ADSORPTION CHARACTERISTICS OF MANGO LEAF (*Mangifera indica)* POWDER AS ADSORBENT FOR MALACHITE GREEN DYE REMOVAL FROM AQUEOUS SOLUTION

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Abstract: *The adsorption of malachite green (MG) dye on mango leaf powder (MLP) was investigated in a batch process. The adsorbent prepared was characterized by Fourier Transform Infrared Spectroscopy. Operational parameters such as initial dye concentration, contact time and solution temperature governing the adsorption process were studied and evaluated. Equilibrium data were fitted to both Langmuir and Freundlich isotherm models, Langmuir model gave the best fit. The maximum monolayer coverage Q_0 was 4.49 mg/g. Kinetic parameters, rate constants, equilibrium sorption capacities, and related correlation coefficients of pseudo-first-order and pseudo-second-order models were calculated and discussed; the pseudo second-order model provided the best correlation with $R^2 \geq 0.99$. Thermodynamic functions such as Standard free energy (ΔG^0), standard enthalpy (ΔH^0), and standard entropy (ΔS^0) were also calculated. The adsorption process was found to be feasible, spontaneous and endothermic in nature.*

Keywords: *Mango leaf powder, Malachite green, Equilibrium, Adsorption, Thermodynamics*

1. Introduction

Water is a vital commodity, one of the most important of all chemical substances with many remarkable and unique properties. Natural water includes rain water, spring water, river water, well water, lake water and sea water and these take over seventy per cent (70%) of the earth (Shakhashiri, 2009). Water pollution is one of the most undesirable environmental problems in the world that requires urgent solution. Textile industries produce a lot of wastewater, which contains different contaminants, including acidic or caustic dissolved solids, toxic compounds and different type of

dyes. These dyes are stable and fast, difficult to degrade, toxic, rendering the water unfit for its intended use.

The greatest environmental concern with dyes is absorption and reflection of sunlight entering the water. Light absorption diminishes photosynthetic activity of algae and seriously affects the food chain. Many dyes and their breakdown products are carcinogenic (Bello and Ahmad, 2011). Due to the damage effluents from factories and industries have caused to the sewer system. There is a need for the removal of these dyes because water must meet some certain basic requirements to make it fit for domestic uses through colour removal to make the effluent/waste water from industries safe for discharge into sewer systems (Bello and Ahmad, 2011). An efficient removal of coloured substance is activated carbon through adsorption process but it is very expensive in its use commercially. For cost-effectiveness and improved efficiency, environmental chemists have devised several methods for the removal of coloured substances (dyes) from wastewater using readily available and cost-effective agricultural wastes as an alternative to activated carbon for efficient removal of dyes using adsorption method. Furthermore, adsorption processes remove/minimize different pollutants; thus, it has a wide applicability in water pollution control (Bhatnagar and Sillanpaa, 2010). Lot of materials have been extensively investigated as adsorbents in water pollution control. Some of the important ones include silica gel (Huang *et al.,* 2011), activated alumina (Singh and Pant, 2004), zeolite (Wang *et al.,* 2009) and activated carbon (Sandeman *et al.,* 2011) etc.

Agricultural materials particularly those containing cellulose, for example, cereals such as rice (Srivastava *et al.,* 2009), maize (Elizalde-Gonz´alez *et al.,* 2006) and corn (Leyva-Ramos *et al.,* 2005) as well as sugarcane-bagasse (Krishnan *et al.,* 2011) shows potential sorption capacity making them economical and eco-friendly due to their unique chemical composition, availability in abundance, renewable nature, low ash content, reasonable hardness and low cost proffering a viable option for water and wastewater remediation. Several studies on the removal of toxic substances from aqueous solution by adsorption using low cost agro-wastes as alternatives to activated carbon abound in literature. A few of recent and relevant studies are on rubber seed coat (Bello and Ahmad 2012), Cocoa shell (Theivarasu *et al.,* 2011), groundnut hull (Bello *et al.,* 2011), unwanted barley and wheat straws (Abdulhamid and Asil, 2011), Cocoa pod husks (Bello and Ahmad, 2011), coconut husk (Abdul Halim and MohdYatim, 2011) e.t.c. Malachite green is traditionally used as a dye. Millions of kilograms of MG and

