





## ORIGINAL RESEARCH ARTICLE

## Adsorption of Malachite Green Dye Using Carbonized Water Lily Leaves: Kinetics, Equilibrium and Thermodynamics Studies

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### ABSTRACT

This study aimed to investigate the potential of carbonized water lily leaves (CWL) as cheap adsorbent for the adsorption of Malachite Green (MG) dye. The CWL characteristics were studied using Fourier Transform Infra-Red (FTIR) spectroscopy, Scanning Electron microscopy (SEM) and point of zero charge (PZC) to establish surface functional groups present, morphology and net neutral charge of the adsorbent. The effects of contact time (15-150min), dosage (20-200mg), initial concentration (20-140ppm), and pH (3-13) on the adsorption process were investigated for the removal of MG by batch adsorption method. The result shows that all the parameters have effect on adsorption process. Compared to the Langmuir, Freundlich, Temkin, and D-R models, the isotherm models were investigated and confirmed to fit well onto the D-R model. Pseudo-second order model best fitted the kinetic data for the different operating temperature (30°C, 40°C, 50°C) of the analysis. Thermodynamics studies clearly indicates that the sorption was spontaneous, endothermic, and increased in the randomness of the systems at adsorbent-liquid interfaces as a result of negative Gibb's free energy ( $\Delta G$ ), positive enthalpy ( $\Delta H$ ) and Entropy ( $\Delta S$ ). Therefore, this study confirmed that carbonized water lily leaves adsorbent could be used as an alternative adsorbent for the adsorption of toxic dyes such as Malachite green dye.

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## INTRODUCTION

Synthetic dyes are cheap, common and widely used in textiles, food, cosmetics and dyeing of plastics, rubbers, leather and paper materials (Dahri *et al.*, 2013). Discharging industrial wastewater containing such dyes to aquatic habitats can pollute surface water bodies and groundwater. This can endanger the aquatic flora and fauna as dyes may be toxic, mutagenic and non-biodegradable (Xu *et al.*, 2011, Kabra *et al.*, 2012). A re-evaluation of these issues of environmental pollution made at the end of the last century shows that waste such as dyes, medicines, disinfectants, contrast media, laundry detergents, surfactants, pesticides, paints etc. released are severe threat to the environment and human health on a global scale (Sharma *et al.*, 2015). These pollutants could interact naturally with the biological system and therefore of particular importance to humans and wildlife even at minute concentrations (Galadima *et al.*, 2015a).

Dyes are substances that impart colour to a material or a coloured substance that has affinity to the substrate to which its being applied (Enenebeaku *et al.*, 2016). A malachite green dye is a toxic chemical primarily used to treat parasite, fungal infections, and bacterial infection in fish and fish eggs (Eko, 2009). Unfortunately, this dye has detrimental effect on liver, gill, kidney, intestine and gonads of the aquatic organism, as contact with skin irritate the gastrointestinal tract and even courses cancer (Pan and Zhang, 2009).

The existing dyes removal methods are expensive, required expertise and often ineffective. This has challenged scientists, engineers, policy makers and some other researchers to developed an alternative, cheap and promising method of dye remediation from contaminated water (Galadima *et al.*, 2015b).

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Adsorption techniques has become a widely used in many industries on a large scale for purification, separation and other compliance purposes (Martins *et al.*, 2014). This technique is widely preferred over other methods due to effectiveness of pollutants removal from real as well as synthetic water, feasibility of low cost adsorbents, easily adaptable, simplicity of design and friendly operations (Ayuba and Abdulmumini, 2022).

Various form of adsorbents were reported to have been used by many researchers for the removal carcinogenic, mutagenic and toxic dyes from waste water such as raw water lily leaves (Ayuba and Abdulmumini, 2022), Bambara nut hull (Sebata *et al.*, 2013), Groundnut shell waste based powder activated carbon (Ramteke *et al.*, 2007), graphene oxide decorated with cellulose and copper nanoparticles (Khawaja *et al.*, 2021), natural zeolite (Eko, 2009), Hydrophilic thiourea-modified poly(acrylonitrile-co-acrylic acid) (Adeyi *et al.*, 2019), Alumina (Ahlafi *et al.*, 2017). In this study, carbonised water lily (CWL) leaves powder was used to remove MG from aqueous solutions. The effect of various parameters such as contact time, adsorbent dosage, initial concentration, pH of the solution and temperature on the adsorption capacity and efficiency of CWL were studied using batch experimental techniques. Thermodynamic and kinetic parameters for MG adsorption onto CWL adsorbent was analysed in addition to isotherms models to proposed suitable mechanism for the adsorption process.

## MATERIALS AND METHODS

### Plant Sample Collection and Adsorbent Preparation

The water lily leaves (WLL) were obtained from Gubi Dam, Bauchi State, Nigeria. The carbonized adsorbents (CWL) were prepared in a muffle furnace. Thus, the leaves were ground and segregated to granular mesh size with an earlier semi-carbonisation for 15 min at initial temperature of 200°C and later the furnace temperature was adjusted to a desired temperature of 500°C for 45 min for the sample to undergo complete carbonization (Anisuzzaman *et al.*, 2014). The sample was cooled, ground and sieved to obtain a working size of 300µm, and the sample was stored in air-tight container for further experimental studies.

### Determination of Point of Zero Charge (PZC)

The pH drift method was adopted according to Nasiruddin and Sarwar (2007). The pH of 0.01M NaCl was adjusted to a value between 2 and 10 using 0.50M HCl or 0.50M NaOH. Adsorbent 0.10g was added to the 50mL of the adjusted solution in a capped vial and equilibrated for 24hours. The final pH was measured and plotted against the initial pH and the pH at which the curves intercepts the pH line was taken as a point of zero charge.

