

Rapid adsorption of malachite green onto a low-cost adsorbent prepared from *Pupalia lappacea* stalk

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Abstract

Water pollution caused by synthetic dyes, such as malachite green (MG), poses significant environmental and health risks, necessitating efficient removal strategies. In this study, we evaluated the potential of raw *Pupalia lappacea* (RPL), an agricultural waste-derived adsorbent, for MG removal from aqueous solutions. The adsorption process was studied under varying conditions of pH, contact time, adsorbent dosage, initial dye concentration, and temperature. Characterization of RPL was done with the aid of scanning electron microscope, Fourier transform infrared spectroscopy and pH-point-of-zero charge. Isotherm, kinetics and thermodynamics analyses were carried out on the experimental data. Optimal adsorption occurred at pH 5, with equilibrium achieved within 120 minutes. Kinetic analysis showed the process followed the pseudo-second-order model. Equilibrium data fitted best with the Freundlich isotherm. Thermodynamic studies revealed an exothermic process ($\Delta H = -1332.86$ J/mol) that was spontaneous at lower temperatures ($\Delta G = -5.39$ kJ/mol at 303 K). These findings establish RPL as an efficient and sustainable adsorbent for MG removal from wastewater.

Keywords: Adsorption; kinetics; malachite green; *Pupalia lappacea*; wastewater

1. Introduction

Human survival on this planet is highly dependent on water, however activities such as industrialization and increasing population have resulted in the contamination of water with organic and inorganic pollutants such as pharmaceuticals, plastics, heavy metals, personal care products, dyes, etc. [1], [2], [3]. Dyes have been extensively studied in recent times due to their widespread applications in various industries. Moreover, their ubiquitous use has however led to their presence in the eco-system [4].

Malachite green (MG), a synthetic cationic dye, falls under the triphenylmethane category of dyes. Malachite green's versatility has led to its widespread adoption across various industries such as food and cosmetics. In addition, MG is employed in aquaculture and fisheries as a treatment for ecto-parasite and fungi. However, this widespread usage has resulted in its accumulation in the 'food chain,' posing significant health risks to humans and animals due to its potential to cause genetic mutations and birth defects. Furthermore, MG is a persistent environmental pollutant that is resistant to biodegradation and capable of accumulating in the eco-systems for extended period of time [5]. According to Lin et al. [6], the European Union's 2002/657/EC mandated a minimum required performance limit (MRPL) of 2 $\mu\text{g}/\text{kg}$ for MG. As such, MG must be effectively removed from wastewater before discharge into the eco-system [4], [7].

Conventional wastewater treatment plants often struggle to completely remove dyes from wastewater due to their intense colors, resulting in significant levels of the contaminants remaining in treated

effluents [8]. Over the past few decades, various techniques have emerged to address this challenge. Among them, adsorption using activated carbon has stood out as an efficient solution due to its straightforward design and cost-effectiveness. However, the high cost of commercial activated carbon (CAC) necessitates the exploration of more affordable alternatives derived from locally sourced and sustainable materials [9], [10].

Several researchers have employed different agricultural wastes materials such as watermelon rind [11], cocoa pod [12], etc., for the removal dyes from aqueous solution. However, these materials often exhibit limitations such as low adsorption capacities, poor regeneration ability, and selectivity challenges. Moreover, different modification techniques such as chemical and physical methods have been employed to improve the adsorption capacity of adsorbents, however, some of these methods require long preparation routes. Hence, the need for sustainable adsorbent materials [5]. In this study, readily available agricultural waste (*Pupalia lappacea*), was used as an alternative adsorbent in its unmodified form for the removal of MG from aqueous medium.

Pupalia lappacea, with the common name Forest burr, is a flowering plant whose leaves have been traditionally used to treat wounds and bone fractures. The leaves are also consumed in certain regions as vegetables however, the stalks are often discarded as waste [13]. A thorough review of literature reveals that *Pupalia lappacea*'s stalks have not been previously investigated as adsorbents. *Pupalia lappacea* stalk as other plant material is likely composed of lignocellulosic materials containing hydroxyl, carboxyl, and other oxygen-bearing function groups that could facilitate the adsorption of cationic species such as malachite green [14]. Possible adsorption mechanisms include electrostatic interactions between negatively charged functional groups and the positively charged MG molecules, pores diffusion and hydrogen bonding. A comprehensive study was conducted to examine the influence of various experimental conditions on the removal of MG. Isotherm, kinetics and thermodynamics of the adsorption process were also investigated.

2. Materials and Methods

2.1 Chemicals used

Analytical-grade chemicals, including malachite green ($C_{23}H_{25}ClN_2$, MW = 364.91 g/mol), sodium hydroxide (NaOH, MW = 40 g/mol) and hydrochloric acid (HCl, MW = 36.5 g/mol) sourced from Kem Light Laboratories, Mumbai, India were utilized in this research. For all the experiments, aqueous solutions were prepared distilled water. A stock solution of malachite green (1000 mg/L) was prepared by dissolving 0.1 g of the dye in a 100 mL volumetric flask. Serial dilution of this stock solution yielded working solutions with concentrations between 100 and 250 mg/L.

