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Adsorption of Malachite Green from Aqueous Solutions by PNSBP: Equilibrium, Kinetic and Thermodynamic Studies

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Abstract: *The objective of this project work is to study the adsorption of Malachite Green dye using Picralima nitida stem bark from aqueous solution. It was found that the potential of Picralima nitida stem bark (PNSBP) for the removal of malachite green (MG) dyes from aqueous solution was high. Batch adsorption studies were conducted and various parameters such as contact time, adsorbent dosage, initial dye concentration, pH and temperature were studied to observe their effects on the dyes adsorption process. The optimum conditions for the adsorption of MG onto the adsorbent (PNSBP) was found to be: contact time (80mins), pH (10.0) and temperature (343K) for an initial MG dye concentration of 50mg/L and adsorbent dose 1.0g. The experimental equilibrium adsorption data fitted best and well to the Freundlich isotherm model. The maximum adsorption capacity was found to be 18.696mg/g for the adsorption of MG dye. The kinetic data conformed to the pseudo-second-order kinetic model. Thermodynamic quantities such as Gibbs free energy (ΔG^0), enthalpy (ΔH^0) and entropy (ΔS^0) were evaluated and the negative values of ΔG^0 obtained indicated spontaneous adsorption process. The positive ΔH^0 and ΔS^0 values obtained for the adsorption of MG indicate endothermic nature and increased in randomness during the adsorption.*

Keywords: *Adsorption, Isotherms, Kinetic, Malachite green***,** *Picralima nitida stem bark, Thermodynamic.*

I. Introduction

Dyes are substances that impart color to a material. Mankind has used dyes since the dawn of civilization till the late nineteenth century [1]. It is a colored substance that has an affinity to the substrate to which it is being applied. All dyes available to man came from natural source most commonly from flowers, vegetables, insects and mollusks [2]. Today, nearly 40.000 dyes and pigment are listed which consist of over 7000, approximately 10,000 different chemical structure [3]. Dyes and pigment are used industrially and over 7×10^5 tonnes are produced annually worldwide [4].

Dyes are widely used in industries such as textile, rubber, paper, plastic, cosmetic, paint, pharmaceuticals, foods, leathers, tannery and printing etc. these industries used wide varieties of dyes in order to color their product. Textile industry rank first among other industries worldwide today in usage of dyes for coloration of fiber, which generate huge volume of waste water every year [5-.6]. Dyes being an important recalcitrant persist for long distance in flowing waters and retards photosynthetic activity of aquatic biota by blocking out the sun light and utilizing dissolved oxygen and also decreases the recreation value of stream [7]. Most of the dyes are carcinogenic and toxic in nature and when discharged into the water they pose serious hazard to the aquatic biota [8]. Nowadays concern has increase about the long term toxic effect of water bodies containing these dissolved pollutants. The waste water discharged from textile industries includes residual dyes, these dyes are not bio-degradable, and therefore they may cause water pollution and serious threat to the environment [9].

II. Materials And Method

Picrilima nitida stem bark powder, PNSBP (adsorbents), Malachite green dye (adsorbate), Hydrochloric acid (HCl) and Sodium Hydroxide (NaOH), Distilled water, Filter paper(Whatmann NO.1), Digital pH meter, Electrical shaker, Electronic weighing balance, Thermostatic water bath, Thermometer, Ultra-violet visible Spectrophotometer (Jenway 6305), Measuring cylinders(1000ml), funnels, Conical flask, (250ml), Beakers(1000ml).

1.1. Preparation of Adsorbent

The Picrilima nitida stem bark powder (PNSBP) was collected from Ahiazu Mbaise Local Government Area of Imo State, Nigeria. These agricultural wastes (PNSBP) were properly washed with running water to remove sand, dirt and other impurities present in them and dried in an oven at 50^0C until all moistures were removed. The dried samples were ground in a mill and sieved in a sieve of particle size 300μm. The samples that passed through the sieve were stored in separate air tight containers and used as adsorbent without any further pretreatment.

1.2. Adsorbate Preparation

Stock solution of Malachite green was prepared by dissolving 1g of the powdered dye in 1L distilled water respectively to have 1000mg/L dye concentration in the solutions. Experimental dye solutions of desired concentrations were obtained by appropriate dilution of the stock solution.

1.3. Scanning Electron Microscopy and Fourier Transform Infrared Studies

Scanning electron studies was carried out on the PNSBP to study the surface features and morphological characteristics of the adsorbent before adsorption, using Phenom ProX Scanning Electron Microscope. The fourier infrared spectroscopy analysis was applied on the PNSBP to determine the surface functional groups by using Fourier transform infrared spectrophotometer (SHIMADZU FTIR-8400S). FTIR of the sample was recorded within 500 cm^1- 4000 cm^1 before and after adsorption.