### Preparation of Stock Solution

A stock solution of Malachite green dye was prepared by dissolving 1g of the dye in a 1000mL volumetric flask at room temperature and shaken until homogenous solution is obtained (Ibrahim and Sani, 2015). The sample of required concentration were prepared by diluting the stock solution with distilled water to a required concentration using dilution formula.

$$C_1V_1 = C_2V_2 \dots\dots\dots (1)$$

The concentration of residual un-adsorbed MG dye was measured at working wavelength ( $\lambda_{max} = 615.50\text{nm}$ ) using UV-visible spectrophotometer (Hitachi 2800 model).

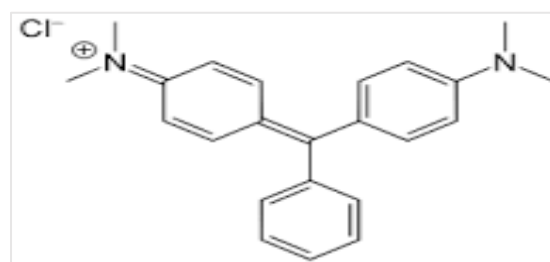


Figure 1: Structure of Malachite Green

## Optimization of Experimental Parameters

### Effect of Contact Time

The effect of contact time on the adsorption of the dyes used in these experiments was conducted at room temperature and initial concentration of the adsorbates of 100mg/L, adsorbents dose of 0.1g for carbonized adsorbent were introduced and shaken at 150rpm (Ara *et al.*,2013). The data generated from this study at 5-120 minutes respectively was used for adsorption kinetics studies.

### Effect of Adsorbent Dosage

Manjunatha and Vagish (2016) method was adopted with little adjustment. The effect of adsorbents dosage was studied and carried out with an initial concentration of 100mg/L at different dosage amount of 0.02g, 0.05g, 0.08g, 0.1g and 0.2g respectively. The weighed samples were taken in polythene bottles with 50mL of the stock solution. The sample was kept in an orbital shaker at room temperature, at the constant speed of 150 rpm at the optimum time.

### Effect of Adsorbate Initial Concentration

Concentration is among the important factors influencing the rate of chemical reactions. The effect of the variation in initial concentration of dyes solution at room temperature using a fixed amount of the adsorbents was determined by using 20, 40, 60, 80, 100 and 120ppm of MG dye initial concentration. The mixture was then shaken at the optimum time, room temperature and adsorbent dosage of 0.02g at speed of

150rpm. The solution was filtered using Whatman filter paper and the filtrate were then taken for UV-spectrophotometric analysis.

**Effect of pH**

The adsorption experiment was carried out at different pH to determine the optimum pH for the adsorption process. The optimum initial concentration and adsorbent dosage were added to five different polythene bottles (50mL) with each bottle conditioned at different pH (3, 5, 7, 9, 11 and 13) and at room temperature. The pH was adjusted to the desired value with 0.1M HCl or 0.1M NaOH solution respectively. The bottles were shake at 150rpm and then filtered. The filtrate was analysed using UV-spectrophotometer to determine the concentration of residual (un-adsorbed) dyes (Majithiya et al., 2013; Oznur et al., 2013).

**Adsorption Equilibrium Experiments**

The batch adsorption was adopted for this experiment because of its simplicity (Shahryari et al., 2010). The batch experiments were conducted to determine the optimum conditions for equilibrium adsorption of MG dye onto CWL. The results obtained after optimization experiments were used to conduct the batch adsorption for the different system at their ideal conditions. The system was run separately in 60cm<sup>3</sup> polyethene sample bottles at 30, 40, 50 and 60°C temperatures. The sample was placed in temperature controlled shaker for the period reported for each system. After reaching equilibrium period, the content was filtered and the filtrate was analysed using UV-visible Spectrophotometer at maximum absorbance wavelength of 615.4nm for MG. The amount of the adsorbed dye was obtained using equation (2):

$$Q_e = \frac{(C_0 - C_e)}{M} \times V \dots\dots\dots (2)$$

While colour removal rate (%Removal) was calculated using equation (3):

$$\%R = \frac{(C_0 - C_e)}{C_0} \times 100 \dots\dots\dots (3)$$

Where: qe is adsorption capacity (mg/g), Co and Ce are the initial and final concentration in (mg/l) respectively for the dyes in the solution, V is the volume of the dye in solution (L) and m is the mass of the adsorbents (Ibrahim and Sani, 2015b; Shahryari et al., 2010b).

**Fourier transform infrared spectroscopy Analysis**

Fourier transform infrared spectroscopy (FTIR) was used to study the surface functional group of the adsorbents so that the chemical structure of the prepared adsorbents is then determined. IR spectra were obtained with a type spectrum 100 series FTIR spectrometer (Agilent Technology Perkin Elmer Spectrum 100, USA) using the transformation of 20 scans with spectral resolution of 4 cm<sup>-1</sup> by attenuated total reflectance method. FTIR spectra were collected in the mid infrared region between 4,000 and 650 cm<sup>-1</sup>. Spectra were acquired using air background correction (Anisuzzaman et al., 2015).

**Scanning Electron Microscope (SEM) Analysis**

Scanning electron microscope (SEM) is an analysis of surface morphology of the adsorbents and was carried by viewing the electron micrographs of the materials (Sartape et al., 2017). Analysis was done with proxy Scanning Electron Microscope (phenom world Eindhoven). The Scanned micrographs of CWL before and after adsorption were taking at an accelerating voltage of 15.00kv and 1500X magnification.

