

# Adsorption Behavior of MB Dye on Activated Usoro (Adenia Lobata) Fiber; Equilibrium, Kinetics and Thermodynamic Studies

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**Abstract-** This paper presents the feasibility of removal of MB dye from aqueous solution using activated carbon prepared from Usoro fiber (*Adenia lobata*). FTIR analysis revealed that many functional groups were present on the surface of the adsorbent. The adsorption Kinetics was analyzed by pseudo first order, pseudo second order and intra particle diffusion kinetics models. Results showed that MB adsorption followed the pseudo first order and intra-particle diffusion models appropriately. Isotherm data were treated according to Langmuir and Freundlich models. The result showed that both models fitted the data reasonably but Langmuir isotherm model fitted better in the temperature ranges studied. The thermodynamic parameters, such as Gibb's free energy change, standard enthalpy change, and standard entropy change were evaluated. The negative values of Gibb's free energy confirmed the feasibility and spontaneity of the adsorption process. The study confirmed the process to be endothermic at lower initial concentrations and exothermic at higher initial concentrations studied.

**Index Terms** - Adsorption, Isotherm, Kinetics, Thermodynamics, Usoro fiber.

## I. INTRODUCTION

Most countries of the world clamour for industrial development. This quest for sustainable industrial development has its own attendant problems. While the government is head over heels in promoting industrial development in all the fields of the economy, little attention is however paid to the consequences of such full-scale industrialization like environmental pollution. Waste water from textile, cosmetics, printing, and pepper making industries are discharged to the environment and this indeed, cause serious environmental problems principally because of their carcinogenic and toxic effects on living things. These colored compounds are not only aesthetically displeasing but also inhibiting sun light penetration into the stream and effecting aquatic ecosystem.

Dyes usually have complex aromatic, molecular structures which make them more stable and difficult to comprehensively biodegrade. High concentration of such dyes causes many water borne diseases and increase the BOD of receiving waters [1]. Consequent of the above, waste water from dyeing industries needs to be treated before discharging into the water bodies

Many methods can be used to remove dyes from waste waters such as coagulation, membrane separation process, electrochemical, chemical oxidation, reverse osmosis, aerobic and anaerobic microbial degradation but these methods have restriction and therefore are not successful for removing the colors completely from waste water [2]. Among all these methods,

Adsorption is preferred due to its low cost and high treatment efficiency [3]. In a good number of adsorption processes, activated carbon is used as adsorbents, but adsorption by commercial activated carbon has some restrictions such as the cost of the activated carbon, the need for regenerations after exhausting and loss of adsorption efficiency after regeneration [4]. In the light of the above, attention of researches has been redirected to low cost alternative adsorbents from agriculture waste [5], [6].

The opportunity offered by agriculture material like Usoro activated carbon fiber is novel and has since engaged the attention of researches as a better adsorbent than granular activated carbons. Activated carbon fibers have micropores, which are directly accessible from the external surface of the fiber. The implication is that adsorption molecules reach adsorption sites through micropores without the additional diffusion resistance of macropores which is usually considered the rate controlling step in the case of granular adsorbents [7].

## II. MATERIALS AND METHODS

### A. Pre - processing of the natural fiber

The fibers were sourced locally from Ebonyi State of Nigeria and were cut into definite smaller sizes, washed and then carefully sorted out to remove every debris and contaminants. It was dried under the sun and packed inside a polythene bag ready for further analysis.

### B. Preparation of the fiber activated carbon.

The fibers were washed thoroughly first with distilled water to remove dust particles and then dried at a temperature of 1000c. The samples were then cut to obtain a uniform size of about 100cm. The preparation was divided into three(s) stages

- Base leaching

- Activation
- Acid washing

First, the fiber was leached with a 0.5M NaOH solution and then boiled in a glass round-bottomed flask at 100°C for 1hr. The base solution was drained and the remaining solid was washed with distilled water to remove the base. This process reduced the pH level to about 7.0, which is neutral. The materials were then dried at 105°C for 24hrs.

Secondary, ZnCl<sub>2</sub> was used as activating agents. A known mass of activating agent was mixed with distilled water, and the fibers were then impregnated in the acidic solution. The impregnated samples were then dried in a sand-bath at high temperature, to remove any residual water and then oven-dried for the next 24hrs. A weighed amount of the impregnated sample was then placed in a fixed bed reactor made of quartz. The reactor was inserted into an electric furnace at a reaction temperature of 400°C and the reaction continued for the next 1hr. The activated carbon were subsequently removed from the furnace and cooled at room temperature.

