulsion between the positively charged sites on the surface of the adsorbent below pH 6.45, the pH_{pzc} , and the positively charged MG ion might be responsible for lower adsorption at low pH values. As pH of the dye solution was raised beyond that of pH_{pzc} , the magnitude of positive charge on the surface of the adsorbent reduced and that of negative charge increased promoting electrostatic attraction between the adsorbent binding sites and the dye ions. This led to increase in the quantity of dye removed at high pH values [24, 25].

3.5. Effect of Temperature

The removal of MG from aqueous solution was favoured at lower temperature as adsorption capacity decreased as temperature was raised as presented in Figure 1(d). The uptake of MG decreased from 9.62 mg/g to 8.35 mg/g when temperature was raised from 303 K to 318 K. This suggests that the adsorption kinetic was exothermic in nature. This observation was opposite to other works that reported endothermic process for uptake of MG by activated carbon from rubber seed coat [20] and banana stalk [26], respectively.

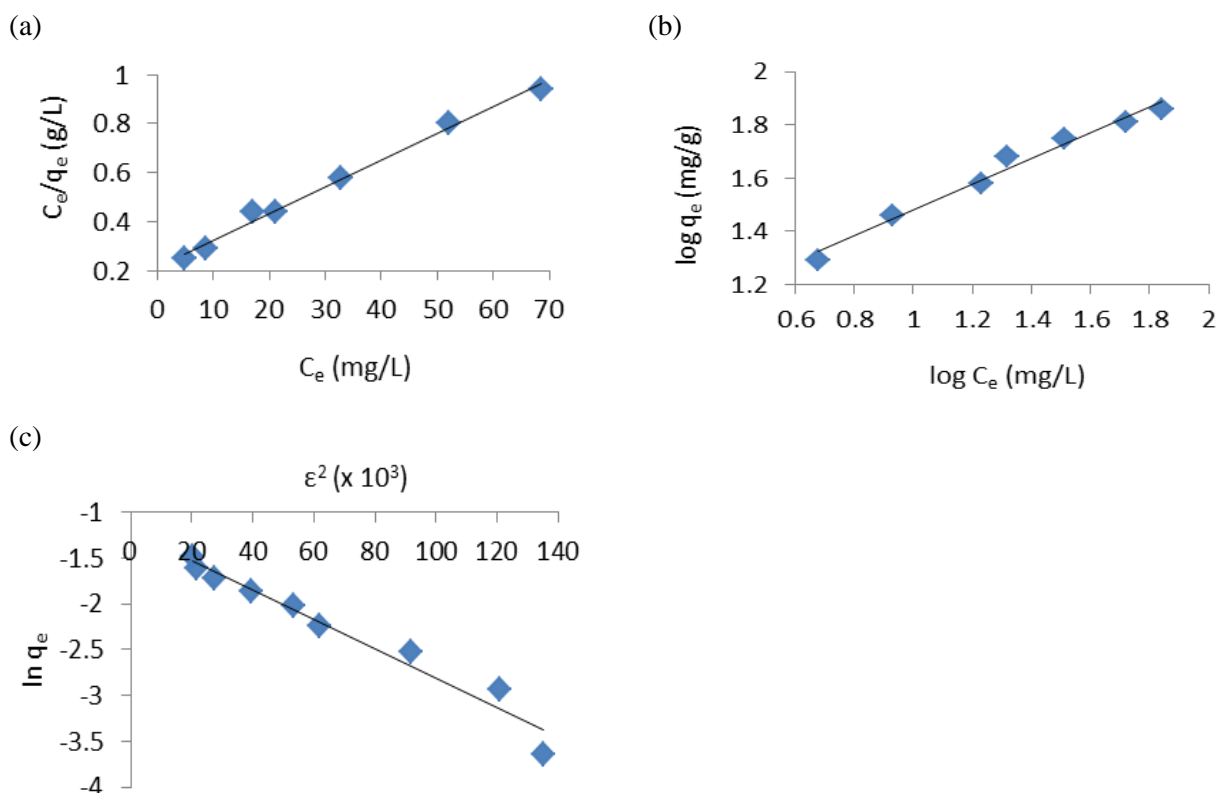


Figure 2. Langmuir (a), Freundlich (b) and Dubinin-Radushkevich (c) isotherm plots for removal of MG by TLLAC at 303 K