**RESULT AND DISCUSSION**

**Characterization of Adsorbents**

**FT-IR Analysis**

The FTIR spectra of CWL before and after adsorption (CWL-MG) given in Fig 2 showed a broad band at 3485cm<sup>-1</sup> due the OH group stretching vibration, while the bands at 2951cm<sup>-1</sup> and 1623cm<sup>-1</sup> were associated with the C-H stretch and carboxylic group respectively. The band at 1582cm<sup>-1</sup> after adsorption implied the formation of new C=C bond. Furthermore, the bond at 1385cm<sup>-1</sup> and 1316cm<sup>-1</sup> are associated with the C-O stretch and aromatic groups respectively. Therefore, these results indicate that major and minor changes had occurred before and after adsorption of MG onto CWL. However, the shift in bonds and wavenumbers before adsorption of the samples confirmed chemical transformation during the adsorption process. However, participation of functional groups during the adsorption process was reported by many authors (Boujaady et al., 2013, Karim et al., 2017, Ayuba & Bridget, 2021, Giwa et al., 2018, Parhi et al., 2018).

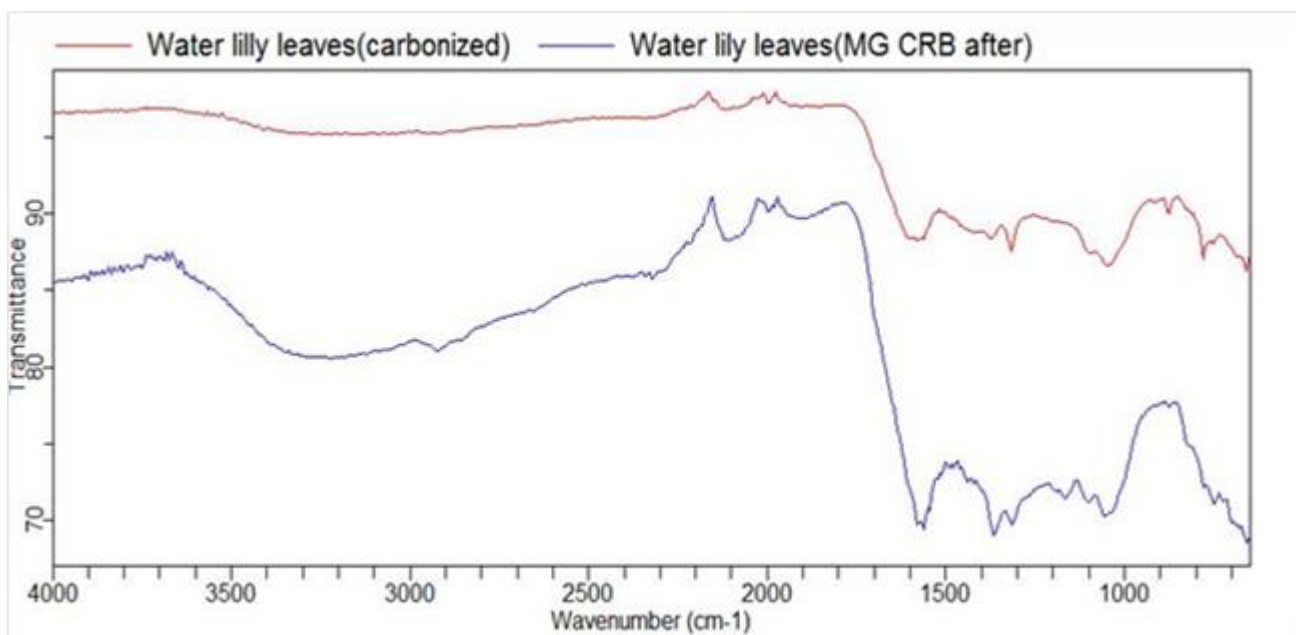


Figure 2: FTIR Spectra for CWL before and after adsorption of MG

Table 1: Functional group recognised before and after adsorption of MG onto CWL

Functional group	Wavelength range (cm <sup>-1</sup> )	Malachite Green (MG).		Differences
		Before Adsorption	After Adsorption	
O-H stretch	3300-3400	3438	3227	211
C-H stretch	2850-2960	2951	2113	838
Carboxylic group	1690-1760	1623	1909	286
C=C aromatics	1500-1700	-	1582	1582
C-O stretch	1080-1300	1385	1316	69
C-H Aromatic	675- 1050	1097	1056	41

**SEM analysis**

The scanned micrographs of CWL before adsorption in Figure 3a shows rough surface morphology with irregular

defects, cracks and cavities. However, the crack widens after adsorption and the pores are filled with deposits of MG molecules adsorbed

