INDIAN SPINACH LEAF POWDER AS ADSORBENT FOR MALACHITE GREEN DYE REMOVAL FROM AQUEOUS SOLUTION

By

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Abstract: *Indian spinach leaf powder (ISLP) was used as an adsorbent for the removal of malachite green (MG) dye from aqueous solution. Adsorption characteristics of the adsorbent were studied using Fourier Transform Infrared spectroscopy. Operational parameters such as initial dye concentration and temperature were studied in batch systems. Experimental data were analysed using Langmuir and Freundlich isotherms and it was found that Freundlich isotherms model fitted the adsorption data most. Adsorption rate constants were determined using pseudo first-order and pseudo-second-order model equations. The result clearly showed that the adsorption of MG dye on ISLP followed pseudo-second-order kinetics model. Thermodynamic functions* ΔG^o, ΔH^o, ΔS^o *were obtained. The adsorption process was found to be endothermic and non-spontaneous. The study shows that ISLP is a good precursor for MG dye removal.*

Keywords: *Indian spinach leaf powder, Malachite Green, Adsorbent, Spontaneous, endothermic.*

1. Introduction

Dye is a coloured substance that has affinity to the substrate to which it is being applied. The dye is generally applied in an aqueous solution and Dyes are one of the most important hazardous species found in industrial effluents which needs to be treated because its presence in water bodies reduces light penetration, precluding the photosynthesis of aqueous flora (Royer *et al.*, 2010; Al-Degs, 2008). Many dyes cause health problems such as allergic dermatitis, skin irritation, cancer and mutation in human. So, the removal of dyes from waste water became of great importance and attracted to a large number of research activities. Several methods have been developed for the decolourisation of waste water including ozonization, flocculation, membrane filtration, catalytic oxidation, ion exchange, irradiation, electrokinetics coagulation and adsorption on stationary phase (Robinson *et al.*, 2001).

Adsorption using commercially activated carbon is costly and rare; hence, improvisation using low cost adsorbent such as readily available agricultural waste becomes imperative. It is worthy of note that the annual production of Indian spinach is on the increase in Ogbomoso metropolis most especially along agricultural land and wastelands as it constitutes one of the major vegetable consumed in Ogbomoso, Oyo State, Nigeria. Despite the essential benefit derived from consuming vegetables, large quantities of its wastes constitute environmental pollution due to lack of proper waste disposal system. This research is designed to study the use of Indian spinach leaf powder in the removal of Malachite green dye from aqueous solution and to offer this adsorbent as alternative to expensive commercial adsorbent material used in dye adsorption.

2. Materials and Method

2.1 Adsorbate

Malachite Green dye has a chemical formula of $C_{52}H_{54}N_4O_{12}$, molecular weight of 927.00 g/mol and Λ_{max}= 618 nm. Stock solutions were prepared by dissolving accurately weighed samples of dye in distilled water.

2.2 Adsorbent

Indian spinach leaves were collected from Osogbo in Osun state. The sample was washed with distilled water to remove dirt from the surface. The washed samples were sun dried until constant weight was attained. The dried sample were then ground using mortar and pestle and sieved using manual sieve of 10nm particle size. The powdered sample was then stored in a container labelled ISLP.

2.3 Modification of Indian spinach leaf powder

A carefully weighed 2.5 g of each sample was put in a beaker containing 50 cm^3 of phosphoric acid. It was thoroughly mixed and heated on a hot plate till it finally forms a paste. The paste was then transfer into an evaporating dish which was placed in a furnace and heated at 350 ^oC for thirty minutes, this was then allowed to cool. It was then washed with distilled water to attain pH 7.0.

2.4 Effect of initial MG Dye concentration and contact time

50 mL of MG dye solution with initial concentrations of 10 – 50 mg/L were prepared in a series of 100 mL Erlenmeyer flasks. An equal mass of 0.50 g of the modified Indian spinach were added into each flask covered with glass stopper and the flasks were then placed in an isothermal water bath shaker at a

temperature of 303 K and varying contact time until equilibrium point was reached. The effect of solution temperature on the MG dye adsorption process was examined by varying the adsorption temperature at 303 K, 313 K, and 323 K respectively, by adjusting the temperature controller of the water bath shaker.