3.6 Adsorption Isotherm

Adsorption isotherm is used to describe the association between the quantity of adsorbate in solution and that removed at equilibrium by adsorbent as a function of concentration and at fixed pH and temperature [27]. Langmuir, Freundlich and Dubinin-Radushkevich isotherm models were used to describe the equilibrium adsorption data at 303 K. Figure 2(a) shows the linear form of the Langmuir isotherm for the removal of MG by TLLAC. Langmuir isotherm is based on the assumption monolayer adsorption, hence an adsorbent ceases to accommodate adsorbate molecules or ions after all binding sites on it have been occupied. Moreover, the adsorption energy is assumed to be constant over the entire surface of the adsorbent [28, 29]. The linearised form of Langmuir equation [30] is

$$\frac{C_e}{q_e} = \frac{1}{q_m} C_e + \frac{1}{q_m K_L} \quad (3)$$

where C_e (mg/L) and q_e (mg/g), respectively, is the concentration and mass of adsorbate removed at equilibrium per unit mass of adsorbent, q_m (mg/g) is the monolayer adsorption capacity of the adsorbent, and K_L (L/mg) is the Langmuir constant related to the rate of adsorption. The values of q_m and K_L are determined from the slope and intercept, respectively, of the linear plot of C_e/q_e versus C_e . A dimensionless constant called separation factor, R_L , can

be used to explain the essential characteristics of Langmuir equation and hence its applicability to an adsorption data. R_L is defined as:

$$R_L = \frac{1}{1 + K_L C_0} \quad (4)$$

where K_L (L/mg) and C_0 (mg/L) are the Langmuir adsorption constant and the highest initial concentration of adsorbate, respectively.

Table 2. Maximum monolayer adsorption capacities of selected low-cost activated carbons for removal of MG by TLLAC

Precursor of Activated Carbon	q_m (mg/g)	Reference
Teak leaf litter (TLLAC)	91.74	This study
<i>Polygonum orientale</i> Linn	480.00	[24]
Rambutan peel	329.49	[25]
Spent tea leaves	256.40	[31]
Coconut shell	214.63	[21]
Banana stalk	141.76	[26]
Rubber seed coat	72.73	[20]
Rice bran	69.00	[32]
<i>Borassus aethiopicum</i> flower biomass	48.48	[33]
Kapok hull	30.16	[34]
<i>Annona squamosa</i> seed	25.91	[35]

Freundlich isotherm assumes uptake of adsorbate molecules or ions from the bulk fluid onto a solid phase with heterogeneous surface [36]. The adsorption process is multi-layer in nature with enthalpy of adsorption decreasing as the fraction of the adsorbent sites occupied increases [27]. The linearised Freundlich adsorption equation is

$$\log q_e = \frac{1}{n} \log C_e + \log K_F \quad (5)$$

where q_e (mg/g) is the mass of adsorbate removed at equilibrium per unit mass of adsorbent and C_e (mg/L) is the concentration of adsorbate removed by adsorbent at equilibrium and K_F (mg/g)(L/mg)^{1/n} and $1/n$ are constants representing the adsorbent capacity and the heterogeneity factor, respectively. A linear plot of $\log q_e$ against $\log C_e$ enables the determination of the values of $1/n$ and K_F from the slope and intercept, respectively. The linear form of the Freundlich isotherm plot for the removal of MG by TLLAC is presented in Figure 2(b). Dubinin-Radushkevich isotherm [37] is used to determine the characteristic porosity of adsorbent, the mean free energy of adsorption and whether an adsorption process is physical or chemical in nature. The linear form of Dubinin-Radushkevich equation is

$$\ln q_e = \ln q_{DR} - \beta \varepsilon^2 \quad (6)$$

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

$$\varepsilon = RT \ln \left(1 + \frac{1}{C_e} \right) \quad (7)$$

where R (8.314 J/mol K) is the gas constant, T (K) is temperature and C_e (mg/L) is the concentration of adsorbate at equilibrium. The values of q_{DR} and β are determined from the plot of $\ln q_e$ against ε^2 which is linear. The mean free energy of adsorption (E , J/mol) is determined using the following equation

$$E = \frac{1}{\sqrt{2\beta}} \quad (8)$$

An adsorption process is said to be physical in nature if $0 < E < 8$ kJ/mol; and chemical in nature if $8 < E < 16$ kJ/mol (Bello *et al.*, 2012). The linear form of the Dubinin-Radushkevich isotherm plot for the removal of MG by TLLAC is presented in Figure 2(c).

