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Effect of Process Factors on the Adsorption of MB Dye Using Adenia Lobata Fiber

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ABSTRACT: This study was undertaken to investigate the adsorptive capacity of Adenia lobata fiber on MB dye. The experiments were carried out in a batch system to study the effects of adsorbent dosage, MB dye initial concentrations, P^H, and contact time on the adsorptive capacity of the activated carbon fiber. The scanning electronic microscopy (SEM) revealed well pronounced porosity which indicated good possibility for the dye to be trapped and adsorbed. P^H did not have much effect on the removal efficiency, the removal efficiency slightly increased as p^H was increased from 2 to 10. The removal efficiency increased with the increase in dosage of the adsorbent while the adsorptive capacity decreased. The increase in initial concentration increased the adsorptive capacity but decreased the removal efficiency. The equilibrium adsorption data fitted well with intraparticle diffusion model but was not the only rate controlling step; boundary layer diffusion controls it to some extent. The thermodynamic parameters indicated the process as feasible and spontaneous. The process was endothermic at lower initial concentration and exothermic at higher initial concentration.

KEYWORDS: activated carbon, Adenia lobata, kinetics, MB dye, SEM,

I. INTRODUCTION

The universe is facing crises of fresh water due to fast depletion of fresh water resources. The industrial and domestic activities have polluted the surface water as well as ground water up to a greater extent [1]. Hence, the cost of removal of organic pollutants from water has been increasing remarkably. Textile industrial uses dyes and pigments to color their products. There are more than 100,000 commercially available dyes with over 7 x 10 tonnes of dyestuff are produced annually [2]. The main sources of wastewater generated by the textile industry originate from the washing and bleaching of natural fibers and from the dying and finishing step [2]. Given the great variety of fibers, dyes and process aids, these processes generate waste water of great chemical complexity and diversity, which are not adequately treated in conventional waste water treatment plant [3].

Dyes are highly colored polymers and low biodegradable. Dye being one of the important recalcitrant, persist for long distances in flowing water, retards photosynthetic activity, inhabit the growth of aquatic biota by blocking out sunlight and utilizing dissolved oxygen and also decreases the recreation value of stream [4]. A literature survey revealed that methylene blue has been used for adsorption studies, not only because of its environmental concern but also for the fact that it has been recognized as a model adsorbate for the removal of organics [5]. Methylene blue is used as model adsorbate for adsorption of organic because of its known strong adsorption to activated carbons [6].

There are many methods available for treating textile waste water, most of which suffer some drawbacks like high capital and operational cost, regeneration cost, and problem of residual disposal. Liquid phase adsorption has been shown to be highly efficient, well established technique for the removal of organic compounds due to its simplicity, adsorbent cost, effectiveness and the availability of wide range of adsorbents. Activated carbon is often the preferred adsorbent for the removal of organic compounds due to its high adsorption capacity. However, it suffers some draw backs, such as high cost and the irreversible nature of adsorption [7]. Thus, the requirement of low cost adsorbent comes here which fulfill all the properties of activated carbon but at the expense of low cost.

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Natural fibers have been attracting the attention of researchers due to the advantages such as low cost, availability, renewability, and biodegradability. In this work, activated carbon was prepared from high abundant Adenia Lobabata (Usoro) fiber.

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 100^0c.The samples were then cut to obtain a uniform size of about 100cm.

The preparation was divided into three(s) stages

1. Base leaching
2. Activation
3. Acid washing

First, the fiber was leached with a 0.5M NaOH solution and then boiled in a glass round-bottomed flask at 100^0C 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 105^0c for 24hrs.

Secondary, $Zncl_2$ 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 400^0c 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 105^0C for 24hrs and then ground very well to form a good porous carbon powder.

C. CHARACTERIZATION OF ACTIVATED CARBON

Scanning Electron microscropy (SEM) (PHENOM PROX) analysis was carried out on the unactiviated lobata and activated Adenia lobtata fiber to study its surface texture before and after activation.