1.4. Batch Adsorption Studies

Batch adsorption experiments were conducted to investigate the parametric effects of contact time, adsorbent dose, initial concentration, pH and temperature for MG adsorption on the adsorbent (PNSBP) with solutions of different initial concentration of MG ranging from 25mg/L to 125mg/L. The adsorbents dose of 1.0 g was added to 100ml of 50mg/L dye solutions. The temperature was controlled at 27^oC. The series of conical flasks were shaken on a rotary shaker at a constant speed of 100rpm. Samples were withdrawn for spectrophotometer analysis at predetermined duration of contact time ranging from 10 to 120 minutes. The equilibrium dye concentrations (C_e) were then measured and the amount of dyes adsorbed per unit weight of the adsorbents at equilibrium (q_e) were determined by

$$q_e = \frac{(C_0 - C_e)V}{M} \qquad \textbf{(1)}$$

Where M is the mass of adsorbent (g), V is the volume of solution (L), C_0 is the initial concentration of MG dye (mg/L), C_e is the equilibrium MG concentration (mg/L) and q_e is the amount of dye adsorbed at equilibrium (mg/g).

The percenaget removal of dyes from the solution was calculated using equation (2):

$$\%\,Removal = \frac{C_0 - C_e}{C_0} \times 100 \qquad \textbf{(2)}$$

Where C_0 is the initial concentration of MG (mg/L) and C_e is the equilibrium MG concentration which is also the equilibrium metal ion concentration of solution in (mg/L).

2.5. Adsorption Kinetics

The Batch adsorption kinetics tests were carried out at known initial dye concentration of 50mg/L for MG dyes. The adsorbent (PNSBP) dose was 1g in $0.1dm^3$ solutions. The temperature was maintained at room temperature (27^0C). Agitations of the samples were carried out at a constant speed of 100rpm on the rotary shaker and the samples were withdrawn at contact time of 10, 20, 40, 60, 80, 100 and 120mins. The agitated samples were filtered using Whatman No. 1 filter paper and the concentration in the supernatant solutions analyzed using UV-visible spectrophotometer (Jenway 6305).

1.5. Thermodynamics Study

The thermodynamic parameters such as change in Gibb's free energy (ΔG^0), change in enthalpy (ΔH^0) and change in entropy (ΔS^0) for the adsorption of MG onto PNSBP have been determined using the following equations:

The Gibb's free energy, ΔG, equation is expressed as follows:

$$\Delta G = -RT\ln K_C \qquad \textbf{(3)}$$

Where T is the temperature (K), R is the ideal gas constant (8.314 J/molK) and K_C is defined by the equation

$$K_c = \frac{C_a}{C_e} \qquad \textbf{(4)}$$

Where C_a (mg/L) and C_e (mg/L) are the equilibrium concentration for solute on the adsorbent and in solution respectively. Also, the Gibbs free energy is related to the enthalpy change (ΔH^o) and entropy change (ΔS^o) at a constant temperature by the Van't Hoff equation, equation (5) [10].

$$\ln K_c = -\frac{\Delta G^o}{RT} = -\frac{\Delta H^o}{RT} + \frac{\Delta S^o}{R} \qquad \textbf{(5)}$$

The values of ΔH^o and ΔS^o are calculated from the slope and intercept of the plot (*ln* K_C versus *1/T*).

III. Results And Discussion

3.1. Scanning Electron Microscopy

The surface morphology of the adsorbent surface shown in fig.1 shows that the adsorbent have considerable number of heterogeneous pores, uneven and rough surface morphology, where there is a good possibility for dye to be trapped and adsorbed [11]. Pores and cavities are responsible for increase in surface area, adsorption capacities and efficiencies [12, 13].