related triarylmethane dyes are produced annually for this purpose (Gessner and Mayer, 2002). It is use to combat the *Oomycete saprolegnia*, which infects fish eggs in commercial aquaculture, and other fungi, and its usage as a parasiticide and antibacterial (Srivastava *et al.,* 2004). MG has frequently been used to catch thieves and pilferers applied on money as bait, sprinkled with the anhydrous powder. The LD_{50} (oral, mouse) is 80 mg/kg. As a leuco-base dye, malachite green is retained in fish muscle much longer, most intake of malachite green would be in the leuco form, it has carcinogenic symptoms, but a direct link between malachite green and liver tumor has not been established (Culp *et al.*, 2002). Numerous niche applications exploit the intense colour of MG. It is used as a biological stain for microscopic analysis of cell biology and tissue samples and in forensic science (Protocol 2.18, 2010). Mango tree, a plant which belongs to the family anacardiaceae (*Mangifera indica*) is an evergreen plant, which is grown in Nigeria. Mango leaves are wastes that are arbitrarily discarded or set on fire. In this paper, the feasibility of mango leaf powder (MLP) as adsorbent for removal of MG dye from aqueous solution was investigated. This disposal results in environmental pollution. The effects of operating parameters on adsorption such as contact time and initial dye concentration were monitored and optimal experimental conditions were determined.

2. Materials and method

2.1 Preparation of the raw mango leaf as adsorbents

Mango leaves were collected from mango tree on LAUTECH campus. They were washed thoroughly with distilled water to remove dust and other impurities and dried at 105 ^{o}C in oven until constant weight was attained. Dried mango leaves were then ground (pulverized), washed to neutrality and dried again in an oven. Dried mango leaf powder was stored in plastic container and labelled as ML for further use.

2.2. Preparation of Malachite green dye solution

The dye used in this study was Malachite Green, it was cationic in nature (purity: 98.7%; colour: green; maximum wavelength of absorption: 618 nm). 500 mg/L of Malachite green dye solution was prepared, from this stock, other working concentrations (10-50 mg/L) were prepared by serial dilution.

2.3. Batch equilibrium method

Batch adsorption process of malachite green dye was carried out by agitating 0.5g of ML with 50 mL of MG dye at various concentrations in 250mL conical flasks. This was done by setting the samples into a bath shaker and the samples were shaken for 48 h at three different temperatures 303, 313 and 323 K until equilibrium was reached. 10 mL of the supernatants were

extracted and filtered using filter paper. The filtrates were analysed using UV–visible spectrophotometer (Model A Analyst 800; Perkin-Elmer) at a wavelength of 618 nm to determine the amount of MG dye adsorbed on mango leaf powder. The amount and percentage of malachite green dye removed was calculated using Equations (1) and (2).

$$q_e = \frac{[C_o - C_e]V}{W} \quad (1)$$

$$\% \text{ Removal} = \frac{[C_o - C_e]}{C_o} \times 100 \quad (2)$$

where q_e is the amount of malachite green dye adsorbed (mg/g) at equilibrium, V is the volume of solution (dm^3), C_o and C_e are the initial and equilibrium concentration of malachite green dye remaining in the solution (mg/L), and W is the dry weight of the mango leaf powder used (g).

2.4. Characterization of the adsorbents

Fourier Transform Infrared spectroscopic analysis was used to study the surface chemistry of the sample. The FTIR spectrum gives information about the characteristic functional groups on the surface of the sample. The analysis was conducted by encapsulating the sample in potassium bromide pellets. The spectrum was measured from 4000 to 400 cm^{-1}.

2.5. Adsorption kinetics

The pseudo-first-order equation was used to test the adsorption data (Lagergren and Svenska, 1898). Plots of ln (q_e-q_t) against t at various concentrations and temperatures resulted in linear graphs. k_1 and q_e were calculated from the slopes and intercepts respectively.