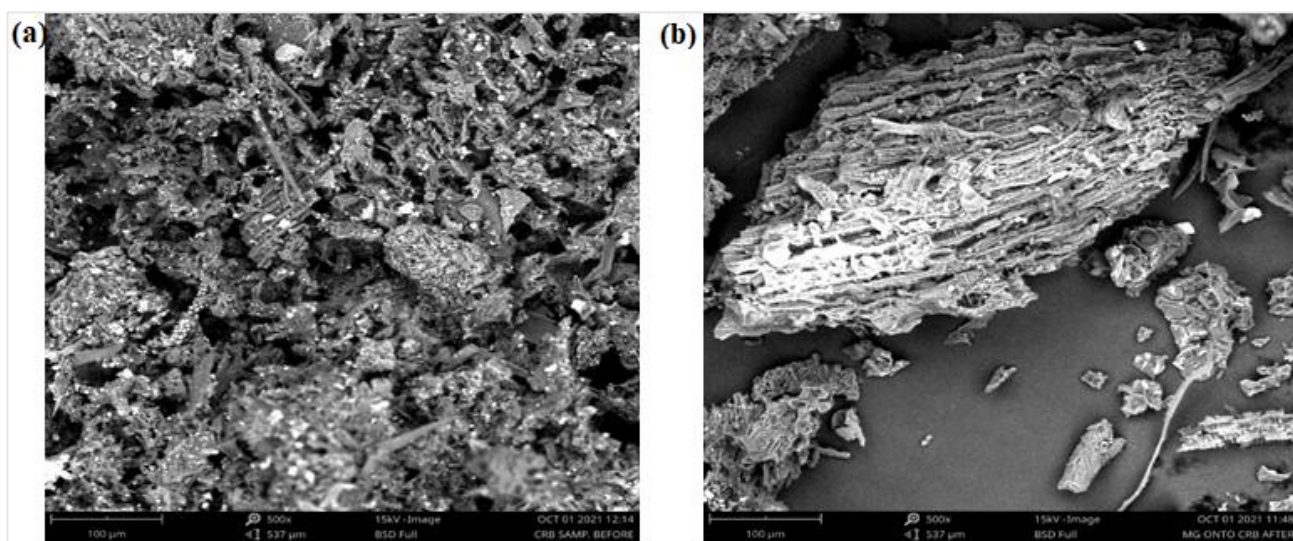
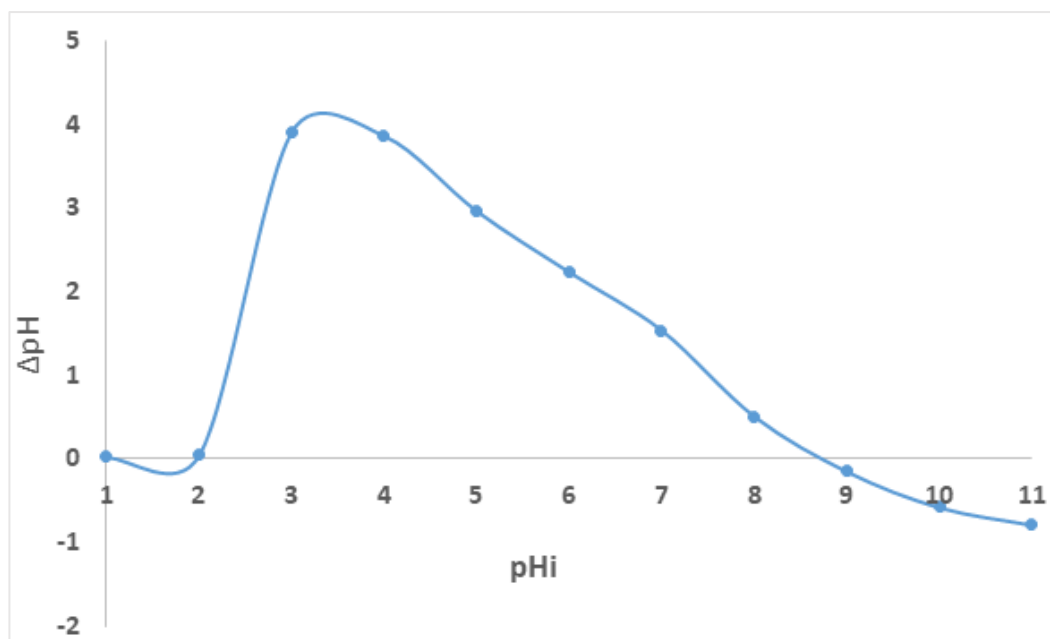


Figure 3: SEM micrograph of CWL (a) Before adsorption (b) After Adsorption of MG.



**Figure 4: Determination of point of Zero Charge ( $\text{pH}_{\text{pzc}}$ ) of CWL adsorbents**

#### Point of Zero Charge (PZC)

The effect of pH on adsorption can be described based on the point of zero charges (PZC), which is the point at which the net charge of the adsorbent is zero (Asim *et al.*, 2019). The PZC of the adsorbent is 8.80 which shows a perfect charge balance in the basic region. However, basic water donates more  $\text{OH}^-$  than  $\text{H}^+$  groups and since the adsorbent has negatively charged surface ( $\text{pH}_{\text{pzc}} = 8.80$ ) it favours the uptake of cationic dyes such as MG due to the increased electrostatic force of attraction.

#### Optimisation of Experimental Parameters

##### Effect of Contact Time

The impact of time on sorption capacity was checked with an initial concentration of 100mg/L at ambient pH, agitation speed of 150rpm, dosage of 0.1g and 50mL dye solution at room temperature. The effect of contact time on the amount of dye adsorbed per unit mass of CWL adsorbent is presented in Figure 5a indicating the efficacy of adsorptions from aqueous solutions (wastewater). The adsorption capacity of adsorbents increases as contact time increases (15-30mins). However, extending the time above 30mins lead to decrease in the sorption capacity probably desorption might have occurred or inaccessibility of the active site. The initial adsorption was rapid at the first stage, and after that, it proceeded at a slower rate (15-150mins) and finally reached equilibrium. The same findings were reported by Amsadi *et al.* (2021) on the study of Malachite Green adsorption on Oil Palm Fruit Bunch.