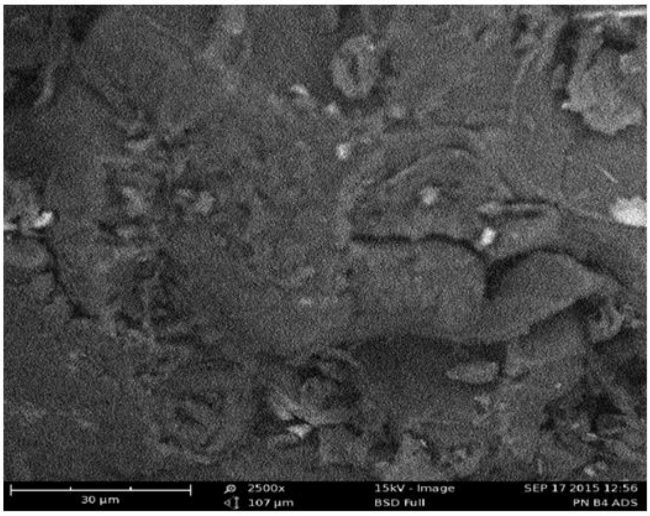

Fig. 1: SEM micrograph of PNSB powder surface at magnification 2500×

3.2. FTIR before and after Adsorption

The FTIR spectra of PNSBP before and after adsorption (Fig.2 & 3) of MG dye were analyzed to determine the vibration frequency changes in their functional groups. For PNSBP before adsorption, various peaks are at 3630.91 cm^{-1} (O-H stretch, free hydroxyl), 3422.94 cm^{-1} (O-H stretch, H-bonded), 2926.71 cm^{-1} (C-H stretch from alkane), 1735.12 cm^{-1} (C=O stretch), 1654.31 cm^{-1} (C=C stretch), 1637.11 & 1559.87 cm^{-1} (N-H bend from 1^{0} amines), 1508.47 cm^{-1} (C-C stretch in rings),1458.51 cm^{-1} (C-H bend), 1425.14 cm^{-1} (CH$_3$), 1246.31 cm^{-1} (C-N), 1030.98 cm^{-1}(C-O stretch) and 668.55 cm^{-1} (C-Br stretch) [14]. After adsorption of MG dye it was found out that some of the functional groups were affected after the uptake process. After adsorption of MG dyes it was found out that most of the functional groups on the adsorbent were affected after the dye uptake process. This is judged from shifts in the position of some of the functional groups to lower or higher frequency or band intensity before and after MG adsorption. The functional groups that moved to lower frequency or band intensity after MG adsorption includes: C=O, C=C, C-C, C-H, and C-Br from 1735.12 cm^{-1}, 1654.31 cm^{-1}, 1508.47 cm^{-1}, 1458.51 cm^{-1} and 668.55 cm^{-1} respectively to 1733.03 &1716.18 cm^{-1}, 1646.69 cm^{-1}, 1507.26 cm^{-1}, 1456.84 cm^{-1} and 668.47 cm^{-1} respectively. The functional groups that moved to higher frequency or band intensity includes: O-H (free hydroxyl), O-H (H-bonded), and C-O from 3630.91 cm^{-1}, 3422.94 cm^{-1}, and 1030.98 cm^{-1} to 3647.82 cm^{-1}, 3501.99 cm^{-1} and 1033.74 cm^{-1} respectively. This indicated involvement of these groups for MG binding to PNSBP [15].

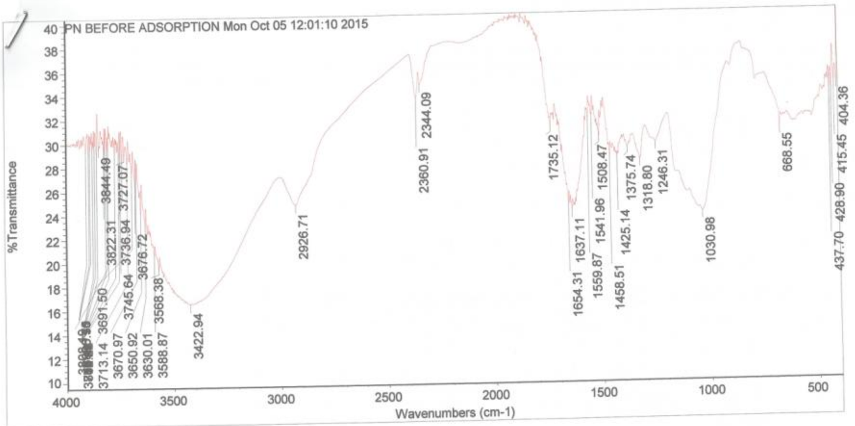

Fig. 2: FTIR Spectra of PNSBP before adsorption

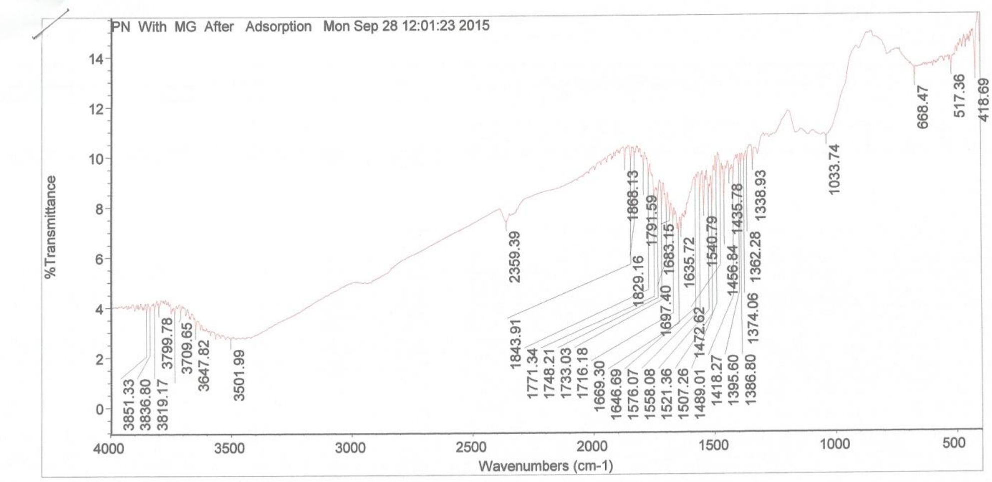

Fig. 3: FTIR Spectra of PNSBP after adsorption of MG

3.3. The Effect of Contact Time on Adsorption Capacity of MG onto PNSBP

Fig. 4 and 5 show the effect of contact time on the adsorption capacity and percentage removal of MG dye. It can be observed in Fig. 4 and 5 that the sorption of MG dyes by PNSBP was rapid in the initial stages and becomes slow in later stages until optimum adsorption (equilibrium time) at 80 minutes. It can be inferred from the rapid sorption at the initial stages that there were abundance of active sites on the external surface of PNSBP which resulted in the rapid dyes removal. The slower rate in the later stages is due to the dyes being diffused into the interior of the adsorbents [16].