2.2 Collection and Identification of *Pupalia lappacea*

For this research, *Pupalia lappacea* plant material was obtained from the premises of Ladoko Akintola University of Technology, Ogbomoso, Nigeria (8.168582° N, 4.265152° E). The plant specimen was subsequently identified and authenticated at the university's herbarium, with the assigned voucher number LHO 827.

2.3. Preparation of raw *Pupalia lappacea* adsorbent (RPL)

This study adopted the methodology of Giwa et al. [15] for preparing the *Pupalia lappacea* adsorbent. The process involved washing 50 g of ground *Pupalia lappacea* stalk with distilled water to eliminate soluble contaminants and achieve a neutral pH. The washed material was dried in an oven at 105 °C for 12 hours and then sieved to obtain different particle sizes and stored as RPL adsorbent in airtight containers.

2.4 Characterization of adsorbent

2.4.1 Surface charge determination

To determine the net surface charge (pH_{pzc}) of RPL 0.05 g of RPL was mixed with 25 mL of 0.1 M NaCl solution. The initial pH of the solution was adjusted to a range of 2 - 12 using 0.1 M HCl or 0.1 M NaOH. All measurements were performed in triplicate, and the average values were reported. The

pH meter was calibrated using standard buffer solutions of pH 4, 7, and 9. The mixture was subjected to agitation at 160 rpm for 8 hours in a thermostatic shaker. After filtration, the final pH was measured. A plot of initial pH versus final pH revealed the pH_{pzc} of the adsorbent.

2.4.2 Functional group analysis

The functional groups present in RPL were examined using a Varian 660 MidIR Dual MCT/DTGS infrared spectrophotometer with an Attenuated Total Reflectance (ATR) attachment. The spectrum was recorded over a wave number range of 400-4000 cm^{-1} . Sample preparation involved mixing RPL with KBr pellets.

2.4.3 Surface morphology analysis

The surface morphology of RPL was investigated with the aid of Hitachi SU 3500 scanning electron microscope. The RPL sample was gold-coated prior to analysis.

2.5 Batch adsorption experiments

Batch adsorption experiments were conducted to investigate the impact of various operational parameters on the adsorption process. The parameters studied included solution pH, contact time, initial malachite green (MG) concentration, adsorbent dosage, and temperature. The experiments were conducted in triplicate, and the mean values were reported.

The experiments were performed by varying one parameter at a time while keeping the others constant. Specifically:

- i. The effect of solution pH was examined over a range of 2 - 8, with initial concentration, temperature, and dosage held constant at 100 mg/L, 30 °C, and 0.015 g, respectively.
- ii. The influence of contact time was studied over a range of 15 - 240 minutes, with other parameters kept constant.
- iii. The impact of initial MG concentration was investigated over a range of 50 - 250 mg/L, with temperature, time, and dosage held constant.
- iv. The effect of temperature was examined over a range of 30 – 60 °C, with other parameters kept constant.
- v. The effect of RPL dosage was studied over a range of 0.01 - 0.035 g.

In all experiments, 25 mL of adsorbate was used. The adsorbate-adsorbent mixtures were placed in a horizontal mechanical shaker at 160 rpm and shaken until equilibrium was established. The shaker's temperature was monitored with the aid of a thermometer. The supernatant was then filtered and analyzed using a UV-visible spectrophotometer at a wavelength of 616 nm.

Malachite green uptake was evaluated using Equation 1, thus:

$$q_e = \frac{C_o - C_e}{M} \times V \quad 1$$

Where C_o = the initial concentration; C_e = concentration at equilibrium; V = volume of (L); M = mass of adsorbent (g); and q_e = quantity adsorbed at equilibrium (mg/g).

2.6 Modelling studies

The data from the experiment were analyzed using various isotherm and kinetic models. Five isotherm models, namely Langmuir (Equation 2), Freundlich (Equation 3), and Temkin (Equation 4), [7], were employed to describe the adsorbent's performance at constant temperature. Additionally, three kinetic models, including pseudo-first-order (equation 5), pseudo-second-order (Equation 6), and Elovich (Equation 7) [8], were utilized to investigate the solute uptake rate and adsorbate-adsorbent interactions. Non-linear forms of the kinetic models were plotted using Origin 2024 software.

$$\frac{c_e}{q_e} = \frac{1}{q_m K_L} + \frac{c_e}{q_m} \quad (2)$$

$$\text{Log } q_e = \log K_F + \frac{1}{n} \log C_e \quad (3)$$

$$q_e = \frac{RT}{b_T} \ln A_T + \frac{RT}{b_T} \ln C_e \quad (4)$$

$$q_t = q_e (1 - e^{-k_1 t}) \quad (5)$$

$$q_t = q_e - e^{-\frac{q_t}{tk_2 q_e}} \quad (6)$$

$$q_t = \frac{1}{\beta} \ln (1 + \alpha \beta t) \quad (7)$$

2.7 Adsorption thermodynamics

Thermodynamic analysis is vital to understanding the adsorption process. Calculating key parameters such as the entropy change (ΔS°), enthalpy change (ΔH°), and Gibbs free energy (ΔG°) helps determine the spontaneity and thermal characteristics of the process [16]. These parameters were evaluated using the following equations:

$$\Delta G = -RT \ln K_0 \quad (8)$$

Where,

$$k_0 = \frac{q_e}{C_e} \quad (9)$$

Also,

$$\Delta G = \Delta H - T \Delta S \quad (10)$$

Therefore,

$$\Delta H - T \Delta S = -RT \ln k_0 \quad (11)$$

Linearized as;

$$\ln k_0 = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \quad (12)$$

3. Results and Discussion

3.1 Characterization of adsorbent

3.1.1 pH Point-of-zero-charge of RPL

The determination of the pH-point of zero charge (pH_{pzc}) is crucial in understanding the surface chemistry of an adsorbent and its interaction with target contaminants in aqueous media [17]. The pH_{pzc} of raw *Pupalia lappacea* (RPL) adsorbent was determined to be 7.3 (Figure 1), highlighting its neutral surface charge at this pH. This value is a critical parameter for understanding the surface behavior of RPL in aqueous solutions. At $\text{pH} < 7.3$, the surface of RPL is positively charged due to protonation of functional groups. In contrast, at $\text{pH} > 7.3$, the surface undergoes deprotonation, resulting in a negative charge that enhances electrostatic attraction [18].

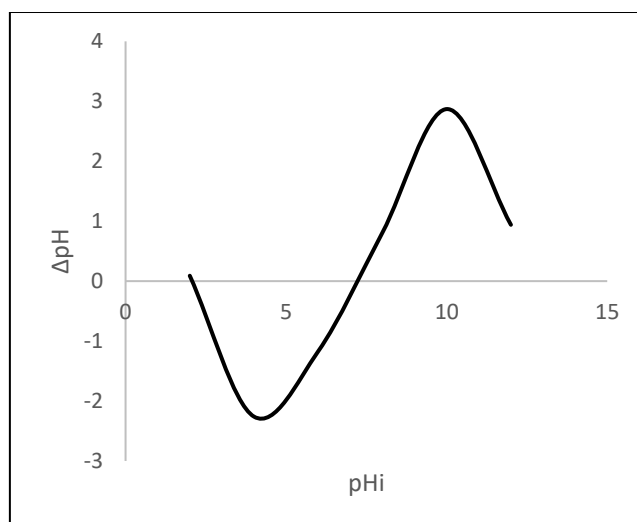


Figure 1: pH_{pzc} of RPL

3.1.2 Fourier transform infrared spectroscopy (FTIR)

The FTIR spectra of raw *Pupalia lappacea* (RPL) both before and after the adsorption are displayed in Figure 2. Before MG adsorption (Figure 2a), the broad peak observed at 3204 cm^{-1} could be attributed to the N-H stretching vibration of alcohol while the peak at 2500 cm^{-1} could be assigned to the S-H stretching vibration of mercaptans and the peak at 2399 cm^{-1} is likely due to the $\text{C}\equiv\text{C}$ stretching vibration of alkynes. The peaks at 1310 and 1100 cm^{-1} could be due to the C-O stretching vibration of alcohols, esters, ethers or carboxylic acid. Peaks appearing 938 , 729 , 684 and 518 cm^{-1} could be as a result of $=\text{C-H}$ bending vibration of alkenes and C-H rocking vibrations alkane, respectively [19]. Following the adsorption of MG onto RPL, there were significant shift in band positions (Figure 2b) and there were appearances of new bands. For example, the bands there was a shift in the band at 3204 cm^{-1} to 3104 cm^{-1} , similarly, there was a bathochromic shift in the band at 2500 to 2510 cm^{-1} . A new band at 1623 cm^{-1} which could be attributed to the C=C stretching vibrations of alkenes was also observed. In addition, there is also the appearance or a shift in the absorption band of the peaks at 1310 cm^{-1} , 1100 cm^{-1} , 938 cm^{-1} , 729 cm^{-1} to 1374 cm^{-1} , 1108 cm^{-1} , 952 cm^{-1} , 790 cm^{-1} . In addition to these shifts, the new peaks observed at 1295 cm^{-1} and 1063 cm^{-1} can be attributed to the C-O stretching esters, ethers or carboxylic acids while the peak at and 881 cm^{-1} could be as a result of C=C bending vibration of alkenes [19].

