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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^{0}C, 40^{0}C, 50^{0}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 (ΔG), positive enthalpy (ΔH) and Entropy (ΔS). 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℃ and later the furnace temperature was adjusted to a desired temperature of 500℃ 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.

$$C_1V_1 = C_2V_2 \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (1)$$

The concentration of residual un-adsorbed MG dye was measured at working wavelength (λmax =615.50nm) using UV-visible spectrophotometer (Hitachi 2800 model).

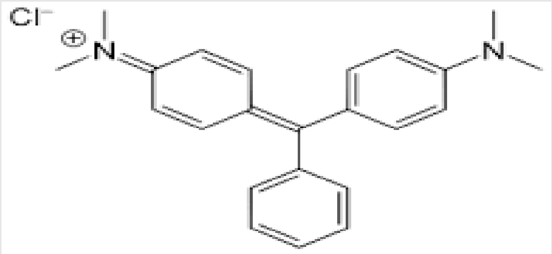

Figure 1: Structure of Malachite Green

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 $60cm^3$ polyethene sample bottles at 30, 40, 50 and 600C 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):

$$Qe = \frac{(CO-Ce)}{M} x\, V \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (2)$$

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

$$\%R = \frac{(Co-Ce)}{Co}\ x\ 100 \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (3)$$

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-1 by attenuated total reflectance method. FTIR spectra were collected in the mid infrared region between 4,000 and 650 cm-1. 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-1 due the OH group stretching vibration, while the bands at 2951cm-1 and 1623cm-1 were associated with the C-H stretch and carboxylic group respectively. The band at 1582cm-1 after adsorption implied the formation of new C=C bond. Furthermore, the bond at 1385cm-1 and 1316cm-1 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).

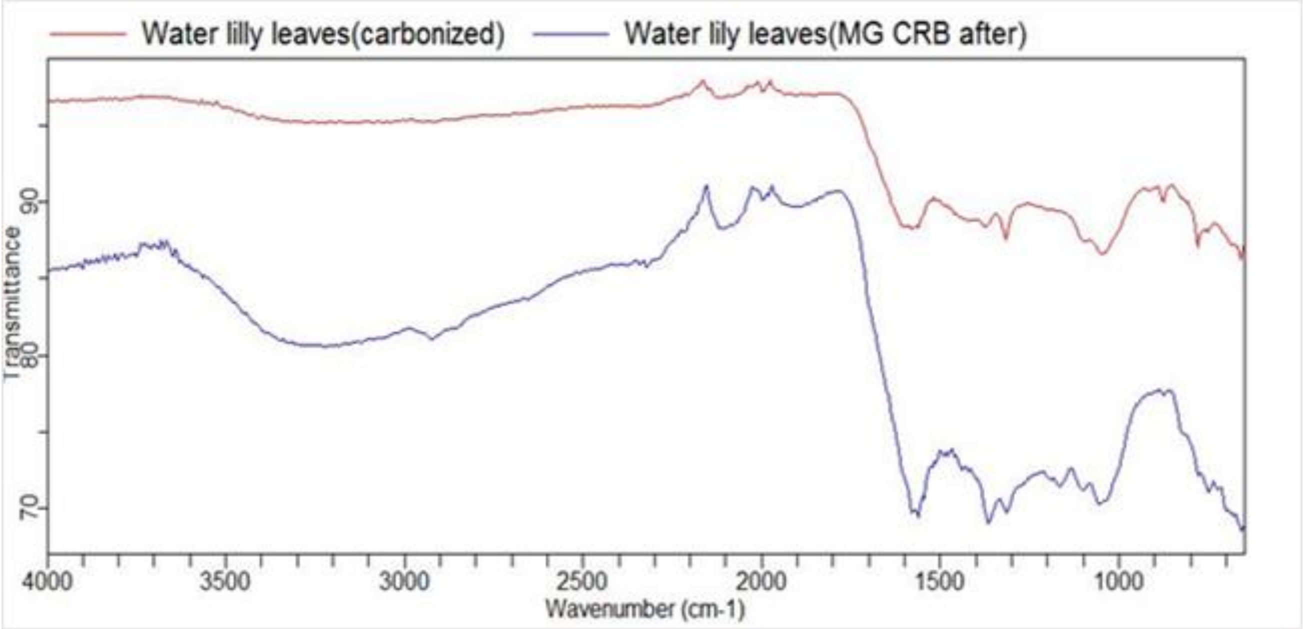

Figure 2: **FTIR Spectra for CWL before and after adsorption of MG**

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

Functional group	Wavelength range (cm^{-1})	Malachite Green (MG).		
		Before Adsorption	After Adsorption	Differences
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