The pseudo-second-order equation was also used to test the adsorption data (Ho and McKay 1999). Plots of t/q_t versus t gave linear graphs from which q_e and k_2 were estimated from the slopes and intercepts of the plot at temperatures 303, 313 and 323 K respectively. The correlation coefficients (R^2) were also calculated from the graphs. The agreement between $q_{e,}$ cal. and $q_{e,}$ exp data were considered.

2.6. Adsorption isotherm

Two important isotherms were selected in this study: Langmuir and Freundlich. The expression of the linearized form of Langmuir adsorption isotherm model (Langmuir, 1916; Freundlich, 1906).

$$\frac{C_e}{q_e} = \frac{C_e}{q_o} + \frac{1}{q_o b} \quad (3)$$

where C_e is the dye concentration in the solution at equilibrium (mg L^{-1}),

q_e is the dye concentration on the adsorbent at equilibrium (mg g^{-1}),

q_o is the monolayer adsorption capacity of adsorbent (mg g^{-1}), and

b is the Langmuir adsorption constant (L mg^{-1}).

The essential characteristics of the Langmuir isotherm can be expressed by a dimensionless constant called equilibrium parameter R_L to confirm the favourability of the process which is defined by Equation (4):

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

The linearized form of Freundlich model is expressed as.

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

where q_e is the amount of dye adsorbed at equilibrium (mg g^{-1}),
C_e is the equilibrium concentration of the adsorbate (mgL^{-1}),
k_f and n are constants incorporating the factors affecting the adsorption capacity and the degree of non-linearity between the solute concentration in the solution and the amount adsorbed at equilibrium, respectively.

3. Results and discussion

3.1. Fourier Transform Infra-red analysis

Table 1: FTIR spectra characteristics of raw mango leaf powder.

IR Peak	ML Wave number (cm^{-1})	Assignment
1	3375-3132	Bonded -OH group
2	2920-2850	Aliphatic C-H stretching
3	1613	C-C Stretching of CH_3
4	1454	Symmetric C-H bending
5	1372	Symmetric C-H bending
6	1031	C=O bonds of ether, phenol, ester
7	560	C=N stretching
8	512	S-O group

As shown in the Table 1, the FTIR spectroscopic analysis indicated broad band at 3375-3132 cm^{-1}, representing bonded -OH groups. The band observed at about 2920-2850 cm^{-1} was assigned to aliphatic C-H stretching group. The peak observed around 1613 cm^{-1} corresponds to C-C stretching region. The peak observed at 1454 cm^{-1} corresponds to the symmetric C-H bending. The peak observed at 1372 cm^{-1} corresponds to symmetric C-H bending. The peak observed at 1031 cm^{-1} corresponds to C=O bonds of ether, phenol, ester. The peak observed at 560 cm^{-1} corresponds to C=N stretching. The spectral

analysis of the raw Mango leaf indicates that mostly the bonded O-H groups, aliphatic C-H groups, symmetric C-H groups will be involved in the adsorption process. The spectrum is as shown in figure 1.