##### Effect of Adsorbent Dosage

Adsorbents dosage is an important factor that influences the adsorption process since it determines the adsorption capacity of the adsorbent at different operating conditions (Chattopadhyaya *et al.*, 2014). The effect of CWL dose on the removal of MG dye was studied in the range of 20-200mg. Figure 5b shows that the adsorption capacity of the adsorbent decreases with increasing dosage in the system. This trend may be partly attributed to the adsorption site's saturation, overlapping or aggregation. Similar result was reported for adsorption of cationic dyes such as Malachite Green and Methylene Blue using oil palm empty fruit bunch (Asmadi *et al.*, 2021) and Carbonised *Prosopis Africana* (CPA) seeds (Ayuba and Olowafemi, 2021). Hence 20mg was chosen for the successive experiments.

##### Effect of Initial Concentration

The percentage removal and adsorption capacity of the dyes as shown in Figure 6a, showed that the removal increased from 88.32% to 94.55%, decreased to 90.48% as the initial concentration of the dye increased from 20 to 140mg/L respectively. In contrast, the dye uptake rises with an increase in dye concentration. For a dilute solution (20mg/L), the amount of dye uptake per unit mass was just 44.13mg/g whereas in the case of concentrated solution (140mg/L) an increase of the uptake to 316.70mg/g was observed. This clearly shows that the adsorption process was highly dependent on the initial dye concentration (Khaled *et al.*, 2009), due to high driving forces capable of overcoming mass transfer resistance (Enenebeaku *et al.*, 2016).

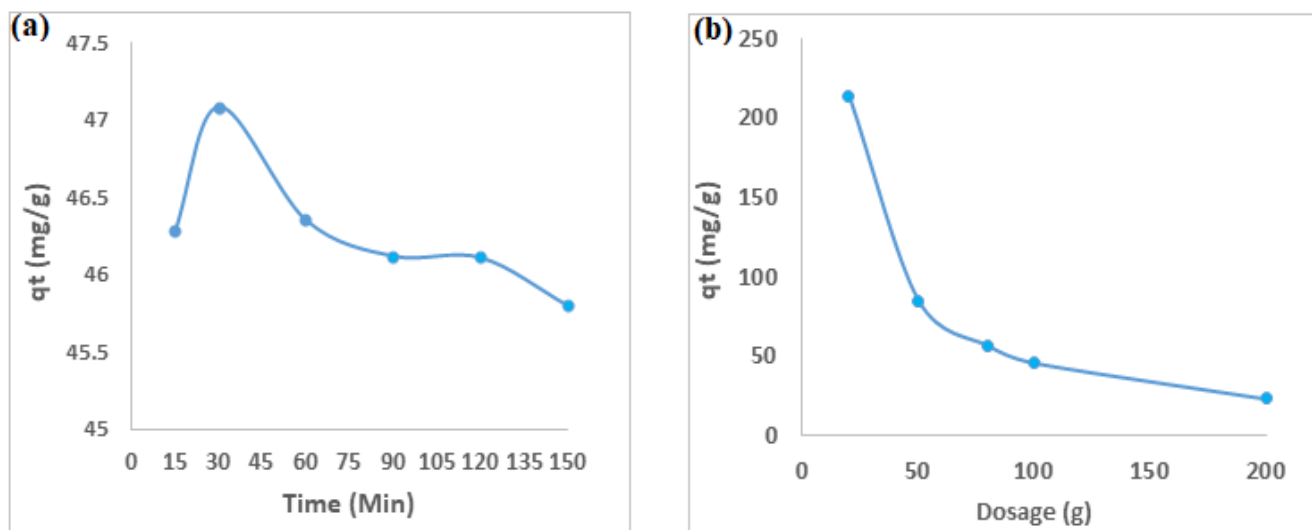


Figure 5: (a) Effect of Contact Time on Adsorption of MG (b) Effect of Dosage on Adsorption of MG.

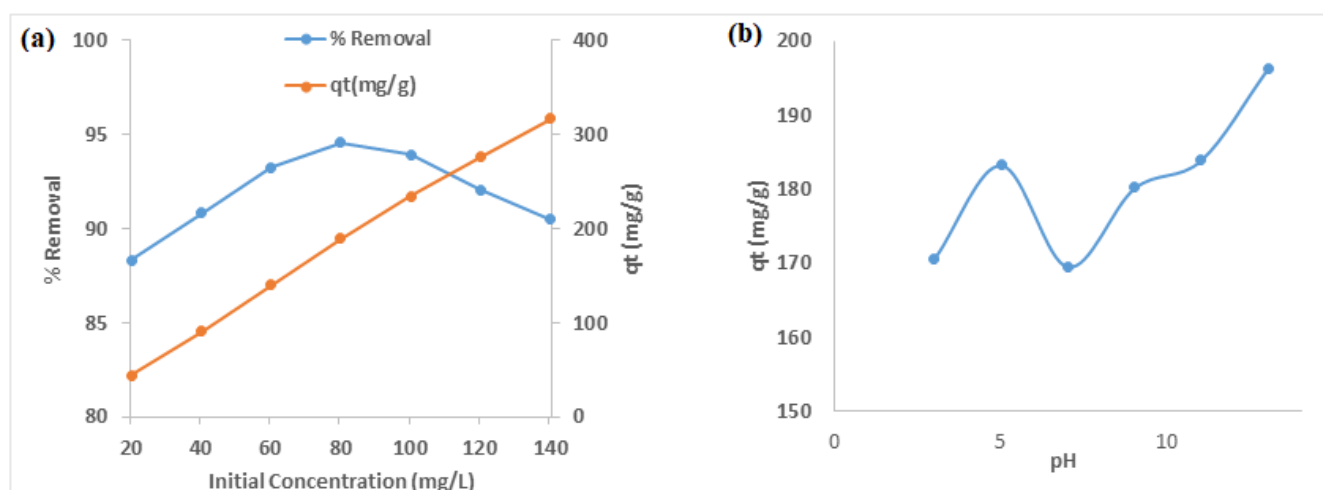


Figure 6: (a) Effect of Initial Concentration on Adsorption of MG (b) Effect of pH on adsorption of MG