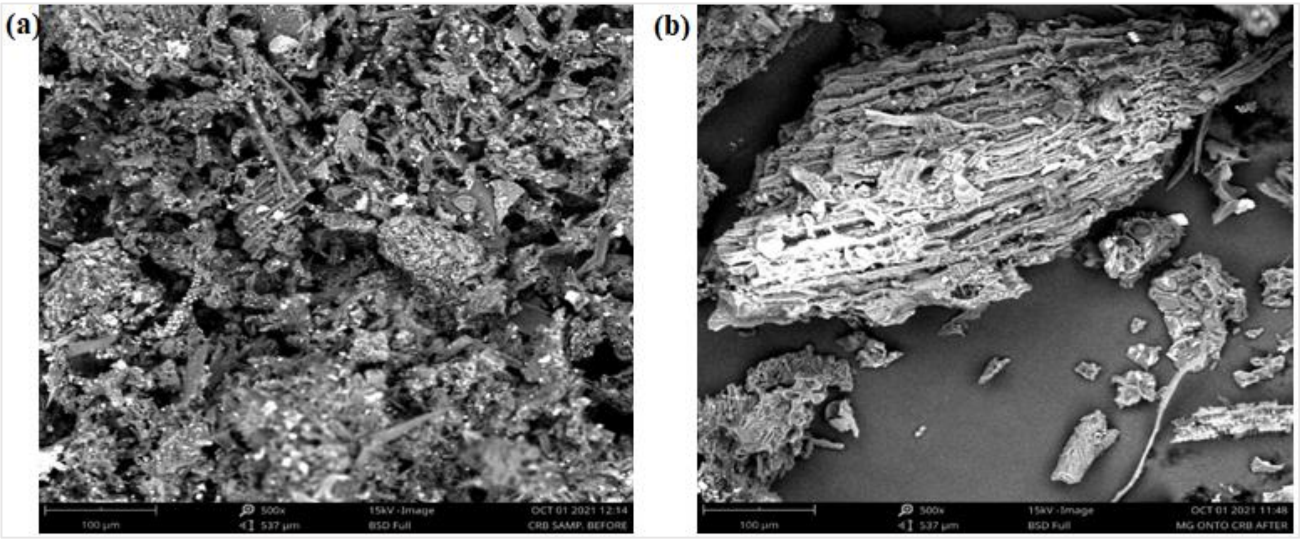

Figure 3: **SEM micrograph of CWL (a) Before adsorption (b) After Adsorption of MG.**