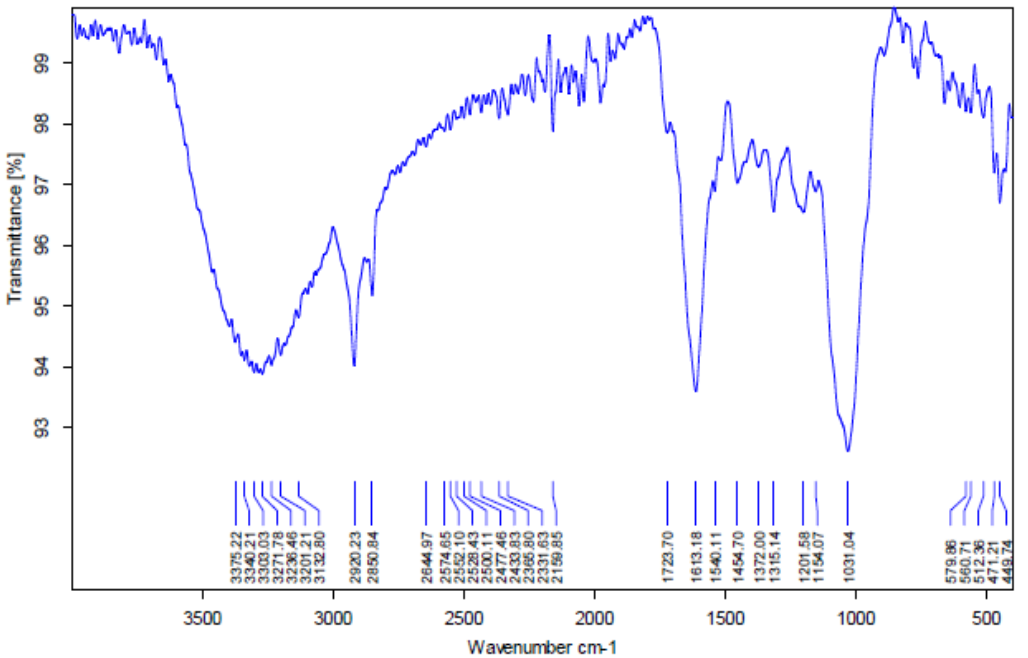

Figure 1: Fourier Transform infra-red spectra of MLP.

3.2. Effect of temperature

The initial malachite green dye concentration was varied from 10–50 mg/L. The amount of dye adsorbed increased as dye concentrations increases with rise in temperature from 303 to 323 K. This is mainly due to the increased surface activity suggesting that adsorption between malachite green dye and mango leaf powder was an endothermic process.

3.3. Adsorption isotherm

A plot of C_e/q_e versus C_e from the Langmuir isotherm model gave linear graph with slope $1/q_o$ and an intercept of $1/q_ob$ (Figure 2). The R^2 values for the Langmuir isotherm, when compared with the Freundlich isotherm, indicate that the adsorption of malachite green dye onto mango leaf powder fits the Langmuir isotherm well. Values of q_o and b are calculated from linear plots and reported in Table 2. The dimensionless constant (R_L) is used to confirm the favourability of the adsorption process, that is ($0< R_L< 1$) favourable, $R_L = 1$ linear, $R_L = 0$ irreversible or $R_L> 1$ unfavourable (Langmuir 1916). The values of $R_L$obtained are reported in Table 3. The fact that all the R_L values for the

adsorption of MG onto MLP are in the range 0.01–0.76 at various temperatures are less than one shows that the adsorption process is favourable. Plots of log q_e versus log C_e gave linear graph (figure not shown). The values of k_f and n from the graph are reported in Table 3. The adsorption data does not fits the Freundlich isotherm when compared with Langmuir model judging from the R^2 values. Values of 1/n less than one indicate that the adsorption is favourable.

3.3.1. Performance of MLP

The comparison of the adsorption capacities of different types of low-cost adsorbents used for the removal of MG (Khan *et al.*, 2010; Khattri and Singh, 2009; Saha *et al.*, 2010; Iqbal and Ashiq, 2007; Kumar and Vasanth 2007) are given in Table 2. The monolayer adsorption capacities of adsorbent, q_o (mg g^{-1}) from Langmuir isotherm are shown. The value of q_o in this study is greater than those reported in previous works. This suggests that MG could be easily adsorbed on MLP.

Table 2: Comparison of adsorption capacities of MG dye onto various adsorbents

Adsorbent	q_o (mg.g^{-1})	Temp. (K)	References
Unsaturated polyester			
Ce(IV) phosphate	1.01	300	Khan *et al.*, 2010
Neem Sawdust	4.35	303	Khattri and Singh, 2009
Tamarind fruit shell	1.95	303	Saha *et al.*, 2007
Activated charcoal	0.18	303	Iqbal and Ashiq, 2007
Lemon peel	3.2	305	Kumar and Vasanth, 2007
Mango Leaf Powder	*4.49*	*323*	*This work*