After activating the sample, 3M Hydrogen chloride (HCL) was used to remove the zinc compound. The activating agents and carbon mixtures were refluxed with hot acidic solution for 1hr. The remaining solid was then washed with distilled water until neutralization was achieved. The washed sample were dried at 105°C for 24hrs and then ground very well to form a good porous carbon powder.

### C. Preparation of Methylene Blue Solution

Double distilled water supplied by Pymotech Research Center and laboratories Abakpa, Enugu State of Nigeria was used for the preparation of the solutions. A 1000mg/l stock solution was prepared and from there, necessary dilutions were made to obtain the desired concentrations.

### D. Characterization of Activated Carbon

The surface functional groups and structure were studied by Fourier transform infrared spectroscopy [Buck 530 IR]. The FTIR spectra of the activated carbon was scanned at a wavelength of 600–4000nm to obtain its spectra lines.

### E. Adsorption Isotherm

Batch isotherm studies were carried out in 250ml conical flask at different temperature of 303K, 313K, 323K and 343K on an Isothermal shaker for 6 hours to ensure equilibrium. 0.02g of the adsorbent was mixed with 50ml of 30mg/l, 50mg/l, 80mg/l and 110mg/l of the solution at different pH of 10. At the end of equilibrium time of 6 hours, the reaction mixture was centrifuged and the residual MB concentration analyzed. The amount of MB adsorbent at equilibrium

qe(mg/g) was calculated from the following equation (1).

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

### F. Adsorption Kinetic Model

The kinetic experiments were performed using a procedure similar to the equilibrium studies. 50mls of known concentration of MB was mixed with 0.02g of the adsorbent in a flask. Then, the flask was agitated in an isothermal shaker for a contact time varied in the range of 0- 120mins at a speed of 200rpm under room temperature. The adsorbent was separated from the solution by centrifugation and the filtrate was analyzed by the same procedure as batch equilibrium studies. The amount of MB adsorbed at each time interval per unit mass of the adsorbent, q<sub>t</sub> (mg/g), was calculated by equation 2:

$$q_t = \frac{(C_o - C_t)}{W} V \quad (2)$$

Where C<sub>o</sub> (mg/L) is initial MB solution, C<sub>t</sub> (mg/L) is its concentration at time t, V (L) is the volume of the solution and W (g) is the mass of the adsorbent.

## III. RESULTS AND DISCUSSIONS

### A. FTIR Analysis

The FTIR spectra was obtained to evaluate qualitatively the chemical structure of the activated carbon. The spectra is shown in fig.1 and was recorded at a wavelength of 600–4000nm. Many sharp and obvious peaks were found, along side with relatively low intensity ones. The functional groups on the adsorbent surfaces were identified by evaluating the spectra using available literature [8], [9], [10], [11], [12]. The absorption peaks at 3830.43354 to 3335.8564cm<sup>-1</sup> are the stretching of the O-H bond of hydroxyl group and NH<sub>2</sub> primary group. The peaks between 2977.43995 and 2806.77927cm<sup>-1</sup> of C-H stretching described the presence of –CH and ≡ CH groups presents in the lignin structure of the fiber. The peaks at 2279.44615 can be attributed to C=C stretching of –COOH groups. The peak at 1701.50914cm<sup>-1</sup> is due to C=O stretching vibration attributed to the presence of carboxyl group on the surface of the adsorbent. The olefinic C=C stretching vibration adsorption caused the band at about 1622.08175cm<sup>-1</sup> while skeletal C=C vibration in aromatic rings caused another band at about 1445.92353cm<sup>-1</sup>. The bands at 1283.00922 and 1075.29014cm<sup>-1</sup> can be assigned to C-O stretching vibrations in alcohols, phenols or ether ester groups. The C-H out of plane bending vibrations in benzene derivatives caused the bands at 816.412717cm<sup>-1</sup>.

Finally, the band caused by O-H out of plane bending vibration is located at 609cm<sup>-1</sup>. The numerous and varieties of functional groups present in the

adsorbent contributed immensely to its massive adsorption activities for the methylene blue dye.