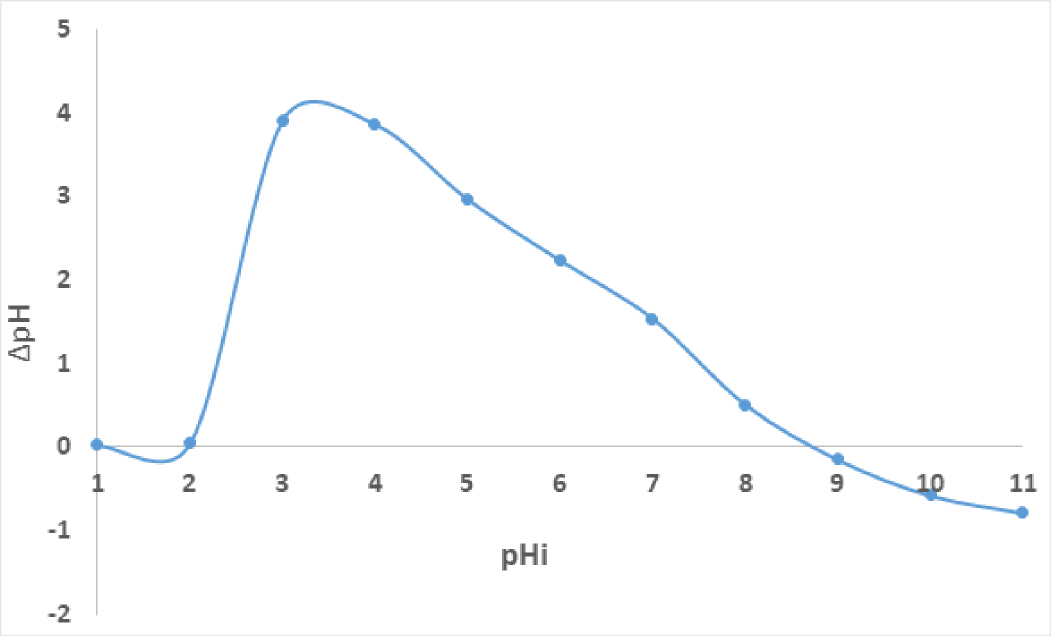

Figure 4: **Determination of point of Zero Charge (pH_{pzc}) of CWL adsorbents**

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 OH- than H+ groups and since the adsorbent has negatively charge surface (pHpzc =8.80) can 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 its determine 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 cunch (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).

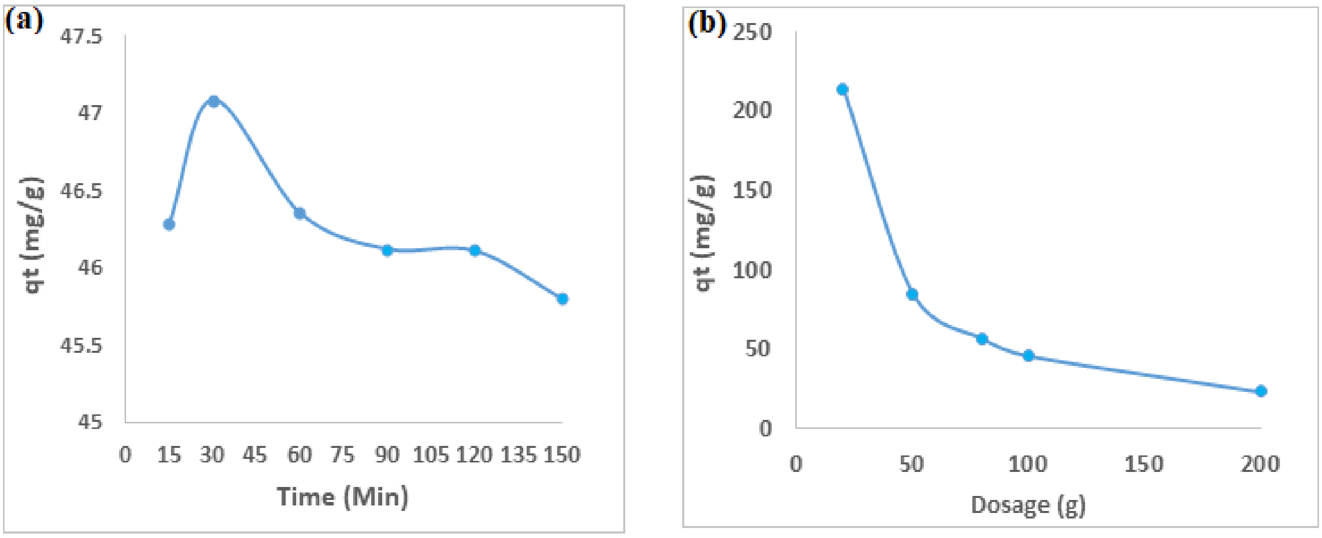

Figure 5: **(a) Effect of Contact Time on Adsorption of MG (b) Effect of Dosage on Adsorption of MG.**