2.5 Characterization

FTIR was used to determine the various functional groups present in the adsorbent. The spectra were measured from 4000 to 400 cm$^{-1,}$

3. Results and Discussion

FTIR spectra analysis indicated a broad band between 3288 cm^{-1} representing O-H bonded. Aliphatic C-H stretching was observed at 2918 cm^{-1} and 2850 cm^{-1}. and C=C of arene was observed around 1600 cm^{-1}, also the peak of C-O of ester, ether and phenol was observed below 1100 cm^{-1}. The spectra analysis of raw and acid activated samples show that the bonded OH group will be involve in adsorption there was clear band shift and decrease in intensity of the band at 3288 cm^{-1}, 1630 cm^{-1}and 1315 cm^{-1} respectively, These are due to the result of high temperature in activation process that broke some intermolecular bonds, this shows that our malachite green will bind mostly at the OH position. The changes of FTIR spectra confirm the effect of acid activation on raw sample suggesting that it will be a good adsorbent for dye removal.

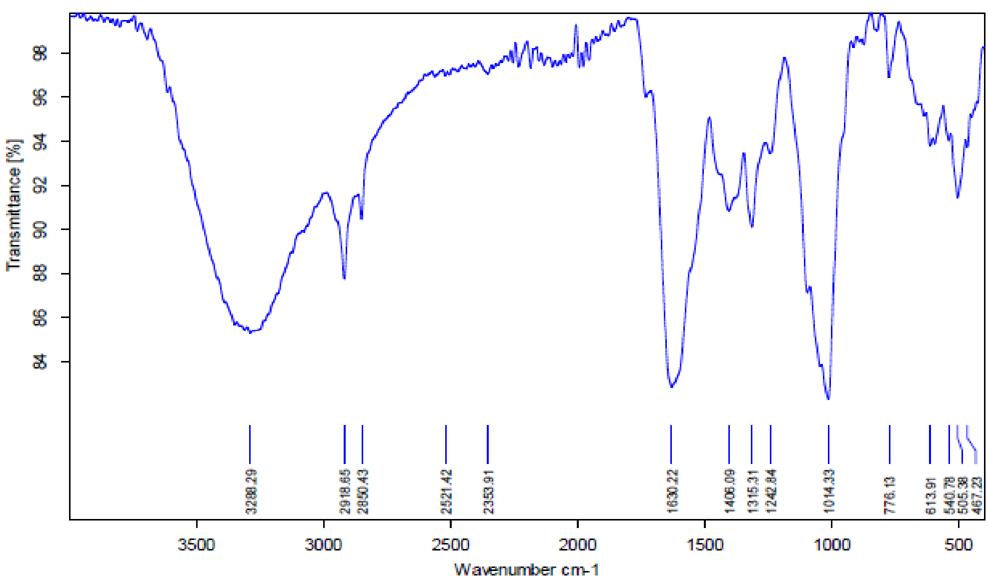

Figure 1: FTIR spectra of raw Indian spinach leaf powder