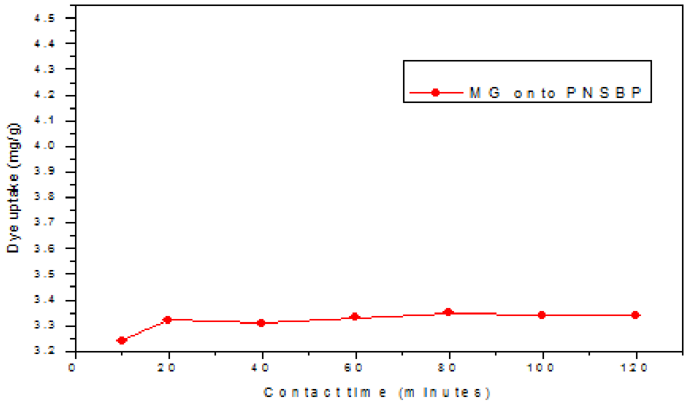

Fig. 4: The effect of contact time on adsorption capacity of MG onto PNSBP

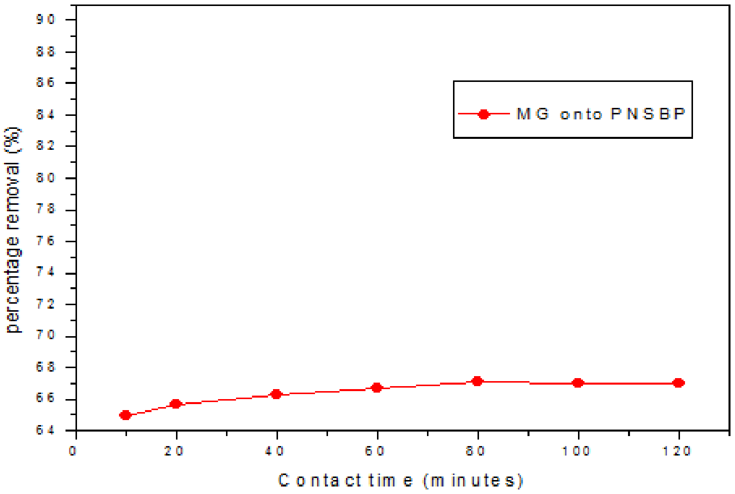

Fig. 5: The effect of contact time on the percentage removal of MG onto PNSBP

3.4. The Effect of Adsorbent Dosage

The effect of adsorbent dosage on the adsorption capacity and percentage removal of MG onto PNSBP is shown in Fig. 6 and 7. The percentage removal of MG dye increased from 83.0% to 89.26%. The adsorption capacity of MG dye decreased from 8.3 to 1.11mg/g. It was observed that as the adsorbents dosage increased, the amount of dyes adsorbed decreased while the percentage removal of the dyes increased. This decrease in adsorption capacity with increase in adsorbent dose is mainly attributed to non-saturation of the adsorption sites during the adsorption process [17]. The increase in percentage removal of the dye with increase in adsorbent dose may be because of the availability of more adsorption sites which increased with increase in adsorbent dose.