D. ADSORPTION ISOTHERM

Batch isotherm studies were carried out in 250ml conical flask at different temperature of 303K, 313K, 323Km 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 the end of equilibrium time of 6 hours, the reaction mixture was centrifuged and the residual MB concentration analysed. The amount of MB adsorbent at equilibrium qe(mg/g) was calculated from the following equation (1).

$$qe = \left(\frac{Co - Ce}{W}\right)V \qquad 1$$

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E. 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 a shaker incubator for a contact time varied in the range 0- 240mins 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_t (mg/g), was calculated by equation 2:

$$qt = \left(\frac{Co - Ct}{W}\right)V \quad (2)$$

Where C_o (mg/L) is initial MB solution, C_t (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. EXPERIMENTAL RESULTS

A. SEM ANALYSIS

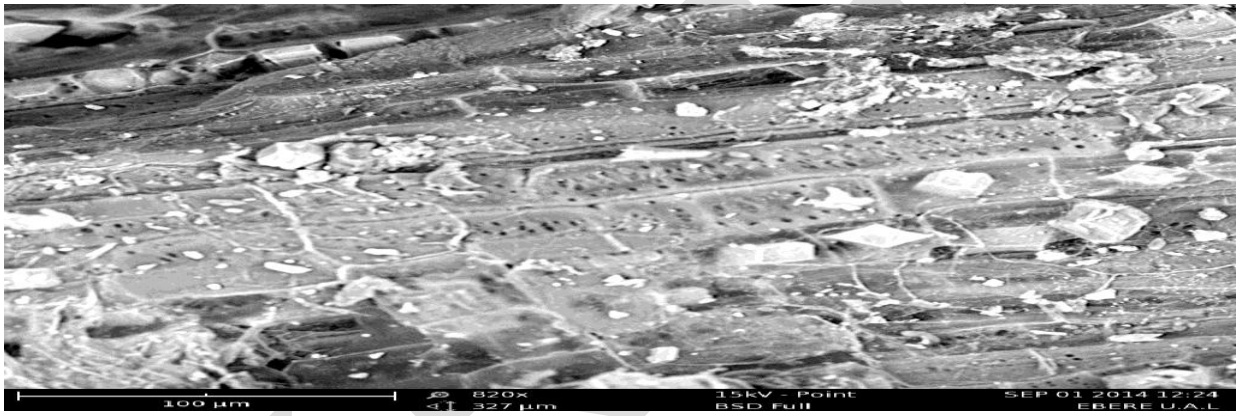

Fig. 1a: SEM analysis of untreated Adenia lobata fiber

The textural structure examination of adsorbent particle can be undertaken by observation of the scanning election microscopy (SEM) images (fig 1a – b). Fig. 1a. shows the SEM image for the unactivated adenia lobtata fiber. There is clear evidence from that image that the surface texture of the inactivated fiber is dense, compact, well covered with substances and without pores. Conversely the SEM image for the activated fiber shown in fig. 1b displays a well pronounced porosity, with a series of irregular cavities distributed over the surface.

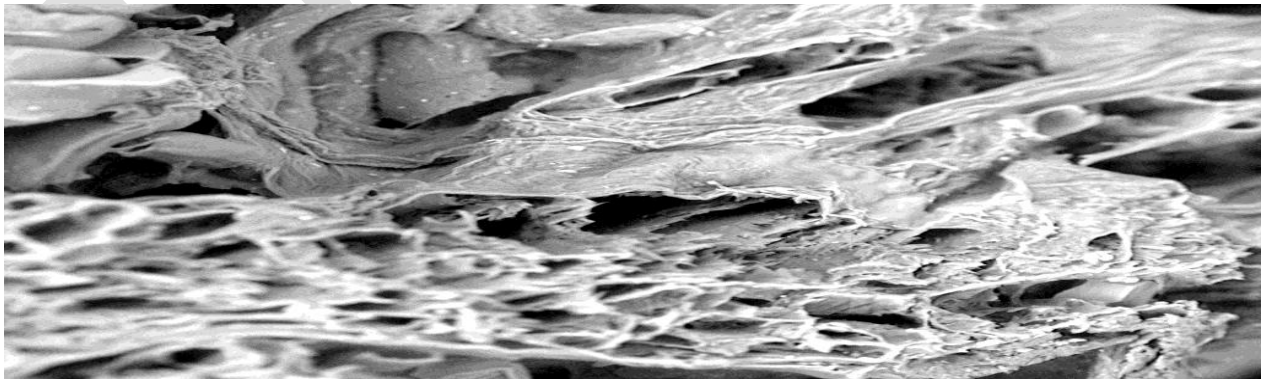

Fig.1b: SEM analysis of activated Adenia lobata fiber

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These cavities were resulted from the evaporation, leaving the space previously occupied by the reagent [8]. It is clear that the activated fiber has considerable numbers of heterogenous layer of pores, indicating good possibility for the dyes to be trapped and adsorbed.