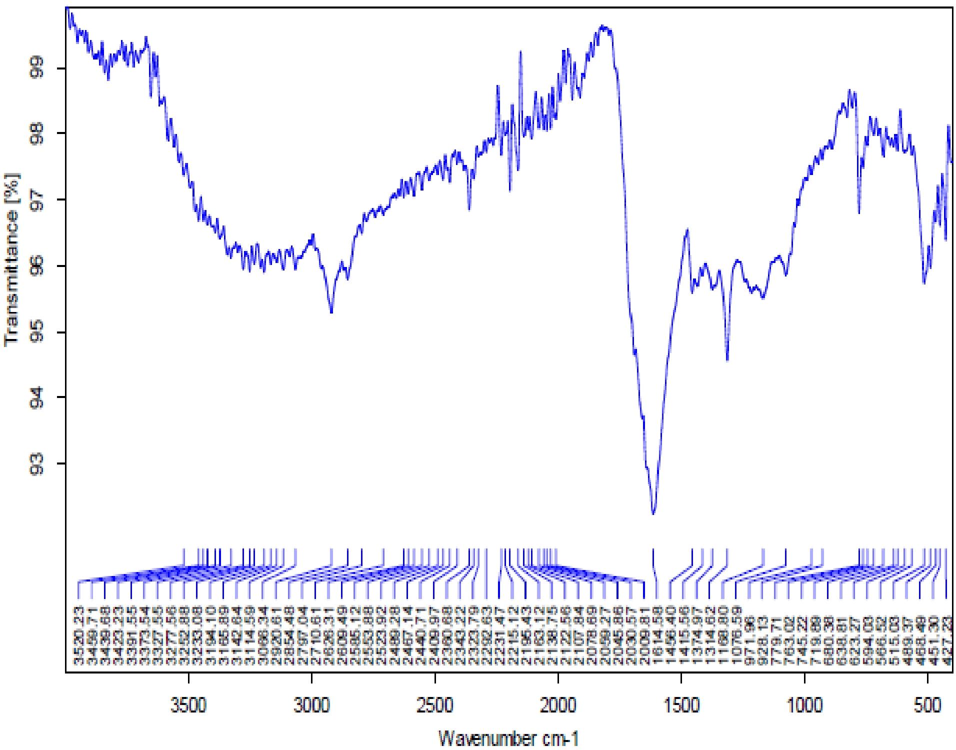

Figure 2: FTIR spectra of modified Indian spinach leaf powder

3.1 Effect of contact time and initial dye concentration

The time-dependent behaviour of malachite green adsorption on modified Indian spinach was measured by varying the equilibrium time in the range of 5-40 min. The concentration of the dye was kept constant at 10, 20, 30, 40 and 50 mg/L respectively while the adsorbent dosage was 0.5 g. From the graph below (fig 3) it is evidence that there is a sharp increase of adsorption from time zero to 10. Followed by a steady increase till around 30-40 min where equilibrium is reached (adsorbate did not show any significant increase wit time). Therefore, a 40 min shaking time was found to be appropriate for maximum adsorption and was used in all subsequent measurements. At this point, the amount of dye adsorbed onto the adsorbent was in a state of dynamic equilibrium with the amount of dye desorbed from the adsorbent. Adsorption capacity increased as the initial dye concentration increases. The adsorption of malachite green dye at different concentrations as a function of contact time is shown in the figure (3) below.