Where;

$K_2$  = the rate constant of the pseudo-second-order model (g/mg/min).

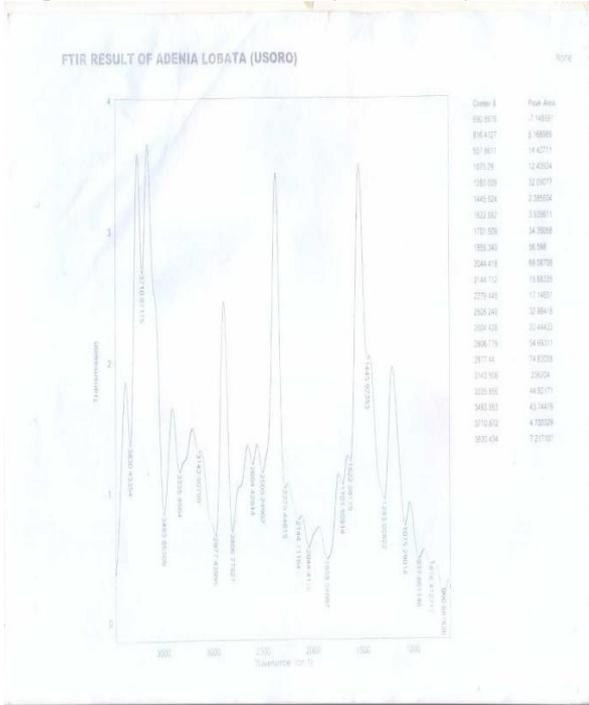


Fig. 1. FTIR of the activated carbon.

**B. Batch adsorption kinetics studies**

In order to analyze the controlling mechanism of the adsorption of methylene blue dye onto the activated carbon fiber, a pseudo- first order equation, pseudo second-order equation and intra particle model were used to fit the adsorption data.

**Pseudo-first- order model**

The pseudo-first-order equation is written as follows

$$\ln (q_e - q_t) = \ln q_e - k_1 t \tag{3}$$

$K_1$  = the rate constant of the pseudo-first-order adsorption.

$q_t$  and  $q_e$  = the adsorbed amount at time  $t$  and at equilibrium(mg/g).

Values of the quantities  $k_1$  and  $q_e$  were obtained from the slope and the intercept of the plot of the graph of  $\ln (q_e - q_t)$  versus  $t$ .

The linear pseudo-first-order plots, for the adsorption of methylene blue dye, onto the activated carbon fiber were used to determine the  $k_1$  and  $q_e$ . From the value of its  $R^2 = 0.7053$ , first- order kinetics fits this study better and more preferably when compared to the second-order-kinetics.

**Pseudo- second-order kinetics**

The pseudo second order equation, which is an extension of the first-order equation, is written as;