Table 3. Isotherm parameters and constants for the adsorption of MG onto TLLAC

Langmuir Isotherm	K_L (L/mg)	q_m (mg/g)	R_L	R^2
	0.050	91.74	0.022	0.992
Freundlich Isotherm		K_F (mg/g)	n	R^2
		9.842	2.061	0.979
Dubinin-Radushkevich Isotherm	β (mmol ² /J ²)	q_{DR} (mg/g)	E (kJ/mol)	R^2
	2.0×10^{-5}	108.72	0.16	0.961

The parameters, constants and correlation coefficients (R^2) obtained from the three isotherm models are collated in Table 3. Langmuir isotherm model best described the removal of MG by TLLAC because its correlation coefficient is closest to unity. The capacity of the adsorbent was calculated to be 91.74 mg/g which is comparable to the reported values for other laboratory-prepared activated carbons in Table 2. The process was favourable as indicated by the values of R_L and $1/n$ which lie between zero and unity. The process was likely physical adsorption because the mean free energy was only 0.16 kJ/mol [26].

3.7. Adsorption kinetics

Adsorption kinetics determines how long adsorbate ions or molecules stay at the adsorbent-adsorbate solution interface. Kinetic studies help to understand an adsorption process, the mechanism and the approach to develop it for commercial application [38]. Pseudo-first order kinetic, pseudo-second order kinetic, intraparticle diffusion and liquid film diffusion models were used to describe the equilibrium adsorption data at 303 K. The pseudo-first order equation [39] is:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (9)$$

where, q_e (mg/g) and q_t (mg/g) are the quantity of MG removed at equilibrium and time, t (min), respectively; and k_1 (1/min) is the pseudo-first order rate constant. The values of k_1 and q_e were determined from the slope and intercept, respectively of the plot of $\ln(q_e - q_t)$ versus t . The pseudo-first order kinetic plot for the removal of MG by TLLAC is presented in Figure 3(a). This model is often valid during the initial period of adsorption when the rate of uptake of adsorbate by adsorbent tends to be fast.

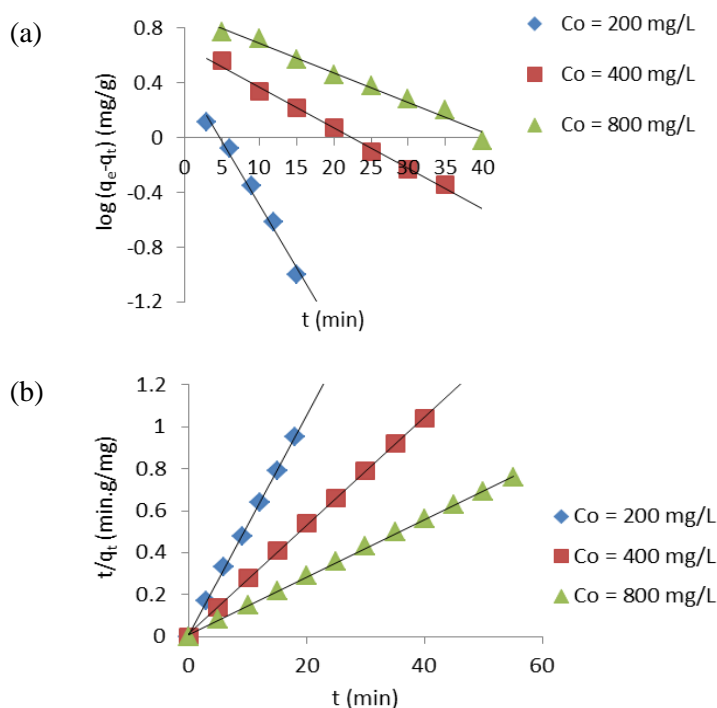


Figure3. Pseudo-first (a) and pseudo-second (b) order kinetics for removal of MG by TLLAC at 303 K

The pseudo-second order model [40] is often applicable over the entire duration of an adsorption process[41]. The equation is

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (10)$$

where, q_t (mg/g), q_e (mg/g) and t (min) are as earlier defined and k_2 (g/mg min) is the pseudo-second order rate constant. The values of q_e and k_2 were determined from the slope and intercept, respectively of the plot of t/q_t against t . The pseudo-second order kinetic plot for the removal of MG by TLLAC is presented in Figure 3(b). The initial rate of adsorption, h , is calculated by applying the following relationship:

$$h = k_2 q_e^2 \quad (11)$$

The value of k_2 is normally inversely proportional to the initial concentration of adsorbate. The ions or molecules adsorbed on the surface of adsorbent particles may move from the surface to the pores of the particles. The influence of pore diffusion is studied by applying intraparticle diffusion equation [42]