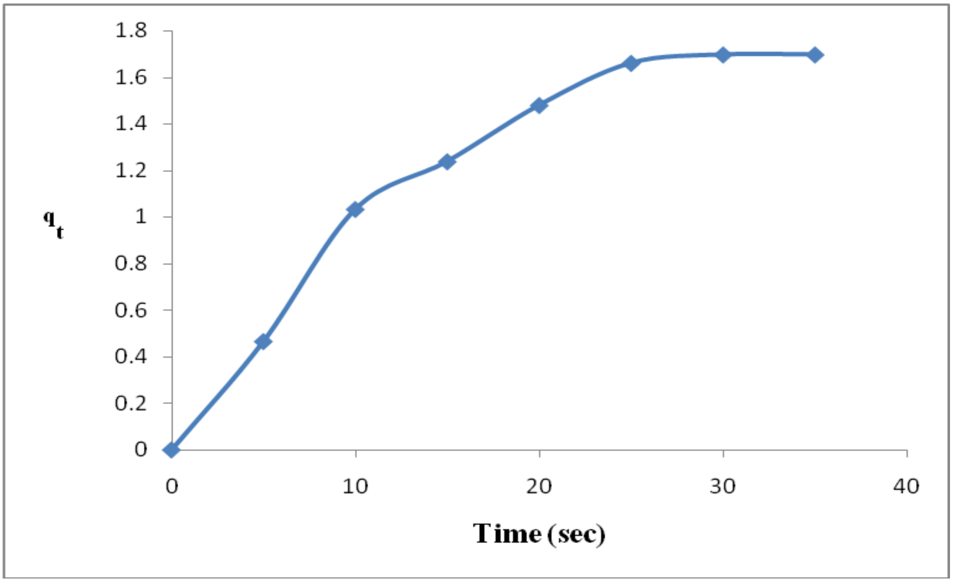

Figure 3: Plot of the effect of contact time at 30 °C for the removal of MG Dye from aqueous solution using ISLP as an adsorbent

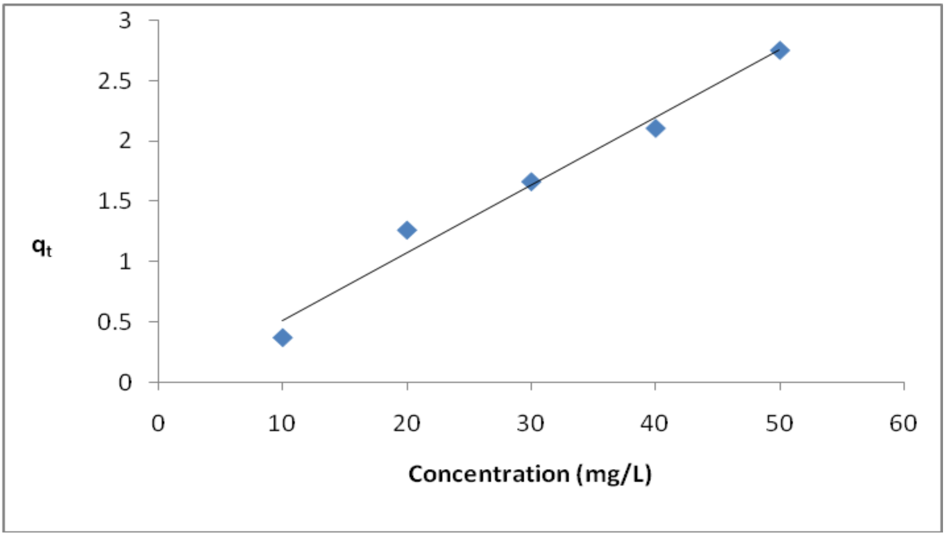

Figure 4: Plot of the effect of concentration as a function of time for the removal of MG dye from aqueous solution using ISLP as an adsorbent

3.2 Kinetic study

The adsorption data were tested using two well-known models: Pseudo-first-order and pseudo-second-order. Pseudo first order equation (Lagergren and Svenska, 1898) is generally expressed using equation (1)

$$\ln (q_e-q_t) = \ln q_e - k_1 t. \qquad (1)$$

where q_e and q_t in mg/g are the adsorption capacities at equilibrium and at time t respectively, k_1 is the rate constant for pseudo-first-order adsorption (h^{-1}). A plot of ln (q_e - q_t) against t at various concentrations and temperatures resulted in graphs with negative slopes shown in equation (5). k_1 and q_e are calculated from the slopes and intercepts, respectively.