$$\frac{t}{qt} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \tag{4}$$

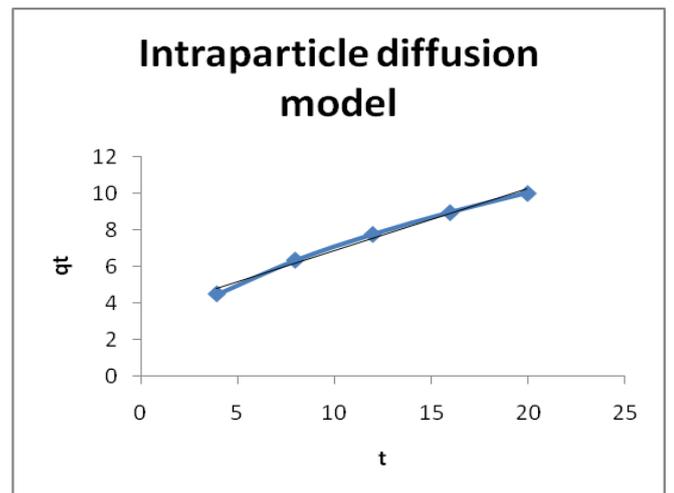
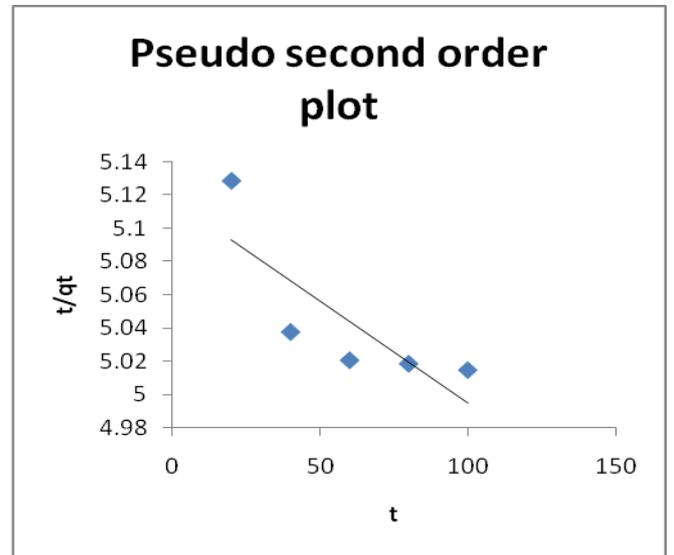
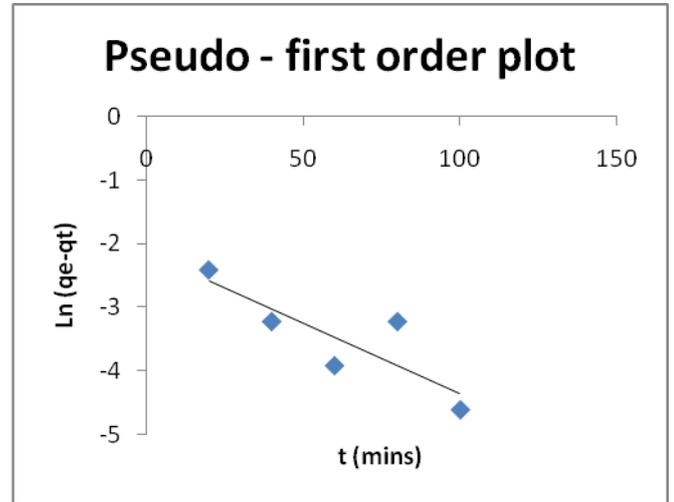


Fig. 2. Kinetic model plots

The slope and the intercept of the plots of the graph of  $\frac{t}{q_t}$  versus  $t$  were obtained to calculate  $k_2$  and  $q_e$ . The  $R^2$  value of the second-order kinetics ( $R^2 = 0.659$ ) was not closer to 1.0 as compared to that of first-order kinetics.

**Intraparticle diffusion model**

The mechanism of adsorption of the methylene blue dye onto the adsorbent is assumed to involve three steps, one or more of which can control the whole adsorption rate. The three steps are [13];

- Mass transfer across the boundary film to the surface of the particle.
- Mass transfer from the exterior surface of the particle to the interior pores via a pore diffusion or intra-particle diffusion mechanism and.
- Diffusion of the adsorbate molecules to active sites either by a pore diffusion process or by a solid surface diffusion mechanism.

The intra-particle diffusion model can be represented by the equation.

$$q_t = k_p t^{0.5} + c_i \tag{5}$$

Where;

$q_t$  = the adsorption capacity at time  $t$  (mg/g)

$k_p$  = the intra-particle rate constant (mg/gmin<sup>0.5</sup>)

$c_i$  = constant related to the thickness of the boundary layer.

The graph of  $q_t$  versus  $t^{0.5}$  gave  $k_p$  as the slope and  $c_i$ , the intra-particle diffusion model constant as the intercept.

As shown by the graph, the straight line didn't pass through the origin. This behavior indicated that more than one process affects the adsorption but only one is the rate limiting within a particular time range [14]. Had it been that the plot passed through the origin, then, intra-particle diffusion will be the sole rate limiting step. Therefore, for this study the intra-particle diffusion is not the only rate controlling step.

Equally, its  $R^2$  value of 0.9876, which is the closest to 1.0 further confirm that it fits this study well.

**C. Isotherm equilibrium studies**

Langmuir isotherm and Freundlich Isotherm models were used to analyze the experimental data. The adsorption isotherm indicates how the adsorption molecules distribute between the liquid phase and the solid phase when the adsorption process reaches an

equilibrium state. The analysis of the isotherm data by fitting them to different isotherm models is an important step to finding the suitable model that can be used for design purposes. Adsorption isotherm is basically important and very critical in optimizing the use of adsorbents.