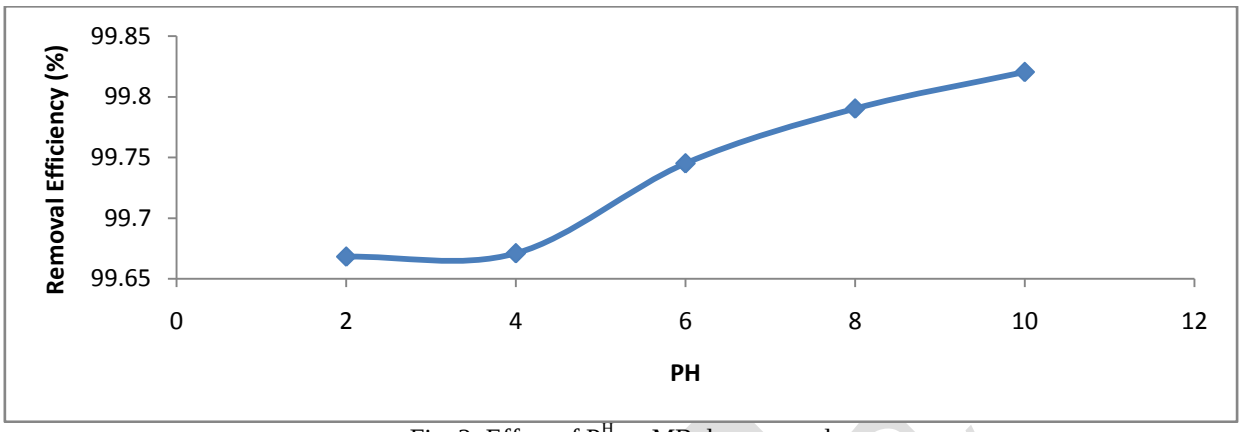


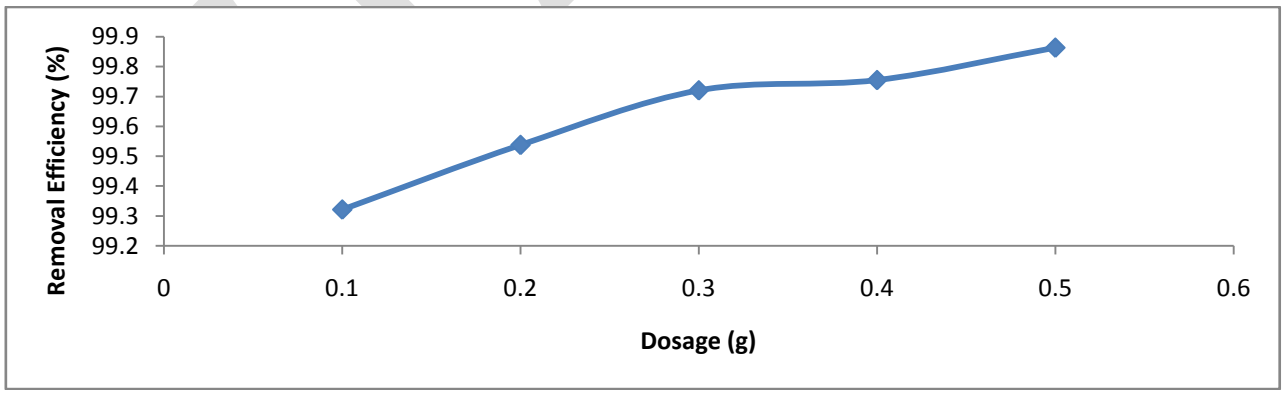
Fig. 2: Effect of P^H on MB dye removal

B. EFFECT OF P^H

P^H of a solution is an important parameter affecting the adsorption process because it affects both aqueous charge distribution and the surface binding site of the adsorbent [9]. From fig. 2, the percentage removal of MB increased from 99.66 to 99.82%, when the p^H of the solution was correspondingly increased from 2 to 10. It was attributed to presence of more negative charges adhering to positive charges of MB which resulted to high MB adsorption. The lower removal efficiencies observed at acidic pH can be attributed to repulsion activities by similar ionic charges present, that is, the prevalence of H^+ in the acidic medium and cations of MB [10].

C. EFFECT OF ADSORBENT DOSAGE

The adsorbent dosage is an important parameter in the adsorption studies because it determines the capacity of the adsorbent for a given initial concentration of dye solution [11], [12]. The result from fig. 3a shows that the removal efficiency increased with increase in adsorbent dosage.