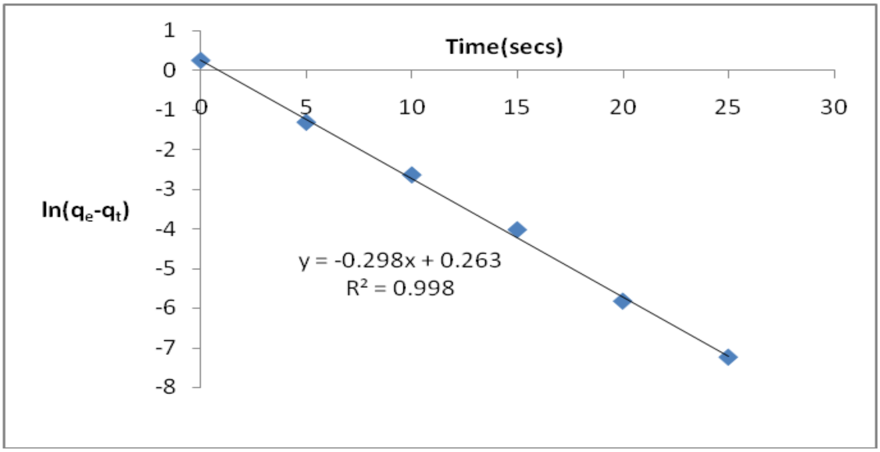

Figure 5: Plot of pseudo-first order kinetic model for the adsorption of MG dye on ISLP at 303 K

The pseudo-second-order kinetic model (Ho and McKay, 1999), the pseudo-second-order equation is expressed in equation (2) as follows

$$t/qt = 1/k_2 q_e^2 + 1/q_e t \qquad (2)$$

where q_e and q_t in mg/g are the adsorption capacities at equilibrium and at time t respectively. k_2 is the rate constant of pseudo-second-order adsorption (g/mg/min). The initial adsorption rate, h (mg/g/min), is h= $1/k_2 q_e^2$. Plots of t/qt versus t gave linear graphs (Figure 6), from which q_e and k_2 were estimated from the slopes and intercepts of the plot at 30 ^{0}C – 50 ^{0}C.

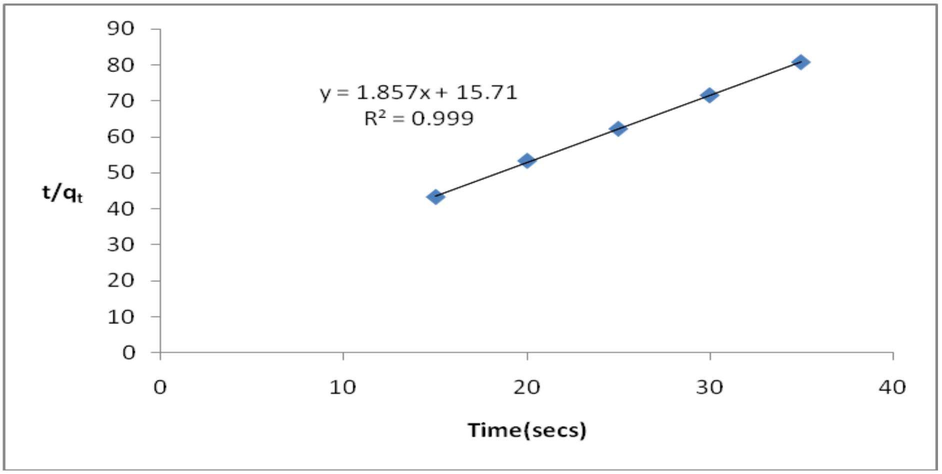

Figure 6: Plot of pseudo-second order kinetic model for the adsorption of MG dye on ISLP at 303 K

Table 1: Comparison of pseudo-first-order and pseudo-second-order adsorption rate constants on malachite green dye at 303 K

Conc. (mg/l)	$q_{e\ exp}$ (mg/g)	Pseudo-first-order model q_e cal (mg/g)	k_1 (min^{-1})	R^2	Pseudo-second-order model k_2 (g/mg min)	$q_{e\ cxp}$(mg/g)	R^2
10	0.438395	1.30447	0.1068	0.9743	54.22289	0.5383	0.9997
20	1.311111	1.19483	0.2825	0.9988	0.580484	1.36407	0.9985
30	2.855072	3.74118	0.1008	0.9967	0.00801	2.867795	0.9989
40	2.213333	85.687	0.4435	1.000	0.132265	2.325041	0.9987
50	1.555106	1.091001	0.0415	0.9932	1.117245	1.785077	0.9985

Comparing the R^2, i.e the correlation between $q_{e\ cal}$ and $q_{e\ exp}$ for both pseudo-first-order and pseudo-second-order model, it is evident that the pseudo second order model fit the adsorption data most as shown in Table 1.