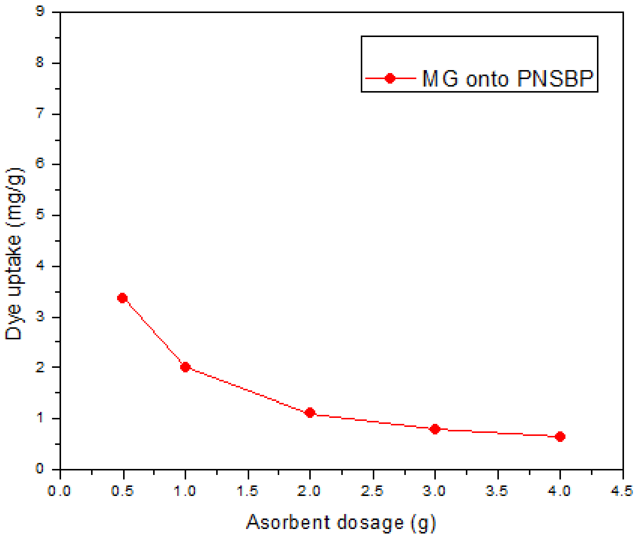

Fig. 7: The effect of adsorbent dosage on adsorption capacity of MG onto PNSBP

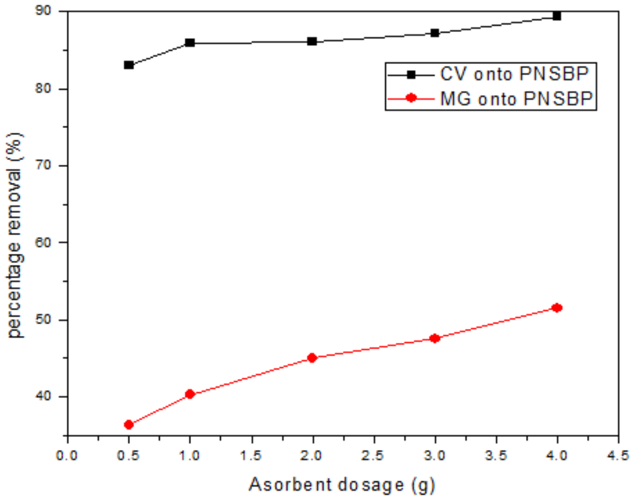

Fig. 8: The effect of adsorbent dosage on the percentage removal of MG onto PNSBP

3.5. The Effect of Initial Concentration

Fig. 9 and 10 show the effect of initial concentration on the adsorption capacity and percentage removal of MG dye onto PNSBP. It can be observed from Fig. 9 and 10 that the adsorption capacities of MG dye increased from 2.41 to 12.26mg/g respectively. While the percentage removal of MG increased from 96.52 to 98.09% as initial concentration increased from 25 to 125 mg/L. The increase in adsorption capacity with increase in initial concentration is due to the high driving force which overcomes the mass transfer resistance at higher initial dye concentration [18]. The increase in percentage removal with increase in dye concentration is due to the fact that, for a given mass of adsorbent, the amount of dye it can adsorb is fixed. Thus, the higher the concentration of the dye the smaller the percentage it can remove [19]. This increase in percentage removal with increase in initial dye concentration may be due to the fact that as the dye concentration is increasing, more dye is available for adsorption on the adsorbent. This is due to the effect of concentration gradient which is the main driving force for the adsorption process.

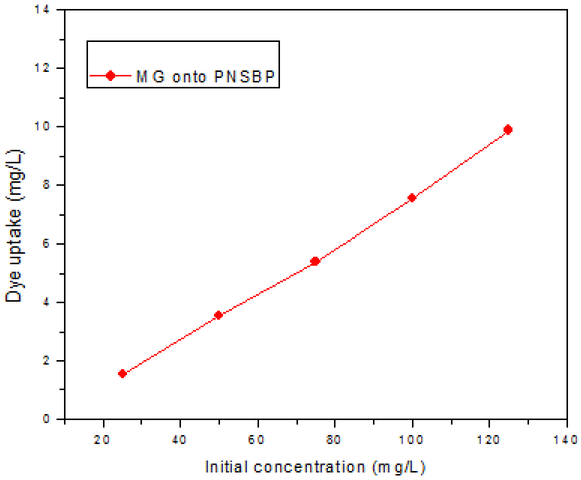

Fig. 9: The effect of Initial concentration on adsorption capacity of MG onto PNSBP

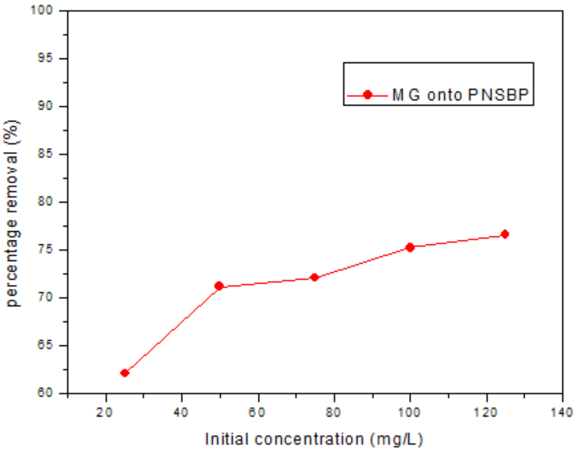

Fig. 10: The effect of initial concentration on percentage removal of MG onto PNSBP

3.7. The Effect of Temperature

Fig. 11 and 12 show the effect of adsorption capacity and percentage removal of MG onto PNSBP. The percentage removal and adsorption capacity increased from 62% to 80.84% and 3.1mg/g to 4.042mg/g for MG onto PNSBP. The removal of dyes with temperatures would increase the mobility of the ions of dyes and produces a swelling effect within the internal structure of adsorbent, thus enabling the large molecules of dyes to penetrate further. The temperature affects the rate of removal of dyes by altering the molecular interactions and the solubility of dyes [20].