The applicability of the isotherm equation to describe the adsorption process was judged by the correlations coefficients,  $R^2$  and  $R_L$  Values as the case may be.

**The Langmuir isotherm**

Langmuir isotherm assumes monolayer adsorption onto a surface containing a finite number of adsorption sites of uniform strategies of adsorption with no transmigration of adsorbate in the plane [15]. The linear form of Langmuir isotherm equation is given as:

$$\frac{C_e}{q_e} = \frac{1}{Q_0 b} + \frac{1}{Q_0} C_e \tag{6}$$

Where:

$C_e$  = the equilibrium concentration of the adsorbate (mg/l)

$Q_e$  = the amount of adsorbate adsorbed per unit mass of adsorbent (mg/l)

$Q_0$  and  $b$  are Langmuir constants related to adsorption capacity and the rate of adsorption respectively.

When  $C_e/q_e$  is plotted against  $C_e$ , a straight line graph with slope of  $1/Q_0$  is obtained. The Langmuir constants  $b$  and  $Q_0$  were calculated using the slope and intercept from the graph.

The essential characteristics of the Langmuir isotherm can be expressed in terms of a dimensionless equilibrium parameter ( $R_L$ )

The parameter is defined by:

$$R_L = \frac{1}{1 + b C_0} \tag{7}$$

Where:

$b$  = the Langmuir constant

$C_0$  = The highest initial methylene blue dye concentration.

The value of  $R_L$  indicates the type of the Isotherm to be either ;

Unfavorable = ( $R_L > 1$ )

Linear = ( $R_L = 1$ )

Favorable = ( $0 < R_L < 1$ )

Irreversible = ( $R_L = 0$ )

Equally, the regression coefficient,  $R^2$  was used to further analyze and determine the suitability and conformity of the Isotherms. The closeness of the  $R^2$  Values to 1.0 determines its level of fit.

The  $R_L$  values and the  $R^2$  values of the Langmuir Isotherm at the 3 different temperatures are as shown in table 2. From the results shown, Langmuir Isotherm at 40<sup>o</sup>c gave the best fit amongst the three temperatures levels studied. This is basically owing to the fact that

its  $R^2$  value was the closest to 1.0. Equally, the  $R_L$  values of the three temperatures were less than 1, confirming the adsorption as favorable.

in Langmuir equation varies as a function of the surface coverage. The well known logarithmic form of the freundlich isotherm is given by the equation;

$$\log q_e = \log k_F + \left(\frac{1}{n}\right) \log C_e \quad (8)$$

Where

$C_e$  = the equilibrium concentration of the adsorbate (mg/l).

$q_e$  = the amount of adsorbate adsorbed per unit mass of adsorbent (mg/g).  $k_f$  and  $n$  are freundlich constants with  $n$  giving an indication of the favorability of the adsorption process.  $K_F$  is the adsorption capacity of the adsorbent which can be defined as the adsorption or distribution coefficient and represents the quantity of methylene blue dye adsorbed onto the activated carbon fiber for a unit equilibrium concentration.

Table 2. Isotherm Parameters

Temperature (oC)	Langmuir constants			Freundlich constants		
	b	$R_L$	$R^2$	1/n	n	$R^2$
30	55.6	0.0004	0.8178	-0.079	-12.5	0.9186
40	11.9	0.002	0.9439	-0.722	-1.4	0.8951
50	9	0.002	0.3093	0.7521	1.3	0.4017

Table 3. Thermodynamic Parameters

Concentrations (mg/l)	$\Delta H \times 10^{-7}$			$\Delta G \times 10^{-7}$			$\Delta S$
	30°C	40°C	50°C	30°C	40°C	50°C	
10	2.7	2.8	2.9	2.7	2.8	2.9	321.3
30	-1.5	-1.6	1.6	1.5	1.6	-1.6	-105
50	-0.8	-0.8	0.9	0.8	0.8	0.9	-29.5

The freundlich isotherm is determined by plotting the graph of  $\ln q_e$  against  $\ln c_e$ .  $K_F$  and  $n$  are determined from the intercept and slope respectively. The value of  $\frac{1}{n}$  ranging between 0 and 1 is a measure of the adsorption intensity or surface heterogeneity, becoming more heterogeneous as its value get closer to zero [16]. A value for  $\frac{1}{n}$  below one indicates a normal Langmuir isotherm model while  $\frac{1}{n}$  above one is indicative of cooperative adsorption, and  $n > 1$  represents favourable adsorption condition. From the freundlich parameters listed in table 2, the values of  $1/n$  for all the temperatures studied were less than 1, indicating normal langmuir isotherm model.