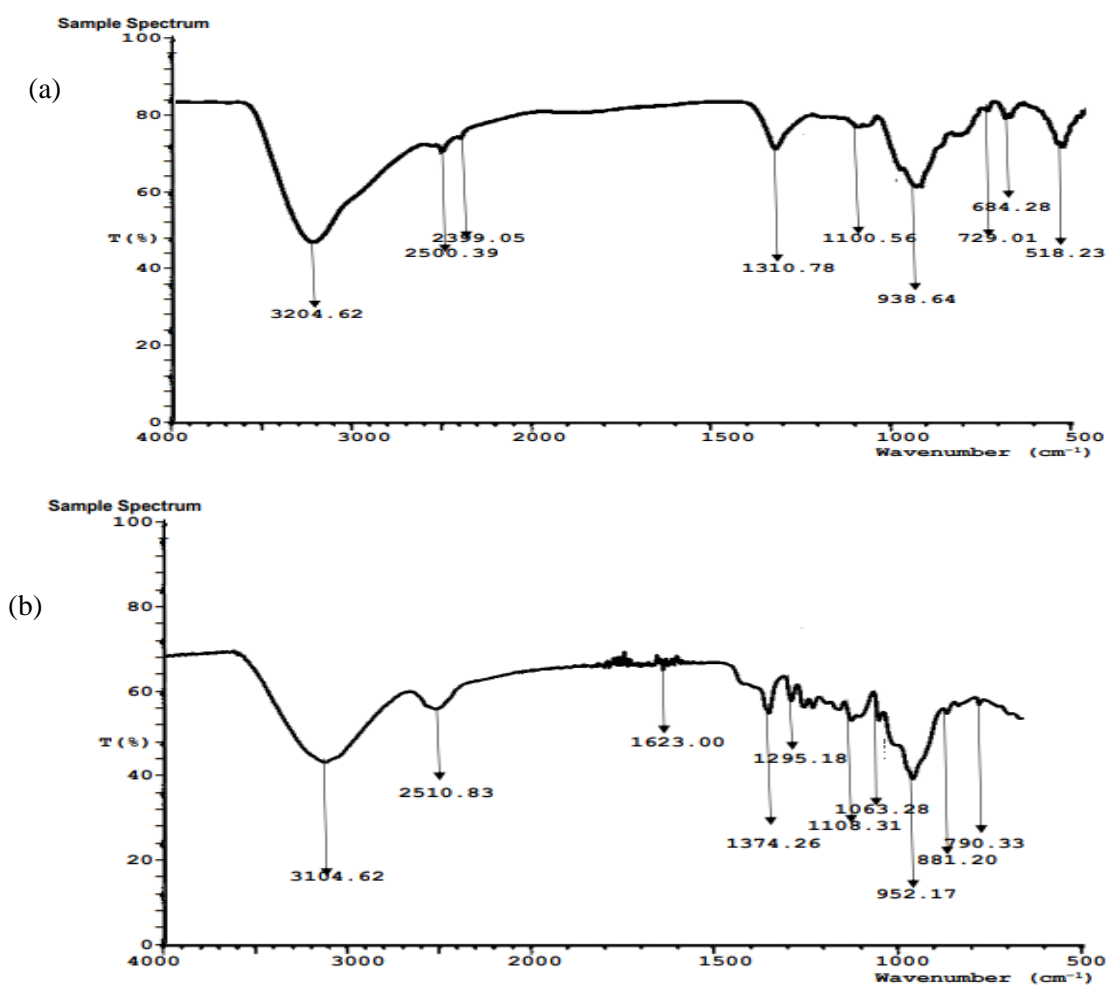


Figure 2: FTIR plots of RPL (a) before adsorption (b) after MG dye adsorption

3.1.3 Scanning electron spectroscopy (SEM)

It can be observed from the SEM micrograph that the surface of RPL appears to consist of sponge-like porous structure with interconnected channels with no cracks or hollows observed (Figure 3a), however, after MG adsorption onto RPL, its surface had undergone major transformation resulting from MG loading onto the adsorbent's surface (Figure 3b)