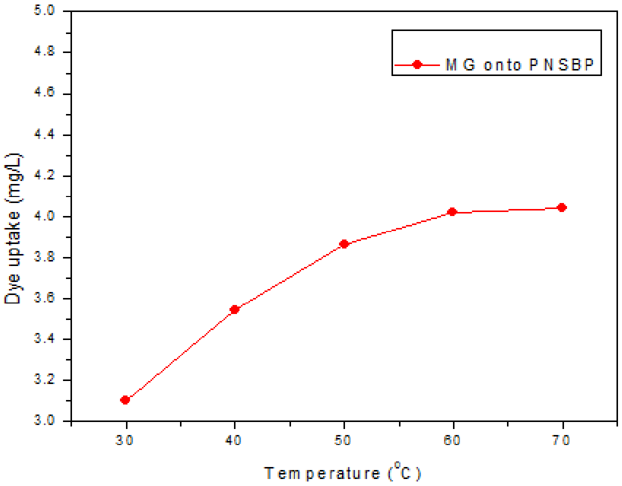

Fig. 11: The effect of temperature on adsorption capacity of MG onto PNSBP

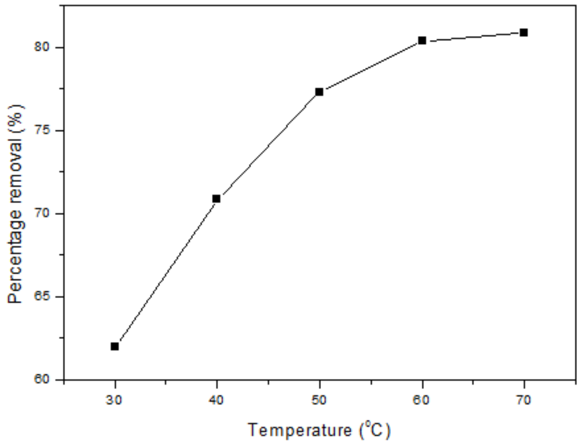

Fig. 12: The effect of temperature on percentage removal of MG onto PNSBP

3.8. The Effect of pH

It can be observed from Fig. 13 and 14 that the adsorption capacity and percentage removal of MG dyes by PNSBP increased from 2.14 to 3.49mg/g and from 43.6% to 89.9% respectively as pH increased from 2 to 10. Optimum sorption was obtained at pH of 10. The increase in percentage removal and adsorption capacity with increase in pH can be attributed to the fact that at low pH values of the solution, the presence of excess hydrogen ion in the solution competes with the cationic groups of the MG dye for the adsorption sites on the adsorbent surface. While at high pH values, the positive charges (H^+) at the solution inter-phase decreases and the adsorbent surface is more negatively charged, thus enhancing attraction of more amounts of the cations of the MG dye [21].

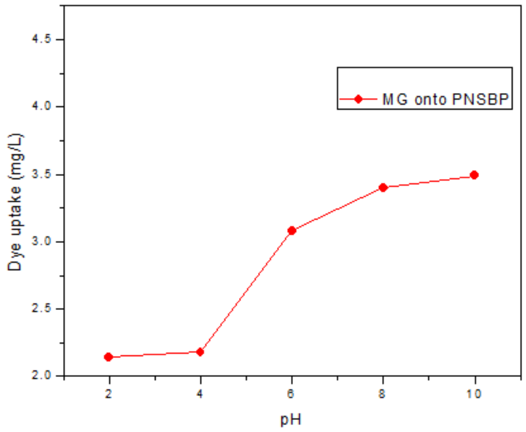

Fig. 13: The effect of pH on adsorption capacity of MG onto PNSBP.

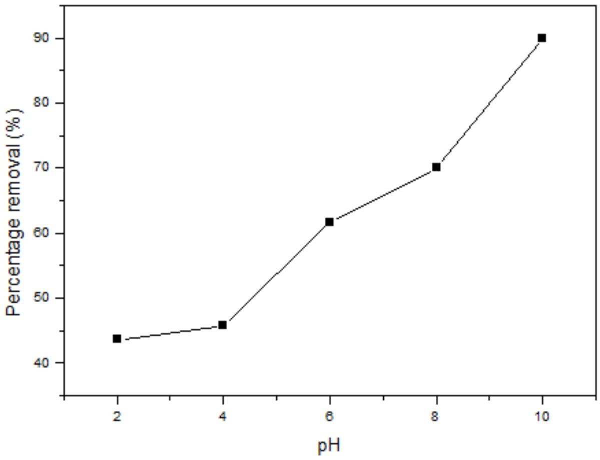

Fig. 14: The effect of pH on percentage removal of MG onto PNSBP.

3.9. Adsorption Isotherms

3.9.1 Langmuir Isotherm

The linear form of Langmuir equation is given as

$$\frac{C_e}{q_e} = \frac{1}{q_m K_l} + \frac{C_e}{q_m} \qquad (6)$$

Where q_e (mg/g) is the amount of dye adsorbed at equilibrium, q_m (mg/g), the amount of dye adsorbed when saturation is attained,
C_e is the equilibrium dye concentration (mg/L) and K_l is Langmuir constant related to the binding strength of dye onto the adsorbent. Fig. 15 shows the Langmuir model plot for the adsorption of MG onto PNSBP. The isotherm parameter and R^2 values are summarized in Table 1.