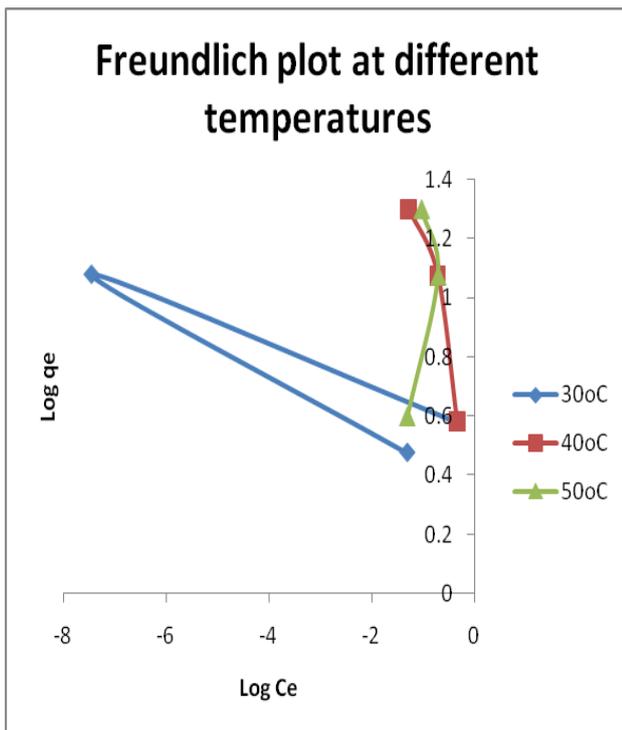
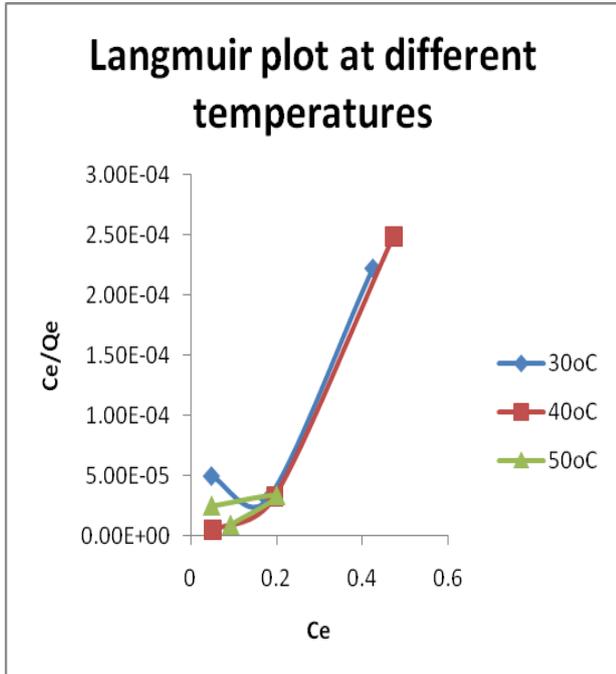


Fig. 3. Isotherm plots

**Freundlich isotherm**

Freundlich isotherm, in other hand assumes heterogeneous surface energy in which the energy term

**D. Thermodynamics studies**

Thermodynamics parameters are extremely important for determining the spontaneity of an adsorption Process. The standard free energy change ( $\Delta G^\circ$ ), standard enthalpy change ( $\Delta H^\circ$ ), and standard entropy change ( $\Delta S^\circ$ ) are associated with the adsorption process. The parameters were calculated from the following equation [17].

$$k_e = \frac{c_a}{c_e} = \frac{c_0 - c_e}{c_e} \tag{9}$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ = -RT \ln k_e \tag{10}$$

$$\ln k_e = -\left(\frac{\Delta H^\circ}{RT}\right) + \frac{\Delta S^\circ}{R} \tag{11}$$

Where  $k_e$  = the equilibrium constant

$c_e$  = Equilibrium concentration of the methylene blue dye in the solution (mg/l)

R = Universal gas constant (8.314 J/mo/k)

T = absolute temperature

The values of  $\Delta S^\circ$  and  $\Delta H^\circ$  were obtained from the slope and intercept of the graph of  $\ln k_e$  versus  $1/T$ . This was done at the three initial concentration values of 10, 30 and 50 (mg/l) and the results are shown in table 3.