### Effect of pH

Figure 6b show a plot of variation of the amount of MG adsorbed against the pH of the solution. The pH was varied from 3-13 by adjusting it with dilute NaOH and HCl respectively. At lower pH ( $H^+$  concentration) the amount of MG adsorbed per unit mass increases from 170.69mg/g at pH 3 to 196.25mg/g at pH 13. This could be attributed to the negative charge surface of the adsorbents (PZC = 8.80). A similar result was reported by other authors using different adsorbents such as alumina (Aazza *et al.*, 2017), and silica (Zang *et al.*, 2012), while different trends were reported by Saechian and Scripongpun (2019) where maximum MG removal was recorded at acidic region probably due to the negatively nature of the adsorbents. The variation of pH values from acidic to alkaline medium makes both the degree of ionization of dyes molecules and the surface properties of the adsorbents vary, affecting the dye adsorption rate (Ibrahim *et al.*, 2015). Therefore, performing adsorption in the basic medium would increase the negative charge on the adsorbents (CWL) surface causing an increase in

electrostatic interaction between the cationic MG molecules and the surface of the adsorbents; hence the increased rate of adsorption.

### Adsorption Isotherms

The adsorption models are significant tools that give insights into the adsorption process and to derive important parameters revealing the adsorption mechanism. Among a number of isotherm models, Langmuir, Freundlich, Temkin and Dubinin-Radushkevich isotherms model are the most commonly used models (Nguyen *et al.*, 2015).

The adsorption data obtained after the adsorption of MG onto adsorbents were fitted into these models to assess the best fit which described the adsorption process. The evaluated parameters were computed and given in Table 2.

#### (i) Langmuir Adsorption Isotherm.

The Langmuir model assumes that monolayer adsorption occurs on the homogenous surface with a finite number

of adsorption sites and little interaction between the adsorbed molecules (Estandiar and Ebadi, 2014). The linear form of Langmuir equations is given below:

$$\frac{1}{q_e} = \frac{1}{q_0} + \frac{1}{q_0 K_L C_e} \dots\dots\dots (4)$$

Where  $C_e$  (mg/L) and  $q_e$  (mg/g) is equilibrium concentration and adsorption capacity respectively.  $q_0$  (mg/g) and  $K_L$  (L/mg) are the maximum monolayer adsorption capacity and rate of adsorption (Langmuir Constant) respectively. The values of  $q_0$  and  $K_L$  were computed from the slope and intercept of the Langmuir plot of  $1/q_e$  vs  $1/C_e$  respectively. The essential features of the Langmuir isotherm may be expressed in terms of equilibrium parameters  $R_L$ , which is dimensionless constant referred to as separation factor or equilibrium parameter.

The essential characteristics of Langmuir isotherm can be interpreted via the dimensionless equilibrium parameters  $R_L$  which is defined by:

$$R_L = \frac{1}{(1+K_L C_0)} \dots\dots\dots (5)$$

Where:  $R_L$  (L/mg) is the Langmuir constant and  $C_0$  (mg/L) is the highest initial concentration. The type of adsorption is determined by  $R_L$  value range: unfavourable ( $R_L > 1$ ), Linear ( $R_L = 1$ ), favourable ( $0 < R_L < 1$ ) and Irreversible ( $R_L = 0$ ) (Nguyen *et al.*, 2015).

**(ii) Freundlich Adsorption Isotherm**

The Freundlich model assumes that molecules are adsorbed on the heterogeneous surfaces of the adsorbent based on different sites with different adsorption energies (Han *et al.*, 2015).

$$\log q_e = \log K_f + \frac{1}{n} \log C_e \dots\dots\dots (6)$$

The constant  $K_f$  is an approximate indicator of adsorption capacity, at the same time  $1/n$  is a function of strength of adsorption in the adsorption process and the adsorption bond is stronger with decreasing  $1/n$  values.

**(iii) Temkin Isotherm Model**

This model considers the interaction between adsorbent materials and adsorbate molecules to be adsorbed and it assumes that the free energy of adsorption process is a function of the surface coverage (Nyijime and Ayuba, 2020). Its expressed by equation 7.

$$q_e = \frac{RT}{bT} \ln A_T + \frac{RT}{b} \ln C_e \dots\dots\dots (7)$$

Where  $R$  is molar gas constant ( $J \text{mol}^{-1} \text{K}^{-1}$ ),  $T$  is temperature in Kelvin,  $b$  is variation of adsorption energy ( $J/\text{Mol}$ ),  $b_T$  is the equilibrium binding constant (L/mg) corresponding to the maximum binding energy. The values of  $\beta$  and  $A_T$  were obtained and tabulated in table 3 from slope and intercept of  $q_e$  against  $\ln C_e$  plot respectively.

**Dubinin-Rudushkevich (D-R) isotherm**

This model is used to determine the adsorption behaviour of MG towards the adsorbates using the Equation 8 (Nica *et al.*, 2020).

$$\ln q_e = \log q_0 - K \epsilon^2 \dots\dots\dots (8)$$

Where  $q_0$  is represent the constant of D-R (mol/g), and  $K$  is the mean free energy of adsorption ( $K_j/\text{mol}$ ). However,  $\epsilon$  can be calculated using the equation below

$$\epsilon = RT \ln \left( 1 + \frac{1}{C_e} \right) \dots\dots\dots (9)$$

Where  $C_e$  is the adsorbate equilibrium concentration,  $R$  is the ideal Gas constant ( $8.314/\text{Mol.K}$ ) and  $T$  is the Temperature in Kelvin. The values of  $q_0$  and  $K$  were obtained using slope and intercept from the plot of  $\ln C_e$  against  $\epsilon^2$  respectively.