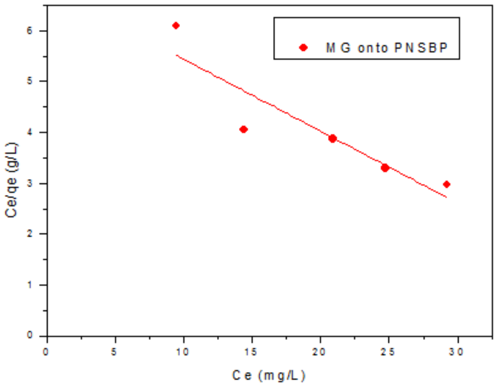

Fig.15: Langmuir isotherm plot for the adsorption of MG onto PNSBP

3.9.2 Freundlich Isotherm

The linearized form of Freundlich equation is expressed as

$$\log q_e = \log K_f + \frac{1}{n} \log C_e \qquad (7)$$

Where K_f and n are the Freundlich constants that represent adsorption capacity and intensity (strength) of adsorption respectively. Fig. 16 shows the Freundlich model plot for the adsorption of MG onto PNSBP. The isotherm parameter and R^2 values are summarized in Table 1.It can be observed from the Fig.16 that a linear plot was obtained for the Freundlich isotherm plot but based on the values of correlation coefficient (R^2), the experimental data fitted best with the Freundlich isotherm model, hence, this shows evidence of the adequacy of the Freundlich isotherm to describe the adsorption of MG onto PNSBP and such adsorptions mainly occurred on the heterogeneous surface of the PNSB powder.

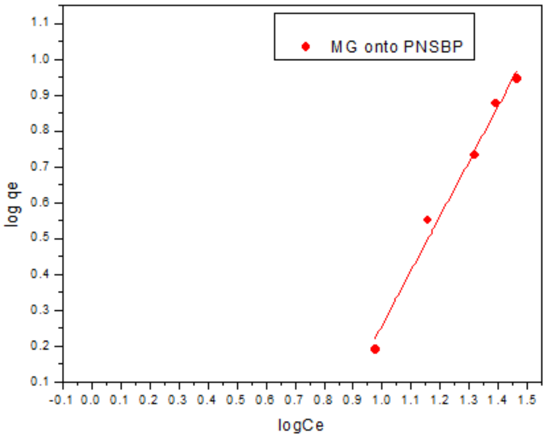

Fig.16: Freundlich Isotherm plot for the Adsorption of MG onto PNSBP

Table 1: Isotherm parameters and correlation coefficient values for PNSBP onto MG

Langmuir			**Freundlich**		
$q_{max(mg/L)}$	K_L	R^2	n	$K_{F(mg/g)(L/mg)}^{1/n}$	R^2
7.07	**0.021**	**0.279**	**0.645**	**18.696**	**0.983**

3.10. Kinetic Studies

3.10.1 Pseudo-First-Order Kinetic Model

The linear form of the pseudo-first-order kinetic model is represented by

$$\ln(q_e - q_t) = \ln q_e - K_1 t \qquad (8)$$

Where q_e and q_t are the values of amount of the dye adsorbed per unit mass on the adsorbent at equilibrium and at various time t, respectively, K_1 is the Pseudo-first-order adsorption rate constant (min^{-1}). The values of K_1 and calculated q_e can be determined from the slope and intercept respectively, of the linear plot of $\ln(q_e - q_t)$ versus t. Fig. 17 shows the pseudo-first-order kinetics for the adsorption of MG by PNSBP. The pseudo-first-order rate constant (K_1) and q_e determined from the model are presented in Table 2. Fig.17 depict that the relationship between the dye solution diffusivity $\text{In}(q_e - q_t)$ against t is non-linear. It can also be observed that the calculated q_e values did not agree with the experimental q_e as shown in Table 2. Therefore, pseudo-first-order model was inadequate in representing the adsorption of MG onto PNSBP.

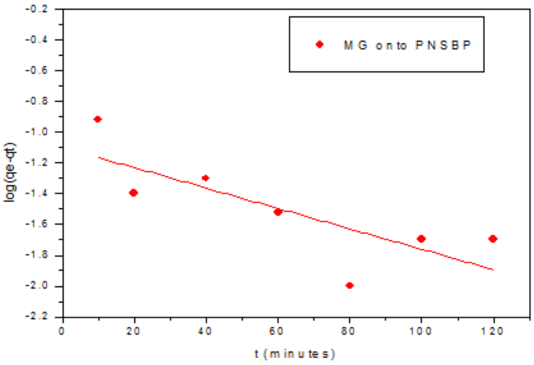

Fig.17: Pseudo first order for the adsorption of MG onto PNSBP.

3.10.2 Pseudo-Second-Order Kinetic Model

The pseudo-second-order kinetic model is expressed by

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \qquad (9)$$

Where K_2 is the pseudo-second-order adsorption rate constant (g/mg/min) and q_e is the amount of dye adsorbed (mg/g) on the adsorbent at equilibrium. The initial adsorption rate, h (mg.g^{-1}.min^{-1}) is expressed as:

$$h = k_2 q_e^2 \qquad (10)$$

The plot of t/q_t versus t gives a linear relationship which allows computation of k_2, h and calculated q_e.Among these models, the criterion for their applicability is based on judgment on the respective correlation coefficient (R^2) and agreement between experimental and calculated values. Fig. 18 shows the pseudo-second-order kinetics for the adsorption of MG dyes onto PNSBP. The pseudo-second-order rate constant K_2, and q_e determined from the model are presented in Table 2. It can be observed from Table 2 that there is good agreement between the calculated q_e values and the experimental q_e values i.e. q_e (cal.) and q_e (exp.) for the adsorption of MG by PNSBP. In addition, highly linear plots with high values of correlation coefficient were also observed for the adsorption of MG dye by PNSBP. It is therefore obvious that pseudo-second-order is the best kinetic model for the description of the adsorption of MG onto PNSBP.