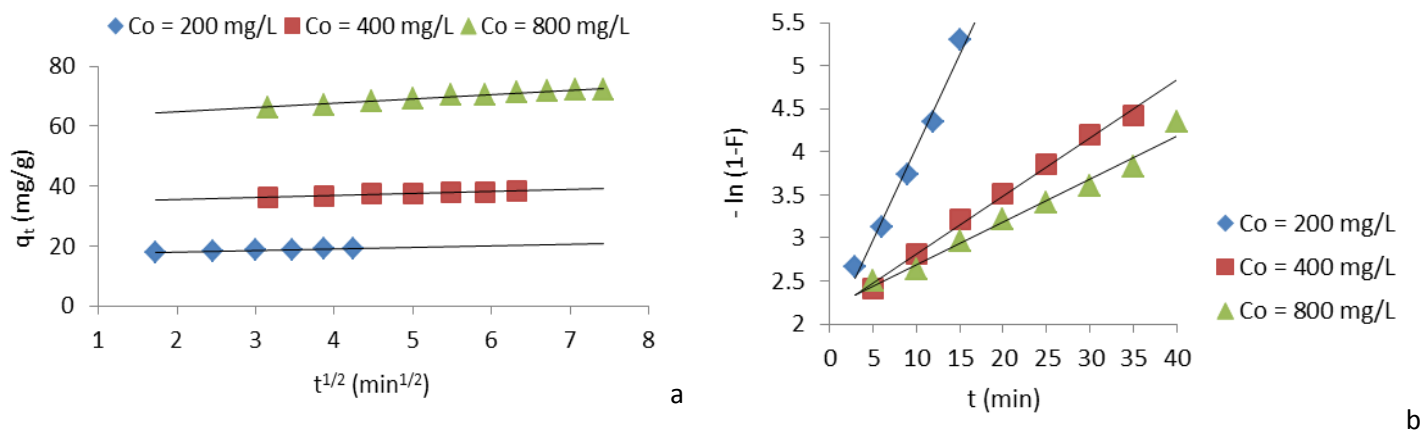


Figure4. Intraparticle (a) and liquid film (b) diffusion kinetics for removal of MG by TLLAC at 303 K

Table 4. Kinetic constants for removal of MG from aqueous solution by TLLAC

Kinetic Models	Co (mg/g)		
	20	40	80
	0	0	0
Pseudo-First Order			
q _e , mg/g (Experimental)	18	38	78
q _e , mg/g (Calculated)	.98	.42	.98
k ₁ , g/mg.min	2.	4.	8.
R ²	754	662	061
	0.	0.	0.
Pseudo-Second Order	212	068	050
q _e , mg/g (Experimental)	0.	0.	0.
q _e , mg/g (Calculated)	986	993	982
k ₂ , g/mg.min			
h, mg/g.min			
R ²	18	38	78
	.98	.42	.98
Intraparticle Diffusion	19	38	72
K _{id} , mg/g.min ^{1/2}	.08	.61	.99
C, mg/g	0.	0.	0.
R ²	319	051	016
	11	76	85
Liquid Film Diffusion	6.2	.03	.25
k _{id} , mg/g.min ^{1/2}	1.	1.	0.
C	000	000	999
R ²			
	0.	1.	2.
	749	631	618
	16	32	61
	.85	.32	.42
	0.	0.	0.
	995	991	977
	0.	0.	0.
	216	068	050
	1.	2.	2.
	888	140	188
	0.	0.	0.
	981	994	980

$$q_t = k_{id} t^{1/2} + C \quad (12)$$

where, q_t (mg/g) and t (min) are as earlier defined, k_{id} (mg/g min^{1/2}) is the intraparticle diffusion rate constant and C is a constant pertaining to boundary layer. The values of k_{id} and C were obtained from the linear plot of q_t against t^{1/2}. The intraparticle diffusion plot for the removal of MG by TLLAC is presented in Figure 4(a). Liquid film diffusion[43] was applied to aid in the elucidation of the rate controlling stage of the adsorption mechanism. The equation is

$$\ln(-F) = -k_{fd} t \quad (13)$$

where, $F = q/q_e$, and k_{fd} (1/min) is the liquid film diffusion rate constant and t (min) is time. The value of k_{fd} was determined from the plot of $-\ln(1-F)$ against t . The liquid film diffusion plot for the removal of MG by TLLAC is presented in Figure 4(b). The parameters, constants and correlation coefficients (R^2) obtained from the models are summarised in Table 4. The experimental and calculated q_e values of are close and the mean correlation coefficient value is unity for pseudo-second order kinetic constants. This suggests the applicability of this model for describing the kinetic data. Intraparticle and liquid film diffusion influenced the mechanism of the adsorption process. However, neither was the rate controlling step because their plots did not pass through the origin.