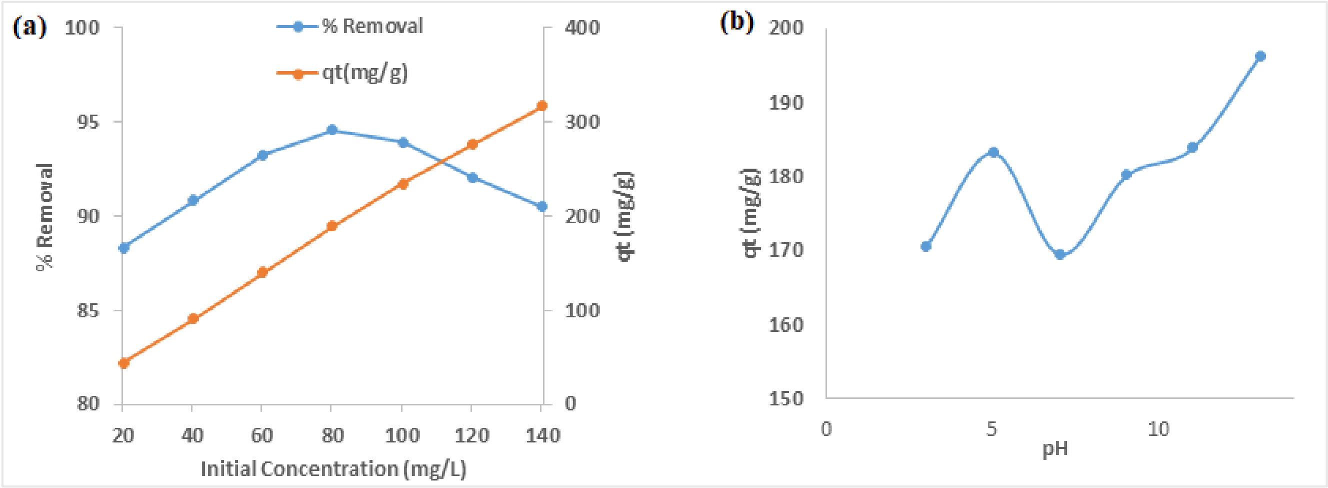

Figure 6: **(a) Effect of Initial Concentration on Adsorption of MG (b) Effect of pH on adsorption of MG**

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:

$$\frac{1}{qe} = \frac{1}{Qo} + \frac{1}{QoKlCe} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \text{(4)}$$

Where Ce (mg/L) and qe (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/qe vs 1/Ce 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:

$$Rl = \frac{1}{(1+KlCo)} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \text{(5)}$$

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).

$$logqe = logKf + \frac{1}{n} logCe \ldots\ldots\ldots\ldots\ldots\ldots \text{(6)}$$

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 is assumes that the free energy of adsorption process is a function of the surface coverage (Nyijime and Ayuba, 2020). Its expressed by equation 7.

$$qe = \frac{RT}{bT} \ln At + \frac{RT}{b} \ln Ce \ldots\ldots\ldots\ldots\ldots\ldots\ldots \text{(7)}$$

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

$$\ln q_e = \log q_0 - K \in^2 \ldots\ldots\ldots\ldots\ldots\ldots\ldots \text{(8)}$$

Where q_o is represent the constant of D-R (mol/g), and K is the mean free energy of adsorption (Kj/mol). However, ϵ can be calculated using the equation below

$$\in = RTln(1 + \frac{1}{C_e}) \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \text{(9)}$$

Where Ce is the adsorbate equilibrium concentration, R is the ideal Gas constant (8.314/Mol.K) and T is the Temperature in Kelvin. The values of q_o and K were obtained using slope and intercept from the plot of $\ln C_e$ against ϵ^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	qs(mg/g)	326.85
	β(mol^2/kj^2)	$3.0\text{x}10^{-6}$
	ϵ (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:

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} \ldots\ldots\ldots\ldots\ldots\ldots\ldots \text{(10)}$$

Where qe and qt are the amount of dyes adsorbed at equilibrium and at time t (mg/g) respectively and k_1 (min^{-1}) is the rate constant of adsorption. The plot of log (qe-qt) vs t should give a linear relationship from which k1 & qe 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;

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

Where k_2 is the rate constant of adsorption (g/mg.min), qe and qt 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 ($1/k_2q_e^2$) and the slope (1/qe) 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				
Pseudo-First Order					
	T (K)	**Q_{exp}(mg/g)**	**Q_{cal} (mg/g)**	**K_1(min^{-1})**	**R^2**
	303	194.84	0.057	5.640x10-2	0.1755
	313	194.23	1.693	9.67x10-3	0.1238
	323	190.10	0.639	1.75x10-2	0.0223
Pseudo-Second Order					
	T(K)	**Q_{exp}(mg/g)**	**Q_{cal} (mg/g)**	**K_2(min-1)**	**R^2**
	303	194.84	192.31	2.08x10-2	0.9936
	313	194.23	188.68	2.00x10-2	0.9928
	323	190.10	185.19	1.82x10-2	0.9937

Adsorption Thermodynamics

The changes in entropy (ΔS), enthalpy (ΔH), and Gibb's free energy (ΔG) parameters are given by equations (12-14). The ΔG parameters were computed using the distribution constant K_c at equilibrium time.