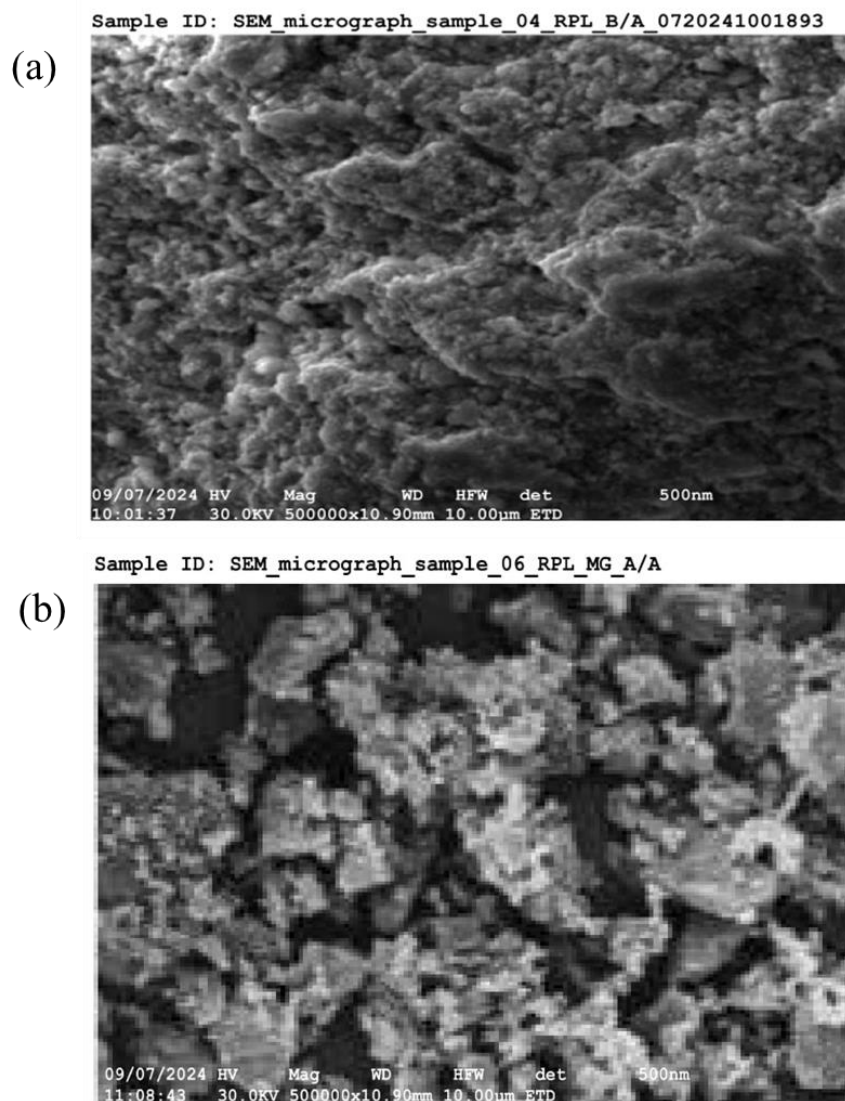


Figure 3: SEM micrographs of RPL (a) before adsorption (b) and MG adsorption

3.2 Batch adsorption studies

3.2.1 Effect of Solution pH

The influence of solution pH on the adsorption capacity of raw *Pupalia lappacea* (RPL) for malachite green (MG) removal was examined between pH 2 - 8. The adsorption capacity exhibited slight upward trend as the pH increases, reaching its peak at pH, as illustrated in Figure 4a. The variation in this trend is likely due to the surface charge properties of RPL and the speciation of MG in aqueous medium. Abewaa et al. [20] reported similar observations for the adsorption of MG onto activated carbon prepared from *Rumex abyssinicus*. The authors reported an optimum removal at pH 6.

3.2.2 Effect of contact time

The study of contact time (15 – 240 minutes) revealed a progressive increase in the adsorption capacity of malachite green (MG) by raw *Pupalia lappacea* (RPL) with time, reaching equilibrium at 120 minutes (Figure 4b). The initial rapid increase in adsorption capacity can be ascribed to the availability of abundant binding sites on the RPL surface, which facilitates the swift adsorption of MG molecules. During this phase, external mass transfer plays a significant role as the dye molecules migrate from the bulk solution to the adsorbent surface. As the contact time exceeds 120 minutes, the adsorption rate slows down, signaling the progressive binding of molecules to the available active sites on RPL, consequently leading to attainment of equilibrium [17].

3.2.3 Effect of initial MG concentration

The adsorption capacity of raw *Pupalia lappacea* (RPL) for malachite green (MG) increased from 30.94 mg/g to 259.79 mg/g as the initial MG concentration was raised from 50 mg/L to 250 mg/L (Figure 4c). This trend can be attributed to the higher driving force provided by the increased concentration gradient at elevated MG levels, which enhances the mass transfer of dye molecules from the bulk solution to the surface of the adsorbent [12]. At lower concentrations, the active adsorption sites on the RPL surface are underutilized due to the limited availability of MG molecules. As the initial concentration increases, more dye molecules are available to interact with the adsorbent, leading to improved utilization of active sites and an increase in adsorption capacity [21].

3.2.4 Effect of adsorbent dosage

The effect of adsorbent dosage (0.01 – 0.035 g) on malachite green (MG) adsorption by raw *Pupalia lappacea* (RPL) showed a gradual decline in the amount of MG uptake with increasing adsorbent dosage (Figure 4d). This trend can be attributed to the fact that as the adsorbent dosage increases, the number of available active sites per unit volume of solution becomes more abundant. Initially, at lower dosages, a higher concentration of MG molecules per unit adsorbent results in efficient interactions and adsorption [22]. However, at higher adsorbent dosages, the concentration of MG molecules remains constant, while the surface area of the adsorbent increases, leading to a reduction in the number of dye molecules available for adsorption per unit mass of RPL [23].

3.2.5 Effect of temperature

The study of temperature (30 – 60 °C) on the adsorption of malachite green (MG) by raw *Pupalia lappacea* (RPL) revealed a decline in adsorption capacity from 139.34 mg/g at 30°C to 24.14 mg/g at 60°C (Figure 4e). This inverse trend suggests that the adsorption of MG onto RPL is exothermic in nature, meaning that increasing temperature adversely affects the adsorption process [24]. Moreover, decline in adsorption capacity at heightened temperatures can be ascribed to reduced surface activity or desorption as higher temperatures increases the movement of dye molecules [21].

3.3 Adsorption isotherm models

The adsorption of MG onto RPL was evaluated using Langmuir, Freundlich and Temkin isotherm models. Isotherm plots are presented in Figure 5. Both the Freundlich and Temkin models exhibited excellent fits with R^2 values of 0.9606 and 0.967, respectively (Table 1), indicating a significant role of heterogeneous surface interaction in the adsorption of MG onto RPL. The Freundlich constant ($n = 3.004$) indicates that the adsorption process was favorable ($1/n$ values less than unity are considered favorable). The Temkin model with its high R^2 value shows the significance of adsorbent-adsorbate interactions. The Langmuir isotherm model on the other hand showed a relative moderate fit with an R^2 value of 0.7347 and Q_m value of 99.09 mg/g. Furthermore, the separation factor R_l was less than 1 (0.09), which further affirms the favorability of the process [25].