3.3 Isothermal studies

Adsorption isotherm model describes how adsorbate interacts with adsorbents, a comprehensive understanding of the nature of interaction is essential for the most effective use of the adsorbent.

Hence two important isotherms were selected in this study, Langmuir (Langmuir, 1916) and Freundlich (Freundlich, 1906) isotherms. The linearized form of Langmuir adsorption model equation (3) is expressed as

$$C_e/q_e = C_e/q_o + 1/q_oK_L \qquad (3)$$

where C_e is the dye concentration in the solution at equilibrium (mg/l), q_e is the dye concentration on the adsorbent at equilibrium (mg/g), q_o is the monolayer adsorption capacity of adsorbent (mg/g) and K_L is the Langmuir adsorption constant (L/mg). A plot of C_e/q_e against C_e gave a straight line with slope $1/q_o$ and an intercept of $1/q_o$ K_L (Figure 7). The R^2 values of the Langmuir isotherm when compared with the Freundlich isotherm indicate that the adsorption of the MG dye onto ISLP fits the Freundlich isotherm well. Values of q_0 and b are calculated and reported in Table 2. It shows that Indian spinach is a good adsorbent for MG dye adsorption. The value of q_o obtained was compared with those from other adsorbents (Table 3).

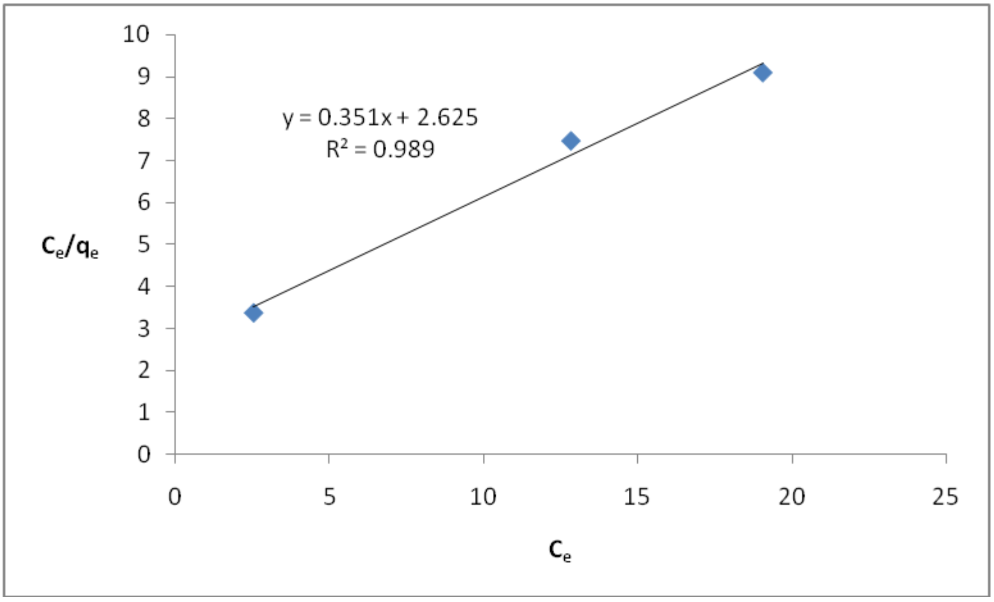

Figure 7: Langmuir isotherm for the adsorption of malachite green on Indian spinach at 40^{0}C

Table 2: Comparison of Langmuir and Freundlich Isotherm values at 40^{0}C

Models	303K	313K	323K
Langmuir			
q_0	2.194426	2.541296	1.052078
k_l	0.506042	0.210958	0.019001
R^2	0.9049	0.9538	0.9894
Freundlich			
K_f	2.647	2.513	2.088
n	2.740	1.956	0.556
R^2	1.000	1.000	0.9872