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

$$\Delta G = -RT\ln K_c \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \text{(13)}$$

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

The ΔH and ΔS 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 ($8.314 jmol^{-1}k^{-1}$).

Table 4: Thermodynamics parameters

T(K)	Ln K_c	ΔG (KJ/mol)	ΔH (J/mol)	ΔS (J/mol.K)
303	3.121	-7.861	19.069	88.19
313	3.163	-8.230		
323	3.484	-9.357		
333	3.778	-10.457		

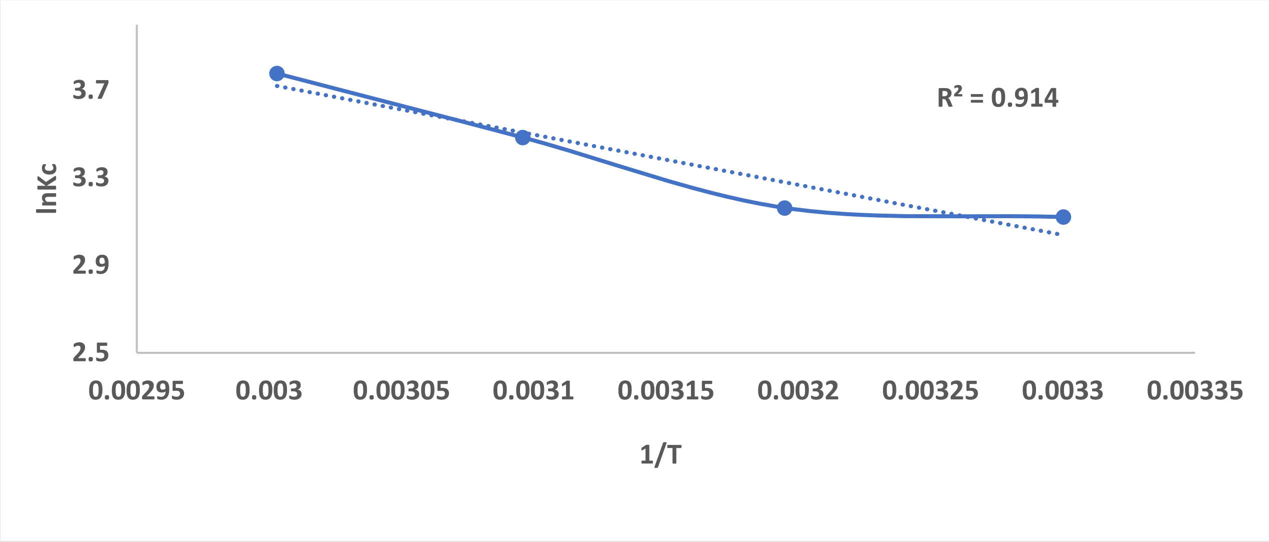

Figure 7: The Van't Hoff plot for Adsorption of MG onto CWL

The values of the thermodynamic functions given in Table 1. As seen from the table 4 reveals that, the negative values of ΔG 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 (-10.46KJmol^{-1}), relative to 323K (-9.36KJmol^{-1}), 313k (-8.23KJmol^{-1}) and 303k (-7.86KJmol^{-1}). The positive value of ΔH demonstrates that the adsorption of MG has endothermic nature (i.e heat absorbed from the surrounding). In contrast, the positive value of ΔS specifies the increased randomness at the adsorbent-liquid interface. Similarly, positive ΔS 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

REFERENCES

Aazza, M., Moussout, H., Marzouk, R., Ahlafi, H (2017). Kinetic & thermodynamics studies of malachite green adsorption on alumina. *Journal of Materials and Environmental Sciences*, vol 8(8), ISSN: 2028-2508, pp 2694-2703.

Abdulmumini, H., Ayuba, A.M. (2022). Reclamation of spent solid matrices used in adsorption of malachite green and methyl violet dyes from aqueous solution. *Journal of Materials and Enviromental Sciences,* 13(06), pp 723-731.