From these values generated from the thermodynamics study, the negative value of  $\Delta G^\circ$  for all the initial concentration values indicates the spontaneity and feasibility of the absorption of methylene blue dye onto the activated carbon fiber under experimental conditions; it equally indicates a physical adsorption process [18]. The positive value of  $\Delta S^\circ$  at lower concentrations shows that an increase in randomness occurs at the interface during the sorption process.  $\Delta H^\circ$  was positive at 10mg/l initial concentration signifying endothermic reaction but was negative at 30 and 50mg/l initial concentrations thereby signifying exothermic in nature. This development may be linked to among other things the variation in the concentrations. As one can say, that 10mg/l initial concentration was not enough to generate the required driving force needed for mass transfer to take place, thus, required additional driving force from temperature. At higher concentration of 30 and 50mg/l, there was enough driving force needed for the mass transfer to take place, thus increase in temperature had little effect. The nature of the adsorption process was equally confirmed by the magnitude of the  $\Delta H^\circ$  values. It is accepted that if magnitude of enthalpy change is less than 84Kj/mol, adsorption is physical, however, chemisorptions takes place from 84 to 420Kj/mol. The range of values of

$\Delta H^\circ$  from table 3 showed that the nature of adsorption is physical

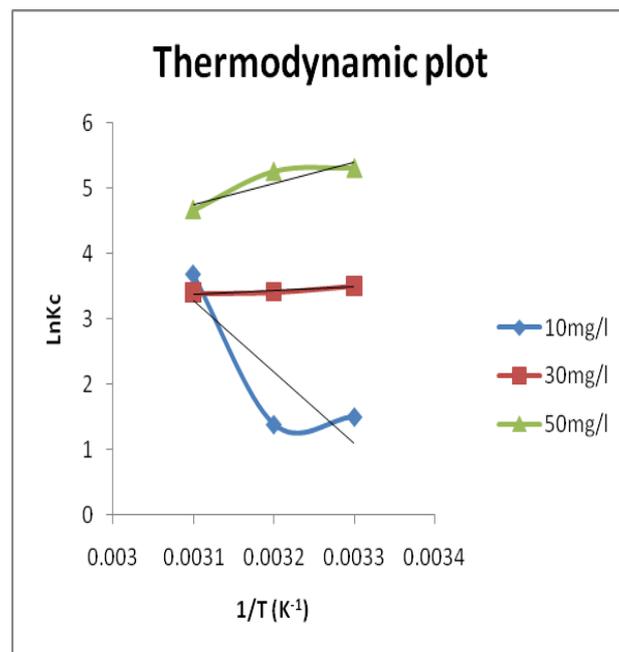


Fig .4. Thermodynamic plot

**IV. CONCLUSIONS**

- The present study confirmed that activated carbon prepared from the Usoro (Adenia lobata) fiber is a promising adsorbent for the removal of methylene blue dye from aqueous solution.
- The Langmuir isotherm model at 40<sup>0</sup>c gave the best fit amongst the temperature levels selected for this study. Thereby, signifying a monolayer adsorption.
- The adsorption capacity decreased with increase in temperature at a higher initial concentration and increased with increase in temperature at lower initial concentration.
- For the adsorption kinetics study, the pseudo-first-order kinetics favored this study.
- The positive  $\Delta S^\circ$  value showed the increased randomness of the process.
- The negative value of  $\Delta G^\circ$  indicated the feasibility and the spontaneous nature of the adsorption of methylene blue dye onto the prepared activated carbon fiber.
- Considering the optimum thermodynamic value that gave the best fit, the negative value of  $\Delta H^\circ$  Confirmed the exothermic nature of the adsorption interaction.
- The intra-particle diffusion kinetics studies confirmed that it is not the only rate limiting step.

**ACKNOWLEDGEMENT**

The authors wish to thank PYMOTEC RESEARCH CENTRE AND LABORATORIES ENUGU, ENUGU STATE NIGERIA for all their facilities used throughout the research work.