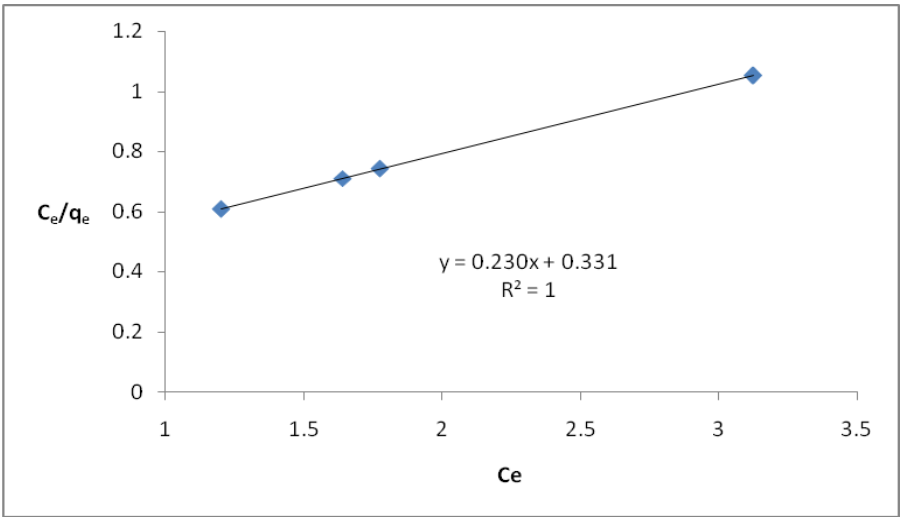

Figure 2: Plot of C_e/q_e against C_e for the adsorption of MG dye onto MLP at 30 ^oC

Table 3: Langmuir and Freundlich isotherm model statistical parameters for the adsorption of malachite green dye onto MLP at different temperatures.

	T(K)		
Model	303	313	323
Langmuir isotherm			
q_0 (mg.g^{-1})	4.333	4.109	4.492
b (L.mg^{-1})	0.697	4.917	0.032
R_L	0.126	0.020	0.755
R^2	1.000	0.999	0.997
Freundlich isotherm			
K_F	1.021	1.005	1.000
n	0.98	0.995	1.000
R^2	0.98	0.995	1.000

3.4 Adsorption kinetics

From the pseudo-first-order equation (Lagergren and Svenska, 1898), a plot of $\ln(q_e-q_t)$ against t at various concentrations and temperatures resulted in graphs with negative slopes (Figures 3 and 4). Although the correlation coefficients were high, comparing q_e calc. to the q_e exp., the values do not agree. The results are presented in Table 4. Therefore the adsorption of malachite green dye onto mango leaf powder (MLP) does not follow the pseudo-first-order kinetics.

Table 4: Parameters of different kinetic models of malachite green dye adsorption onto MLP

Temperature K	$q_{e,(exp)}$ (mg/g)	Pseudo first-order model		Pseudo second-order model				
		k_1 (min^{-1})	R^2	$q_{e,(cal)}$ (mg/g)	k_2 (g/mg min)	$q_{e,(cal)}$ (mg/g)	h_i (mg/g min)	R^2
303	1.993	0.0457	0.999	0.0559	2.099	1.999	8.389	1.000
313	1.995	0.0696	0.998	0.0995	2.477	2.000	9.911	1.000
323	1.992	0.0216	0.999	0.0201	3.391	1.996	13.514	1.000