Adeyi, A.A., Jamil, M.A.N.S., Abdullah, L.C., Choong, Y.S.T (2019). Adsorption of malachite green dye from liquid phase using hydrophilic thiourea-modified poly (acrylonitrile-co-acrylic acid): Kinetic and isotherms studies. *Hindawi journal of chemistry, volume 2019, articles ID 4321475, 14 pages. https://doi.org/10.1155/2019/4321475*

Allen, S.J., Mckay, G., Porter, J.F (2004). Adsorption isotherm models for basic dyes by peat in single and binary component systems. *Journal of Colloids*

Interface Sciences, 280(2), pp 322-333. https://doi.org/10.1016/j.jcis.2004.08.078

Altintig, E., Yenigun, M., Sari, A., Altuntag, H., Tuzen, M., saleh A.T (2020). Focile Synthesis of Zinc oxide nanoparticles loaded activated carbon as an eco-friendly adsorbent for ultra-removal of malachite green from water. *Journal of pree-proof environmental technology and innovation (2020). https://doi.org/10.1016/j.eti.2020.101305*

Anisuzzaman, S.M., Joseph, G.C., Daud, AMSBW., Krishnaiah, D., Yee, H.S (2014). Preparation and characterization of activated carbon from typha orientalis leaves. *International Journal of Industrial Chemistry*, 6:9-21. https://doi.org/10.1007/s40090-014-0027-3

Ara, B., Shah, J., Jan, M.R., Aslam, S (2013). Removal of Metribuzin herbicide from aqueous solution using corn cob. *International Journal of Science, Environment and Technology,* 2(2), pp 146-161

Arinyanto, E (2009). Adsorption of malachite green on natural zeolite. *The reaktor,* 12(3), pp 161-165.

Asim, N., Amin, M.H., Alghoul, M.A., Sulaiman, S.N.A., Razali, H., Akhtaruzzaman, M., Amin, N., Sopian, K (2019). Developing of Chemically Treated Waste Biomass Adsorbent for Dyes Removal. *Journal of Natural fibers,* 00, pp 1-10. https://doi.org/10.1080/15440478.2019.1675214

Ayuba, M.A., Bridget, I (2021). Cowpea husk adsorbent for the removal of crystal violet dye from aqueous solution. *Arabian Journal of Chemical Research.* 8(1): pp114-132.

Ayuba, A.M., Abdulmumini, H (2022). Raw water lily leaves (*Nymphaea Lotus)* poder as an effective adsorbent for adsorption of malachite green dye from aqueous solution. *Chemical Review and Letters,* 5, pp 250-260

Dahri, K.M., Kooh, R.R.M., Lim, L.B.L (2013). Removal of methyl violet 2B from aqueous solution using casuamina equisetifolia needle. Hindawi publishing cooperation ISRN *Environmental Chemistry*, article ID: 619819, page 8. https://doi.org/10.1155/2013/619819

Ejder-Korucu, M., Gurses, A., Dogar, C., Sharma, K.S., Acikyildiz, M (2015). Removal of Organic dyes from Industrial Effluents: An Overview of Physical and Biotechnological Applications. *Sanjay K. Sharma (ed) Green Chemistry for Dyes Removal from wastewaters,* pp 1-34. https://doi.org/10.1002/9781118721001.ch1

El-Boujaady, H., Mourabet, M., Bennani-Ziatni, H., Taitai, A (2014) Adsorption/Desorption of Direct yellow 28 on apatitc phosphate: mechanism, Kinetics and Thermodynamics. *Journal of the Association of Arabs Universities for basic and applied sciences.* Vol 16, pp 64-73.

Eko, A (2009). Adsorption of malachite green on natural zeolite. *Reaktor,* 12(3), pp 161-165.

Enenebeaku, K.C., Okorocha, J.N., Enenebeaku, E.U., Okolie, I.J., Anukum, B (2016). Adsorption of malachite green from aqueous solution by PNSBP: equilibrium, kinetic and thermodynamics studies. *IOSR Journal of applied Chemistry*, vol 9 **(9),** e-ISSN: 2278-5736, pp 28-38. https://doi.org/10.9790/5736-0909012838

Estandiar, N., Ebadi, T (2014). Removal of Mn (II) from Groundwater by Sugarcane Bagasse and Activated Carbon (a Comprative Study): application of response surface methodology (RSM). *Journal of Industrial and Engineering Chemistry,* 2(05), pp 3726-3736. https://doi.org/10.1016/j.jiec.2013.12.072

Galadima, L.G., Wasagu, R.U., Lawal, M., Aliero, A.A., Magaji, U.F., Sulaiman, H (2015). Biosorption Activity of *Nymphaea Lotus* (Water Lily). *The International Journal of Engineering and Sciences (IJES),* 4(3), pp 66-70.