**Table 2: Langmuir, Freundlich, Temkin and Dubinin-Rudushkevich Isotherm Constants for the adsorption of MG onto CWL adsorbents**

Isotherms	Parameters	Values
Langmuir	$q_0$ (mg/g)	270.30
	$K_L$ (L/mg)	0.068
	$R_L$	0.095
	$R^2$	0.8623
Freundlich	$1/n$	1.0648
	$N$	0.9391
	$K_F$	26.345
	$R^2$	0.8235
Temkin	$A_T$	0.5942
	$b_T$	15.3811
	$B$	161.08
	$R^2$	0.9372
D-R	$q_s$ (mg/g)	326.85
	$\beta$ ( $\text{mol}^2/\text{kJ}^2$ )	$3.0 \times 10^{-6}$
	$\epsilon$ (kJ/mol)	0.179
	$R^2$	0.9500

From Table (2), the isotherms data tested by the four common models i.e Langmuir, Freundlich, Temkin and D-R Models. The data tested was best fitted onto the D-R model base on linear regression coefficient ( $R^2$ ) obtained for each model under a wide range of initial concentration. The order of the fit was D-R>Temkin> Freundlich> Langmuir. In the case of Langmuir isotherm, the value of dimensionless parameters  $R_L$  was employed to predict the nature of the adsorption process, whereas for freundlich isotherm, the heterogeneity factor  $n_f$  which represent the deviation from linearity of adsorption was employed. On the other hand, Temkin and Dubinin-Radushkevich (D-R) isotherms the energy parameters  $b_T$  and  $E$  expresses the

adsorption as physical or chemical processes (Ibrahim *et al.*, 2015).

**The Kinetics Studies**

A study of the kinetics of adsorption is desirable as it provides information about the mechanism of adsorption, which is important for the efficiency of the process (Chattopadhyaya *et al.*, 2016). To understand the process two kinetic models (i) pseudo-first order model (ii) pseudo-second order model equations were applied to analysed the experimental data:

(i) Pseudo-first order model: the linearized form of pseudo –first order kinetic model can be written as:

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

Where  $q_e$  and  $q_t$  are the amount of dyes adsorbed at equilibrium and at time  $t$  (mg/g) respectively and  $k_1$  ( $\text{min}^{-1}$ ) is the rate constant of adsorption. The plot of  $\log(q_e - q_t)$  vs  $t$  should give a linear relationship from which  $k_1$  &  $q_e$  were determined from the slope and intercept of the plot as presented in Table 3. The  $R^2$  values calculated

were not close to unity and  $Q_{cal}$  were lower than the experimental ( $Q_{exp}$ ) one at all temperature of the experiment, indicating that pseudo-first order model was not fit to described the kinetic data.

(ii) pseudo-second order model: This adsorption kinetics model can be written as;

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

Where  $k_2$  is the rate constant of adsorption (g/mg.min),  $q_e$  and  $q_t$  are the amount of dye adsorbed at equilibrium and at time  $t$  (mg/g) respectively. The values of  $k_2$  and  $Q_{cal}$  were calculated from the intercepts ( $1/k_2 q_e^2$ ) and the slope ( $1/q_e$ ) of the plots  $t/q_e$  vs  $t$  respectively and presented in Table (3). The correlation coefficient of pseudo-second order was close to unity, and  $Q_{cal}$  values computed from pseudo-second order equations showed good agreement with experimental data, indicating the applicability of pseudo-second order kinetic models for the CWL-MG system at all the temperatures of the experiments. Therefore, this model fits to describe the kinetic data of the systems.

**Table 3: Kinetic Models parameters for adsorption of MG onto CWL**

Kinetic Model	Parameters				
<b>Pseudo-First Order</b>	<b>T (K)</b>	<b><math>Q_{exp}</math>(mg/g)</b>	<b><math>Q_{cal}</math> (mg/g)</b>	<b><math>K_1</math>(<math>\text{min}^{-1}</math>)</b>	<b><math>R^2</math></b>
	303	194.84	0.057	$5.640 \times 10^{-2}$	0.1755
	313	194.23	1.693	$9.67 \times 10^{-3}$	0.1238
	323	190.10	0.639	$1.75 \times 10^{-2}$	0.0223
<b>Pseudo-Second Order</b>	<b>T(K)</b>	<b><math>Q_{exp}</math>(mg/g)</b>	<b><math>Q_{cal}</math> (mg/g)</b>	<b><math>K_2</math>(<math>\text{min}^{-1}</math>)</b>	<b><math>R^2</math></b>
	303	194.84	192.31	$2.08 \times 10^{-2}$	0.9936
	313	194.23	188.68	$2.00 \times 10^{-2}$	0.9928
	323	190.10	185.19	$1.82 \times 10^{-2}$	0.9937

**Adsorption Thermodynamics**

The changes in entropy ( $\Delta S$ ), enthalpy ( $\Delta H$ ), and Gibb's free energy ( $\Delta G$ ) parameters are given by equations (12-14). The  $\Delta G$  parameters were computed using the distribution constant  $K_c$  at equilibrium time.