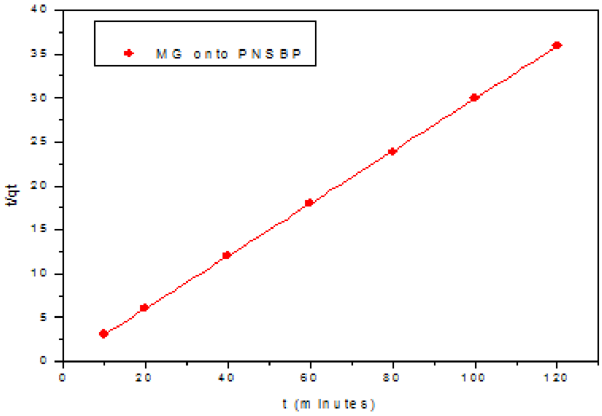

Fig.18: Pseudo second order for the adsorption of MG onto PNSBP

Table 2: First order and second order parameters for the adsorption of MG onto PNSBP

Pseudo-first order model				**Pseudo-second order model**			
q_e (exp) (mg/g)	**k_1 (g.mg^{-1}min^{-1})**	**q_e (cal) (mg/g)**	**R^2**	**h (mg.g^{-1}min^{-1})**	**k_2 (g.mg^{-1}min^{-1})**	**q_e (cal) (mg/g)**	**R^2**
4.48	**0.015**	**0.08**	**0.5432**	**1.152**	**0.103**	**4.39**	**0.998**

3.11.Adsorption Thermodynamics

Fig.19 shows the linear Van't Hoff equation plot for the adsorption of MG onto PNSBP. Negative ΔG^0 values obtained at all temperatures indicate the feasibility and the spontaneous nature of MG dye adsorption onto PNSBP. The positive ΔH^o value obtained for the adsorption of MG onto PNSBP confirms the endothermic nature of the adsorption process while the positive ΔS^0 value obtained for the adsorption of MG onto PNSBP indicate increased randomness during the adsorption process.

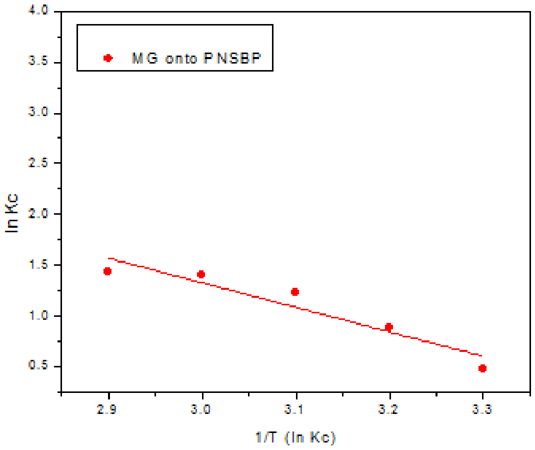

Fig.19: Van't Hoff plot for Adsorption of MG onto PNSBP

Table 3: Thermodynamic parameters for the adsorption of MG dye onto PNSB powder

Temperature (K)	**ΔG (KJ/mol)**	**ΔH (KJ/mol)**	**ΔS (J/mol. K)**
303	**-1.26**		
313	**-2.26**		
325	**-3.30**	**71.384**	**20.120**
333	**-3.87**		
343	**-4.07**		

IV. Conclusion

The potential of Picralima Nitida stem bark (PNSB) powder as an effective adsorbent for the removal of MG dye from aqueous medium has been identified. The adsorption of MG onto PNSB powder was found to be influenced by contact time, adsorbent dose, initial MG concentration, temperature and initial pH of the solution. The optimum adsorption of MG dye was found at pH 10. Maximum adsorption capacity was 18.70mg/g at 50mg/L initial MG dye concentration. Temperature had strong influence on the adsorption processes and the maximum removal was observed at 343K for the adsorption of MG. The equilibrium time was attained at 80min, after which there was no increase in dye adsorption. The kinetic studies revealed that the adsorption of MG dye onto PNSBP followed the pseudo-second-order kinetic model. The study on equilibrium sorption revealed that Freundlich isotherm model gave the best fit to the experimental data. The calculated thermodynamic parameters indicated a spontaneous adsorption. The adsorption of MG dye was endothermic in nature with increase in entropy. The present study showed that PNSB powder can be effectively used as an inexpensive and efficient adsorbent without any pretreatment or modification for the removal of malachite green dye from aqueous solutions and waste water.

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