3.4 Adsorption kinetic models

The kinetic data for malachite green (MG) adsorption onto raw *Pupalia lappacea* (RPL) were evaluated using pseudo-first-order, pseudo-second-order, and Elovich models to understand the adsorption mechanism. Kinetics plot is presented in Figure 6 below. Among the models, the pseudo-second-order model provided the best fit for the experimental data with the highest coefficient of determination ($R^2 = 0.956$) (Table 2). The close agreement between the experimental equilibrium adsorption capacity (Q_e ,

exp = 141 mg/g) and the calculated value ($Q_e, \text{calc} = 144 \text{ mg/g}$) further supports this model's applicability. The results imply that chemisorption, involving exchange of electrons between MG and RPL is the rate-determining step [26]. The pseudo-first-order model showed a moderate correlation with an R^2 value of 0.894 and a slight deviation between the experimental and calculated Q_e values ($Q_e, \text{calculated} = 137 \text{ mg/g}$). The Elovich model, often used to describe heterogeneous surface adsorption, also showed a good fit with an R^2 value of 0.921. The parameters A (36720) and B (0.127) suggest a rapid initial adsorption rate followed by a gradual decrease as the surface sites become occupied [27].

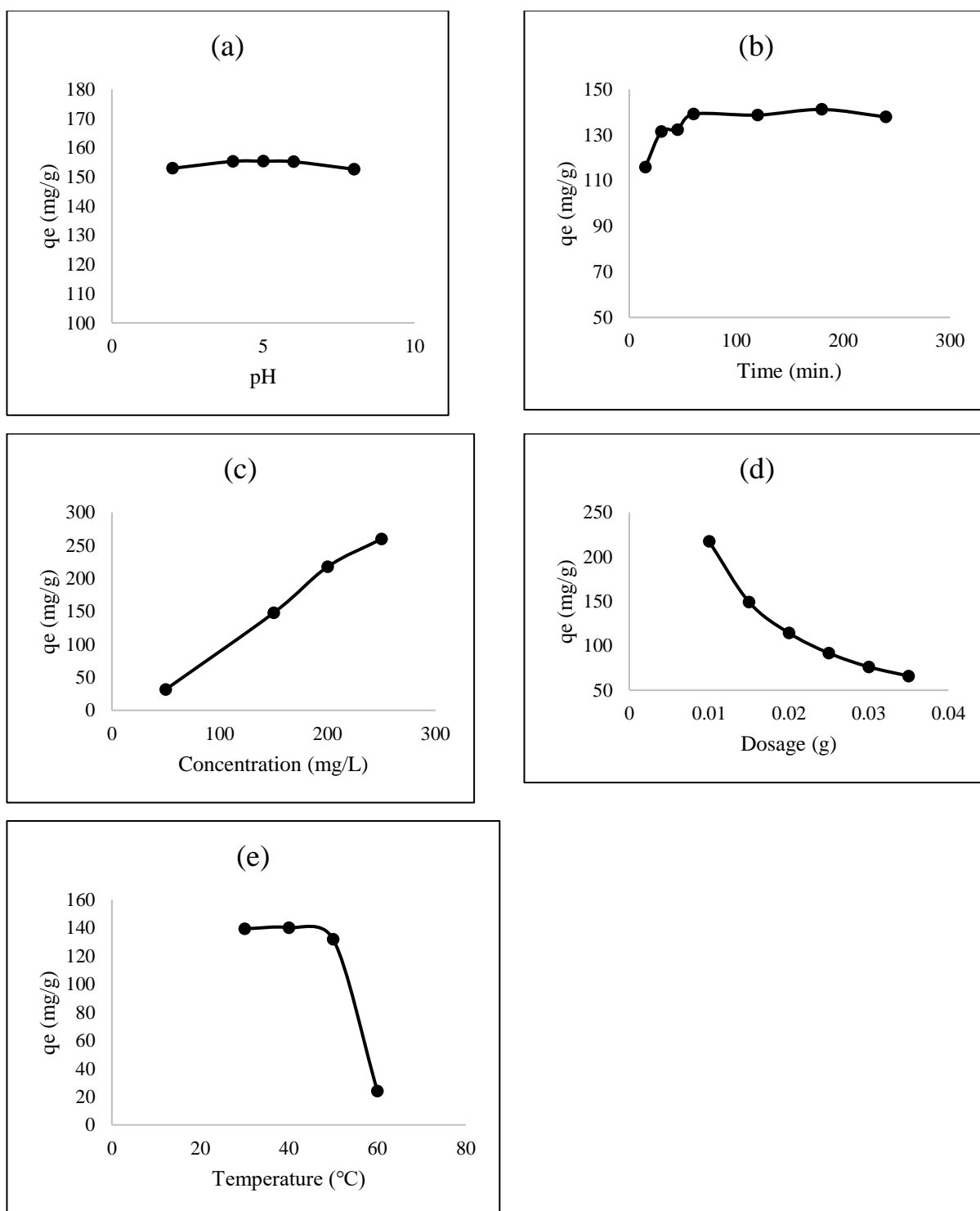


Figure 4: Effect of (a) solution pH, (b) contact time, (c) initial concentration, (d) adsorbent dosage and (e) temperature on the removal of MG onto RPL