Giwa, S.O., Moses, J.S., Adeyi, A.A., Giwa, A (2018). Adsorption of Atrazzine from aqueous solution using Desert Date Seed Shell activated Carbon. ABUAD *Journal of Engineering Research & Development (AJERD)*, 1(3). Pp 317-325.

Han, X., Yuan, J., Ma, X (2013). Adsorption of Malachite Green from aqueous solutions onto lotus leaf: Equilibrium, Kinetics and Thermodynamics Studies. *Desalination and water Treatment*, 52(2). Pp 5563-5574. https://doi.org/10.1080/19443994.2013.813102

Ibrahim, M.B. and Sani, S (2015). Neem (*azadirachta indica*) leaves for the removal of organic pollutants. *Journal of Geosciences and Environmental protection,* 3, pp 1-9. https://doi.org/10.4236/gep.2015.32001

Ibrahim, M.B., Sulaiman, M.S., Sani, S (2015). Assessment of adsorption properties of neem leaves waste for the removal of congo red and methylene orange. 3rdn international conference on biological, chemical and environmental sciences (BCES-2015) September 21-22, 2015 Kuala Lampur, Malaysia.

Kabra, A.N., Khandare, R.V., Waghmode, T.R., Covindawar, S.P (2012). Phytoremediation of textile effluents and mixture of structurally different dyes by *Glandulania pulchella* sweet) Tronc. *Chemosphere,* 87(2), pp 265-272. https://doi.org/10.1016/j.chemosphere.2011.12.052

Karim, B.A., Mounir, B., Hachkar, M., Bakasse, M., Yaacoubi, A (2017). Adsorption/Desorption behaviour of cationic dyes on Moroccan Clay: equilibrium & Mechanism. *Journal of Materials and Environmental Sciences*. **8(3)**. Pp 1082-1096.

Kushwaha, K.A., Gupta, N., Chattopadhyaya, M.C(2014). Removal of Cationic Methylene Blue and Malachite Green Dyes from Aqueous Solution by Waste Materials of *Daucus carota. Journal of Saudi Chemical Society,* 18, pp 200-207. https://doi.org/10.1016/j.jscs.2011.06.011

Khawaja, R., Ramteke, D.S., Wate, S.R (2007). Graphene oxide decorated with cellulose and copper nanoparticle as an efficient adsorbent for the removal of malachite green. *International journal of biological macromolecules,* 167, pp 23-34. https://doi.org/10.1016/j.ijbiomac.2020.11.137

Mafra, M.R., Igarashi-Mafra, L., Zuim, D.R., Vasques, E.C., Ferreira, M. A (2013). Adsorption of Ramazol Brilleint Blue on an Orange Peel Adsorbent. *Brazilian Journal of Chemical Engineering,* 30(3), pp 657-665. https://doi.org/10.1590/S0104-66322013000300022

Manjunatha, K.R., Vagish, M (2016). Study on adsorption efficacy of neem leaves powder in the removal of reactive red dye colour from aqueous solution. *International Research Journal Engineering & Technology,* 3, 12-24.

Majithiya, D., Yadav, A., Tawde, S (2013). Comparative studies of *Azidirachta indica* (Neem) leaf powder and activated carbon as an adsorbent for removal of chromium from an aqueous solution, *Journal of environmental science and sustainability (JESS),* 1(1): 21-27

Malik, R., Ramteke, D.S., Wate, S.R (2007). Adosrption of malachite green on ground nut shell waste based powdered activated carbon. *Waste management,* 27, pp 1129-1138. https://doi.org/10.1016/j.wasman.2006.06.009

Martins, O.O., Jonathan, O.B., Emanuel, U.I (2014). Regeneration strategies for spent solid matrices used in adsorption of organic pollutants from surface water: A critical review. *Desalination and water treatment,* 57(2), pp 518-544. https://doi.org/10.1080/19443994.2014.967726