**REFERENCES**

[1] Tunay O., Kabadasli I., Eremektar. G., Orhan D. "Color removal from textile wastewater". Water Sci. Technol. Vol34, pp. 9-16, 1996.

[2] Sulak. M.T., Demirbas. E. Kobya M. "Removal of Astrazon Yellow 7GL from aqueous solutions by adsorption onto wheat bran "Bioresour. Technol. 98, pp. 2590-2598, 2007.

[3] Qadeer R. "Adsorption behavior of ruthenium ions on activated charcoal from nitric acid medium" Colloids surf. A. 293, pp. 217-223, 2007.

[4] Srivastava .V.C. Mall I. D., Mishra I. M. "Adsorption thermodynamics and isosteric heat of adsorption of toxic metal ions onto bagasse fly ash (BFA) " and rice husk ash (RHA)", Chem. Eng. J. 132, pp.267-278, 2007.

[5] Allen S. J. "Equilibrium adsorption isotherms for peat", fuel 66, pp. 1171-1175, 1987.

[6] Allen S. J., Gan. Q., Matthews R. and Johnson P. A. "Comparison of optimized isotherm models for basic dye adsorption by Kudzu" Bioresour. Technol. 88, pp. 143-152, 2003.

[7] Carlos Moreno- Castilla. "Adsorption of organic molecules from aqueous solutions on carbon materials", Carbon, 42, pp. 83-94, 2004.

[8] Juan, Yang, Keqiang Qju. "Preparation of Activated carbon from Walnut Shell via Application for Methylene Blue Removal". Chemical Engineering Journal 162, pp. 209 – 219, 2010.

[9] J.M. Salman, V.O. Njoku, B.H. Hameed. "Batch and Fixed – Bed Adsorption of 2, 4-dichloro Phenoxyacetic Acid onto Oil Palm Frond Activated carbon". Chemical Engineering Journal 174, pp.33 – 40, 2011.

[10] A.A. Ahmad, B.H. Hameed. "Reduction of COD and Colour of Dyeing Effluent from a Cotton Textile Mill by Adsorption onto Bamboo-based Activated carbon". J. Hazard. Mater. 172, pp.1538 – 1543, 2009.

[11] W. Tongpothorn, M. Sriuttha, P. Homchan, S. Chanthai, C. Ruangviri Yachai. "Preparation of Activated Carbon Derived from Jatropha Curcas Fruit Shell by Simple Thermo-Chemical Activated and Characterization of Their Physico Chemical Properties", Chem. Engr. Res. Des. 89, pp.335 – 340, 2011.

[12] Z. Zhang, M.XU, H. Wang, Z.Li. "Enhancement of CO<sub>2</sub> Adsorption on High Surface Area Activated carbon Modified by N<sub>2</sub>, H<sub>2</sub> and Ammonia", Chem. Eng. J. 160, pp. 571-577, 2010.

[13] Witek- Krowiak, A. " Analysis of influence of process conditions on kinetics of malachite green biosorption onto beach saw dust" Chemical Engineering Journal 171, pp. 976-985, 2011.

[14] Li, Y., Wu, T., Warg, B. and Li, X. "Adsorption properties of Aluminum magnesium mixed hydroxide

for the model anionic dye reactive brilliant red K-2BP" Journal of hazardous materials 164, pp. 1089-1104, 2009.

[15] Kumar, B. G. P, Miranda, L. R and Velan, M. "Adsorption of Bismark Brown dye on activated carbon prepared from rubber saw dust using different activation methods" Journal of Hazardous materials, vol 126, pp.63-70, 2005.

[16] Haghseresht, F. and Lu, G. O. "Adsorption characteristics of phenolic compounds into coal-reject-derived adsorbents" Energy and fuels, vol. 12, no.6, pp.100-107, 1998.

[17] Hameed, B. H., Din, A. T. M., Ahmed, A. C. "Adsorption of methlene blue onto bamboo based activated carbo. Kinetics and equilibrium studies", Journal Hazardous Mat., vol.141, pp. 819-825, 2007.

[18] Moussavi, G. and Khos ravic, R. "The removal of cationic dyes from aqueous solutions by adsorption onto pistadio hill waste". Chemical Engineering Research and design, vol. 89, pp. 2182- 2011.