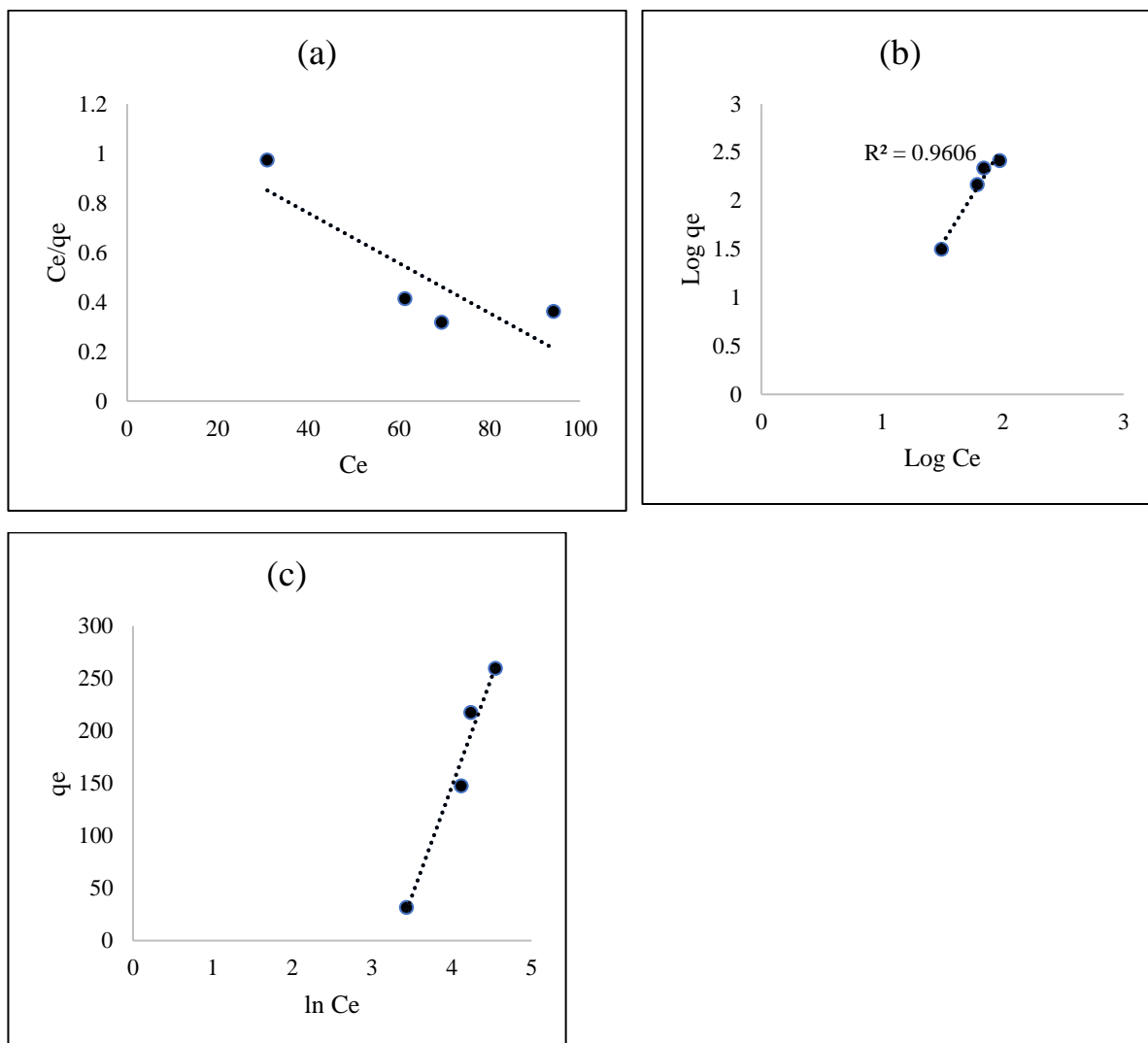


Figure 5: (a) Langmuir (b) Freundlich (c) Temkin Isotherm plots for MG removal onto RPL

Table 1: Isotherm parameter for MG adsorption onto RPL

Isotherm model	Parameters	Values
Langmuir	q_m (mg/g)	99.1
	K_L (L/mg)	1.09
	R_L	0.090
	R^2	0.735
	RMSE	0.327
Freundlich	K_f (mg/g)	3.66
	n	3.00
	R^2	0.961
	RMSE	0.282
Temkin	B_T (J/mol)	136
	A_T (L/mg)	0.0633
	R^2	0.967
	RMSE	39.0