$$K_c = \frac{C_s}{C_e} \dots\dots\dots (12)$$

$$\Delta G = -RT \ln K_c \dots\dots\dots (13)$$

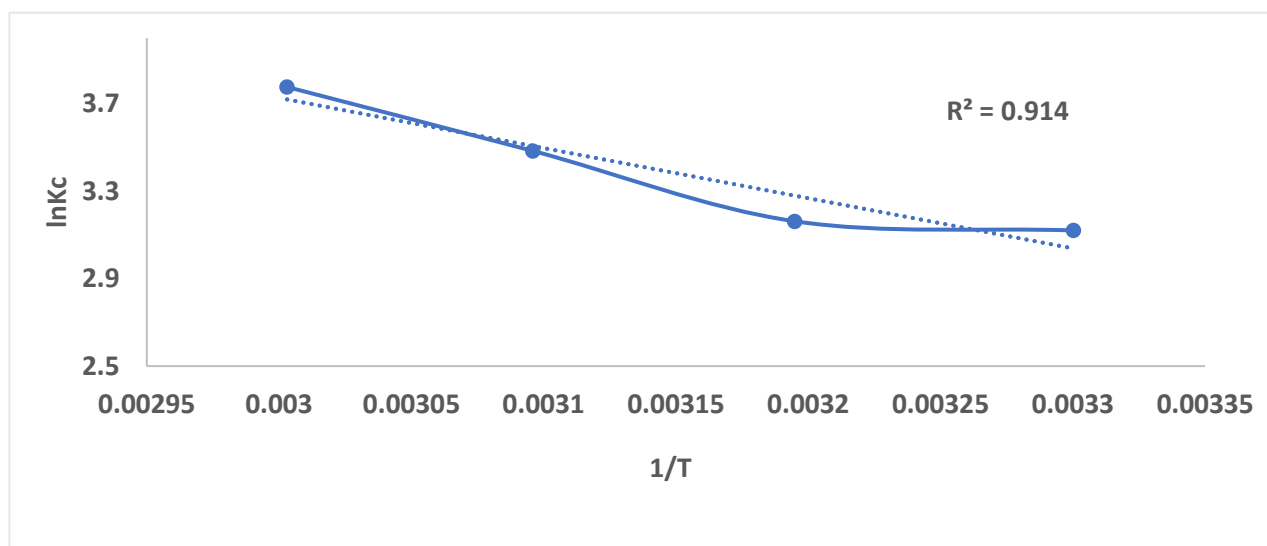
$$\ln K_c = -\frac{\Delta H}{RT} + \frac{\Delta S}{R} \dots\dots\dots (14)$$

The  $\Delta H$  and  $\Delta S$  functions were determined from the slope and the intersection point of  $\ln K_c$  versus the  $1/T$ - plot. Whereas  $C_s$  is the amount of adsorbate in the adsorbed phase and  $C_e$  signifies the remaining dyestuff

concentration (mg/L) in the liquid phase at equilibrium time,  $T$  and  $R$  are Temperature (K) and Gas constant ( $8.314 \text{ J mol}^{-1} \text{ K}^{-1}$ ).

**Table 4: Thermodynamics parameters**

T(K)	$\ln K_c$	$\Delta G$ (KJ/mol)	$\Delta H$ (J/mol)	$\Delta S$ (J/mol.K)
<b>303</b>	3.121	-7.861	19.069	88.19
<b>313</b>	3.163	-8.230		
<b>323</b>	3.484	-9.357		
<b>333</b>	3.778	-10.457		



**Figure 7: The Van't Hoff plot for Adsorption of MG onto CWL**

The values of the thermodynamic functions given in Table 1. As seen from the table 4 reveals that, the negative values of  $\Delta G$  expresses the spontaneity of MG adsorption onto CWL adsorbents. The high negative value with increasing temperature implies more suitability of the process (Sara and Tushar, 2012). Therefore, adsorption of this dye was more favourable at 333K ( $-10.46\text{KJmol}^{-1}$ ), relative to 323K ( $-9.36\text{KJmol}^{-1}$ ), 313k ( $-8.23\text{KJmol}^{-1}$ ) and 303k ( $-7.86\text{KJmol}^{-1}$ ). The positive value of  $\Delta H$  demonstrates that the adsorption of MG has endothermic nature (i.e heat absorbed from the surrounding). In contrast, the positive value of  $\Delta S$  specifies the increased randomness at the adsorbent-liquid interface. Similarly, positive  $\Delta S$  also demonstrated that the solid-liquid interface randomness increased during adsorption of MG (Altintig *et al.*, 2020). Similar adsorption character was reported for adsorption of three basic dyes onto peat (Allen *et al.*, 2004), Congo red from water over pine cone powder (Sara and Tushar, 2012), Malachite Green from synthetic wastewater using banana peel (Saechiam and Scripongpun, 2019), Remazol brilliant blue on the orange peel (Igarashi-Mafra, *et al.*, 2013).

## CONCLUSIONS

The present work shows that carbonized water lily leaves derived adsorbent was an effective adsorbent for the adsorption of malachite green from aqueous solution. Characterization of the adsorbent surface using SEM and FTIR before and after adsorption confirmed the success the adsorption process. The parameters such as the contact time, dosage, initial concentration, pH were found to affect the adsorption of the adsorbates. Kinetically, the MG adsorption onto CWL followed pseudo-second order kinetic model, and D-R isotherm model. Whereas the thermodynamic studies confirmed the process to be spontaneous, endothermic, and

increased in randomness of system on the adsorbent-liquid surface.

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## CONFLICT OF INTEREST

The authors declare no conflict of interest

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