The linearized form of Freundlich model is represented by equation (4)

$$\log q_e = 1/n \log C_e + \log K_f \qquad (4)$$

where q_e is the amount of MG dye adsorbed at equilibrium (mg/g), C_e is the equilibrium concentration of the adsorbate (mg/L); 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. Plots of log q_e versus log C_e gave linear graphs (Figure 9) with high R^2. Comparing the R^2 values with the ones obtained from Langmuir Isotherms, the adsorption data fits the Freundlich isotherm well (Table 2). Values of K_f and n obtained from the slopes and intercepts of the graph reported in Table 2, it shows the heterogeneity of the material as well the possibility of multilayer adsorption of MG dye through the percolation process, the values of n greater than one indicates that the adsorption is favourable.

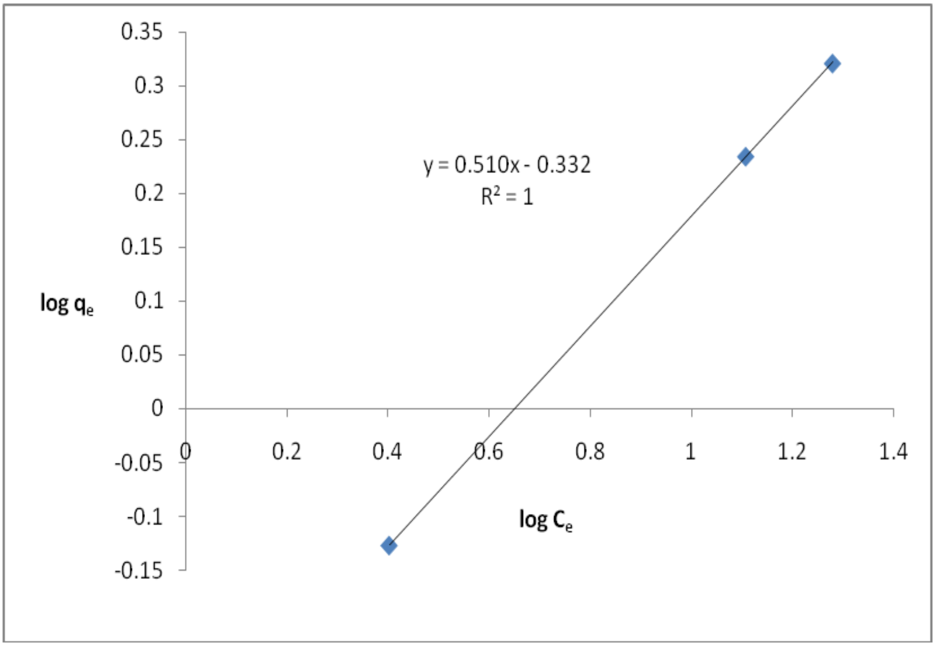

Figure 5 Plot of Freundlich Isotherm for the adsorption of Malachite green dye on Indian spinach leaf powder (ISLP) at 313 K.

Table 3: Comparison of adsorption capacities of malachite green onto various adsorbents

Adsorbents	q_o (mg/g)	Temp (K)	References
Cellulose powder	2.42	298	Sekhar *et al.*, 2009
Carbon prepared from arundo donax root	8.69	303	Zhang *et al.*, 2008
Tamarind fruit shell	1.95	303	Saha *et al.*, 2010
Unsaturated polyester Ce (IV) phosphate	1.01	300	Khan *et al.*, 2010
Neem sawdust	4,35	303	Khattri and Singh 2009
Wood apple shell	34,56	299	Sartape *et al.*, 2013
Chlorella-based biomass	18.4	298	Parthasanthy *et al.*, 2011
Indian spinach leaf powder	*2.54*	*313*	*This work*

3.4 Thermodynamic study

In thermodynamics studies, there are three thermodynamic functions that need to be considered to characterise the adsorption process; they are: ΔH, ΔG and ΔS due to transfer of one mole of solute from the solution onto solid liquid inter phase. The value of ΔH and ΔS can be calculated respectively from the slope and intercept of the Van Hoff plot (Figure 9).