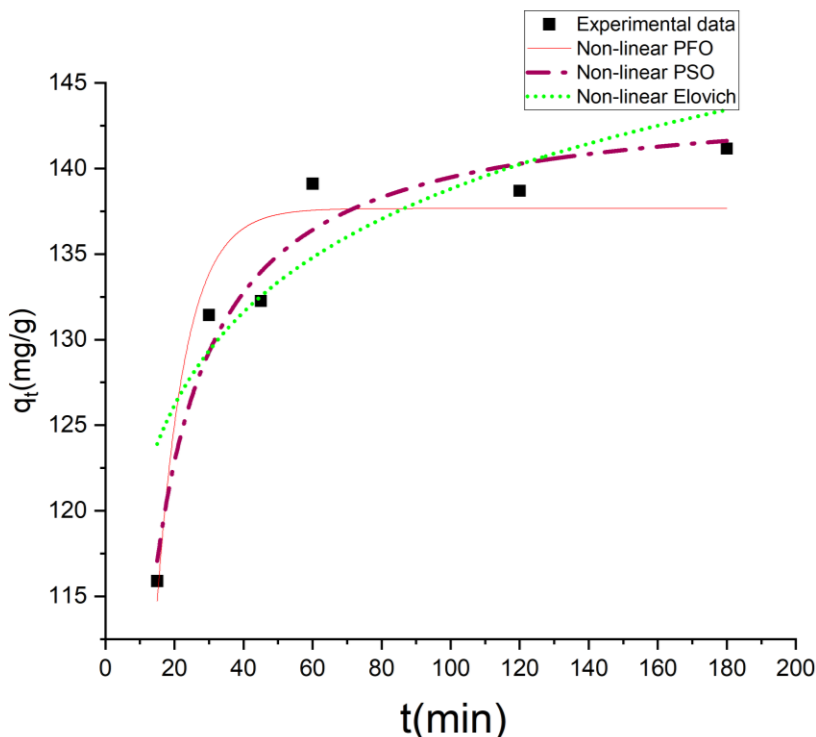


Figure 6: Kinetic plot for MG removal onto RPL

Table 2: Kinetic parameters of MG adsorption onto RPL

Kinetic model	Parameters	Values
Pseudo-first order model	R^2	0.894
	K_1 (min^{-1})	0.119
	q_{ecalc} (mg/g)	138
	q_{eexp} (mg/g)	141
	RMSE	3.38
Pseudo-second order model	R^2	0.956
	K_2 ($\text{g mg}^{-1} \text{min}^{-1}$)	0.002
	q_{ecalc} (mg/g)	144
	q_{eexp} (mg/g)	141
	RMSE	2.17
Elovich	R^2	0.921
	A ($\text{g min}^2 \text{mg}^{-1}$)	36720
	B (g min mg^{-1})	0.127
	RMSE	1.44

3.5 Adsorption thermodynamics

The thermodynamic parameters for the adsorption of malachite green (MG) onto raw *Pupalia lappacea* (RPL) reveal important insights into the feasibility, spontaneity, and nature of the adsorption process (Table 3). The negative value of enthalpy change ($\Delta H^\circ = -1332.86 \text{ J/mol}$) indicates that the adsorption of MG onto RPL was exothermic [26]. This suggests that the adsorption becomes less favorable at elevated temperatures, as observed in the temperature studies where adsorption capacity decreases with increasing temperature. The entropy change ($\Delta S^\circ = -21.48 \text{ J/mol}\cdot\text{K}$) is negative, signifying a reduction

in disorder at the solid-liquid boundary during adsorption. The negative ΔS° value implies that the adsorption of MG onto RPL involved a more structured binding mechanism [28]. The Gibbs free energy change (ΔG°) values further confirm the nature of the process. The negative ΔG values at lower temperatures (e.g., -5.39 kJ/mol at 303 K and -5.67 kJ/mol at 313 K) indicate that the adsorption is spontaneous under these conditions. However, as the temperature increases, ΔG becomes less negative and eventually positive at 333 K (3.49 kJ/mol), indicating that the process becomes non-spontaneous at higher temperatures [29].

Table 3: Thermodynamic parameters obtained for the adsorption of MG onto RPL

Temperature (K)	ΔG° (J/mol)	ΔH° (kJ/mol)	ΔS° (J/mol/K)
303	-5.39	-1332.86	-21.48
313	-5.67		
323	-4.49		
333	3.49		

4. Conclusion

This study demonstrated the potential of raw *Pupalia lappacea* (RPL) as an effective adsorbent for removing Malachite green (MG) from wastewater. The adsorption process was influenced by pH, contact time, adsorbent dosage, initial dye concentration, and temperature. Optimal adsorption occurred at pH 5 and equilibrium was reached within 120 minutes. The adsorption capacity increased with initial dye concentration but decreased with higher adsorbent dosages. Kinetic analysis revealed that the pseudo-second-order model best described the process, suggesting chemisorption as the dominant mechanism. The Freundlich isotherm provided the best fit, indicating multilayer adsorption on a heterogeneous surface. Thermodynamic studies confirmed the process was exothermic, with spontaneity decreasing at higher temperatures. These findings establish RPL as a cost-effective and environmentally friendly adsorbent, suitable for MG removal under optimized conditions, with implications for wastewater treatment applications.

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Competing interests

None declared.

Authors' contributions

Conceptualization: A.A Giwa and M.A Oladipo; Methodology: A.A Giwa; Supervision: D.O Aderibigbe, A.A Giwa and M.A Oladipo; Writing—original draft: O.S Dabo; Writing—review & editing: D.O Aderibigbe

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