Nasiruddin, K.M., and Sawar, A. (2007). Determination of point of charge of natural and treated adsorbents. *Surface review and letters,* 14(3), pp 461-469. https://doi.org/10.1142/S0218625X07009517

Nguyen, T.H.N., Bui, T.P.Q., Pham, T.T.T., Hoang, N.B., Bach, L.G (2015). Pre-treated fruit peels as adsorbent for the removal of dyes from water. *IOP Conf. Series:* Earth and Environmental Sciences, *159, pp 1-9.*

Nyijime, T.A., Ayuba, A.M (2020). Kinetic and equilibrium studies of paraquat dichloride adsorption of raw Bambara groundnut (*Vigna subterranean)* shells. *Applied Journal of environmental engineering, 6N⁰1, pp 1-13.*

Oyeyode, O.J., Ayuba, A.M (2022). Adsorption of Methyl Orange Dye from Aqueous Solutions by Carbonised Iron Tree (*Prosopis Africana)* Seeds: Kinetic, Equilibrium & Thermodynamics Studies. *Applied Journal of Environmental Engineering Science,* 8N⁰(2), pp 130-147.

Oznur, D., Fatma, I., Kadir, T., Mahmure, O (2013). Sumec leaves as a Novel low cost adsorbent for removal of basic dyes from aqueous solution. *Hindawi publishing corporation (ISRN) analytical Chemistry,* Article ID. 1210470, 9 pages. https://doi.org/10.1155/2013/210470

Pan, X., Zhang, D (2009). Removal of malachite green from water by firmiana simplex wood fiber, *e-Journal of biotechnology,* 12(4), pp 1-10. https://doi.org/10.2225/vol12-issue4-fulltext-4

Parhi, P.K., Bindhari, B.K., Mohapatra, R.K., Das, S., Behera, S.S., Murmur, B.M (2018). Extensive Investigation on the study for the adsorption of Bromocresol Green (BCG) dye using activated phragmites karka. *Indian Journal of Chemical Technology,* Vol 25. Pp 409-420.

Rohani, M., Amsadi, A., Gunasangkari, S., Anis, A.A.Z., Mohamad, A., Muhammad, H.C.H., Sofiah, H (2021). Removal of Malachite Green Dye Using Oil Palm Empty Fruit Bunch as Low-Cost Adsorbents. *Biointerface Research in Applied Chemistry,* 11(6), pp 14998-15008. https://doi.org/10.33263/BRIAC116.1499815008

Saechian, S., Sripongpun, G (2019). Adsorption of malachite from synthetic wastewater using banana peel adsorbents. *Songularakarin journal of Science and Technology*, 41(1), pp 21-29.

Sara, D., Tushar, K.S (2012). Removal of an anionics dye congo red from aqueous solutions by raw pine and acid-treated pine cone powder as adsorbent: Equilibrium, Thermodynamics, Kinetics, Mechanisms and process designs. *Water Resources,* 46, pp 1933-1946. https://doi.org/10.1016/j.watres.2012.01.009

Sartape, S.A., Mandhare, M.A., Jadhav, V.V., Raut, D.P., Anusa, A.M., Kolekar., S.S (2017). Removal of malachite green dye from aqueous solution with sorption techniques using *Limonia Acidissima* (wood apple) Shell as low cost adsorbents. *Arabian Journal of Chemistry,*10, pp 3229-3238. https://doi.org/10.1016/j.arabjc.2013.12.019

Shahryari, Z., Goharrizi, S.A., Azadi, M (2010) Experimental study of methylene blue adsorption from aqueous solution onto a carbon nano tubes. International *Journal of water Resources and environmental engineering,* 2(2), pp 016-028.

Tang, H., Zhou, W., Zhang, L (2012). Adsorption Isotherms and Kinetics Studies of Malachite Green on Chitin Hydrogels. *jOurnal of Hazardous Materials,* 209-210, pp 218-225. https://doi.org/10.1016/j.jhazmat.2012.01.010

Xu, R.K., Xiao, S.C., Yuan, J.H., Zhao, A.Z (2011) Adsorption of methyl violet from aqueous solutions by the biochar derived from crops residue. *Bioresources Technology,* 102(22), pp 10293-10298. https://doi.org/10.1016/j.biortech.2011.08.089