ΔH= slope *R= 27752.13

ΔS= intercept*R= 70.03381

The positive value of ΔS shows an increase rate of disorderliness at the solid/solution interphase indicating the affinity of the adsorbent towards the malachite green dye molecules. Also the positive value of ΔH shows that the reaction is endothermic and also ΔG for malachite green dye adsorption was positive showing that the adsorption process is non-spontaneous.

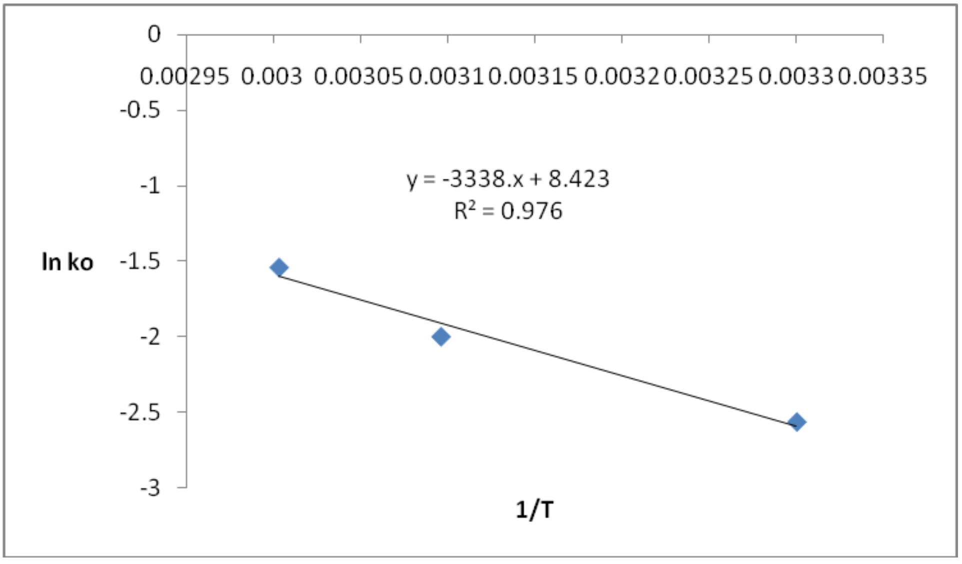

Figure 9: A plot of ln k_o versus 1/T, for the adsorption of MG dye on ISLP

Table 4: Thermodynamic function values for the adsorption of MG dye using ISLP at different temperatures

Temp (K)	ΔG J mol^{-1}	ΔH kJ mol^{-1}	ΔS J $mol^{-1}K^{-1}$
303	- 6465.272	27.752	70.034
323	-5371.661		
333	-4265.664		

4. Conclusion and Recommendation

From this study, it can be inferred that Indian spinach leaf powder has properties similar to that of other adsorbents due to it adsorptive features and capacities and thus can be used as an adsorbent for the removal of dye mixture from aqueous solutions and industrial waste water. The FTIR analysis revealed that the acid modification create more functional group, hence increasing the adsorption site. Adsorption equilibrium data were fitted to Langmuir and Freundlich isotherm models. The higher R^2 values of Freundlich isotherm when compared with Langmuir isotherm indicate that the adsorption of the Malachite green dye onto Indian spinach leaf powder fits the Freundlich isotherm better. The kinetic data were fitted to pseudo first order and pseudo-second-order kinetic model. The adsorption kinetics was found to follow the pseudo second order kinetic model. Various thermodynamic functions such as standard enthalpy change (ΔH°), standard entropy change (ΔS°) and standard free energy change (ΔG°) were evaluated. The adsorption of MG onto Indian spinach was found to be non-spontaneous and endothermic in nature. It is therefore recommended that Indian spinach should be used as an adsorbent in the removal of dye from aqueous solutions.

5. Acknowledgements

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