3.8 Adsorption Thermodynamics

Standard enthalpy (ΔH° , kJ/mol), standard entropy (ΔS° , J/mol K), and standard free energy (ΔG° , kJ/mol) were determined by conducting experiments at various temperatures. The following relationships were employed:

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (14)$$

$$\Delta G^\circ = -RT \ln K_d \quad (15)$$

$$K_d = q_e / C_e \quad (16)$$

$$\ln K_d = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \quad (17)$$

where, R is the gas constant (8.314 J/mol K), T (K) is temperature, K_d is the distribution coefficient, q_e (mg/g) is the quantity of adsorbate removed at equilibrium and C_e (mg/L) is the quantity of adsorbate remaining in solution at equilibrium. Equation (15) was used to determine the values of ΔG° at various temperatures. The values of ΔH° and ΔS° were estimated from the slope and intercept, respectively, of the linear plot of $\ln K_d$ versus $1/T$ (Figure 5).

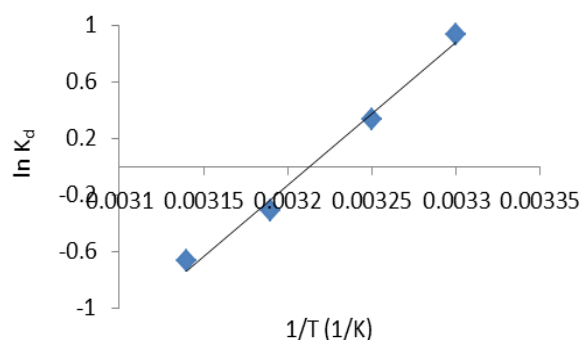


Figure 5. Plot of $\ln K_d$ versus $1/T$ for removal of MG by TLLAC

Table 5. Thermodynamic parameters for the removal of MG from aqueous solution by TLLAC

ΔH° (kJ/ mol)	ΔS° (kJ/mol K)	ΔG° (kJ/mol)			
		3 03 K	3 08 K	3 13 K	318 K
-	-0.27	-	-	+	+1.7
83.82		2.34	0.84	0.82	8

The calculated thermodynamic values are collated in Table 5. The values of ΔG° are positive for temperatures from 313 K and higher implying that the adsorption process was only spontaneous and thermodynamically favourable below this temperature. The sign and value of ΔH° (-83.82 kJ/mol) implies an exothermic process with possibility of some influence of chemical adsorption in the system. The negative value of ΔS° was a reflection of the reduced randomness at the TLLAC-MG solution interface (Sun et al., 2008).

4. Conclusions

TLLAC was prepared from abundant but disregarded TLL. The quality of the adsorbent did not fully meet the specification for commercial activated carbons. However, it might be better if the activation process is conducted in an inert environment and the preparation conditions optimised. The removal of MG from aqueous solution by TLLAC was feasible though temperature, pH and initial concentration of dye solution as well as dosage and contact time influenced the process. The higher the initial concentration of MG the higher the time required for equilibrium to be attained and the quantity of dye removed. The removal of MG from aqueous solutions increased up to pH 10 and optimum TLLAC dosage for adsorption was 0.5 g/L.

Langmuir isotherm model best described the removal of MG by TLLAC at 303 K. The capacity of the adsorbent was found to be 91.74 mg/g which is comparable to the reported values for other laboratory-prepared activated carbons. The adsorption process was best described using pseudo-second order kinetic model at 303 K. The mechanism of uptake of MG by TLLAC was jointly influenced by both liquid film and intraparticle diffusion but neither was the rate controlling step. The exothermic process was spontaneous below 313 K. The value of ΔH° (-83.82 kJ/mol) implies possible influence of chemical adsorption in the system. TLLAC exhibited potentials to remove MG from aqueous solutions.

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