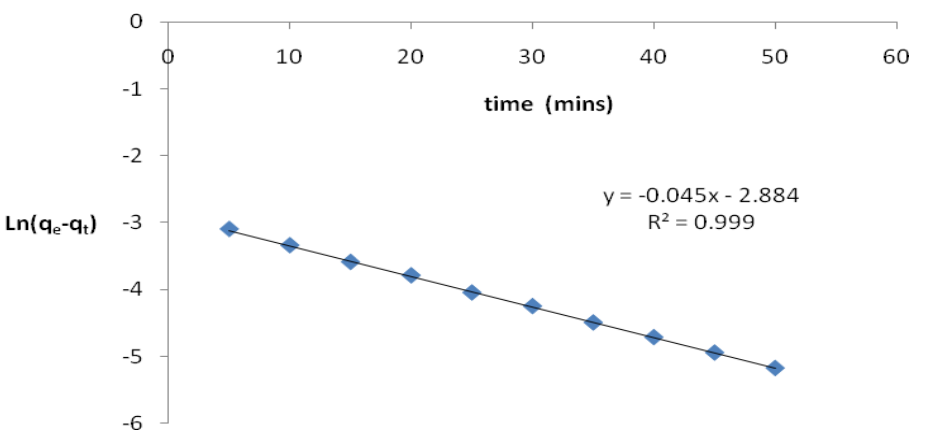

Figure 3: Plot of pseudo-first order kinetic model for the adsorption of MG dye on MLP at 303 K

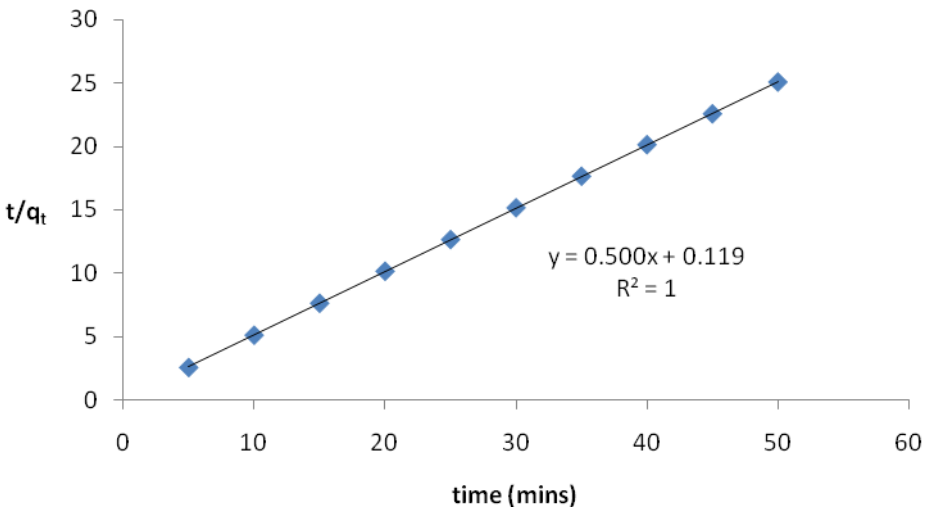

Figure 4: Plot of pseudo-second order kinetic model for the adsorption of MG dye on MLP at 303 K

3.5 Thermodynamic studies

Three thermodynamic parameters are considered to characterize the adsorption process: the standard enthalpy (ΔH^0), standard free energy (ΔG^0), and standard entropy (ΔS^0) due to the transfer of one mole of solute from the solution onto solid–liquid interface. The positive value of ΔH^0, 5.8×10^1 KJ mol^{-1} indicates that the adsorption process was endothermic in nature. The positive value of standard entropy change, ΔS^0, 0.15952 KJ $mol^{-1}K^{-1}$ shows increased randomness at the solid/solution interface occurring in the adsorption process reflecting the affinity of the adsorbent toward the malachite green dye molecules. Values of free energy change, ΔG^0, for malachite green dye adsorption were negative (-1.8×10^3, -1.3×10^4, and -8.7×10^1 J mol^{-1} at 303 K, 313 K, and 323 K, respectively) as shown in Table 5, shows that the adsorption process is spontaneous.

Table 5: Thermodynamic parameters for the adsorption of malachite green dye adsorption onto MLP at different temperatures.

Temp (K)	ΔG J mol^{-1}	ΔH J mol^{-1}	ΔS J mol^{-1} K^{-1}
303	-1754.96	57496.3	159.5207
313	-12795.9		
323	-86.9352		

4.0 Conclusion

From the studies of the preparation, characterization, kinetics, isothermal and thermodynamic studies, Langmuir isotherm was found to correlate most with the adsorption data. Kinetic studies showed that the adsorption profile followed a pseudo-second-order model. This study revealed that mango leaf powder can be used as alternative adsorbents for the removal of malachite green dye from aqueous solutions.

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