(a)

This can be attributed to increase of the available sorption sites. A reverse trend was observed with adsorptive capacity which decreased as the adsorbent dosage was increased (fig. 3b). This can be attributed to particle interaction, such as

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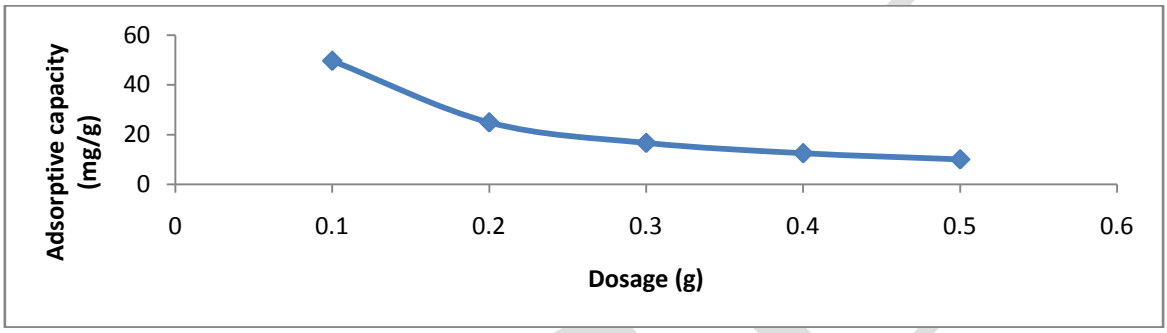
aggregation, resulting from high adsorbent dosage, such aggregation would lead to decrease in the total surface area of the adsorbent and increase in diffusional path length [13].

D. EFFECT OF INITIAL DYE CONCENTRATION

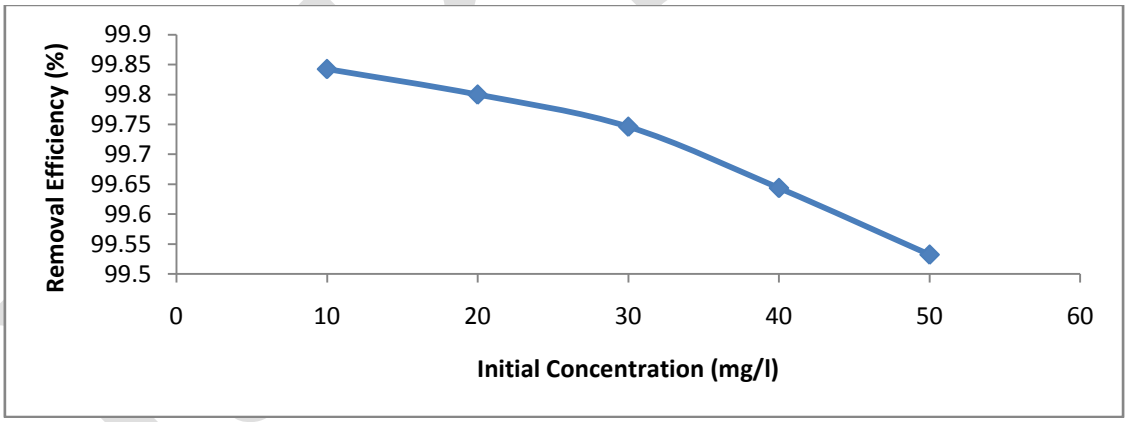
The initial dye concentration played important role on the adsorption capacity of MB on the adsorbent. From the result in fig. 4a, increase in initial dye concentration decreased the percentage amount of dye removed. At a constant dosage, the decrease in the adsorption percentage is probably due to the saturation of the active binding sites on the adsorbent surface at higher MB concentrations.



(b)

Fig. 3: Effect of adsorbent dosage on (a) Removal Efficiency (b) Adsorptive Capacity

On the other hand by increasing the initial dye concentration, the actual amount of dye adsorbed per unit mass of adsorbent increased (fig. 4b). The higher initial concentration of MB provided an additional driving force to overcome the mass transfer resistance for MB transfer between the solution and the surface of the adsorbent [12], [14].



(4a)

E. EFFECT OF CONTACT TIME

The effect of contact time on the dye removal efficiency is shown in fig. 5. From the result, it can be said that the effect of time on the removal efficiency occurred in two phases.

First, an initial rapid phase where the adsorption of dye molecules was fast and rapid, the second phase was a slow stage in which the contribution to the total dyes removal efficiency was relatively small, and finally the removal of dye reached equilibrium [15], [16]. This is as a result of more vacant site been available at the initial stage of the process but became difficult to occupy at the later stage due to repulsive forces between the adsorbate molecules on the solid phase.

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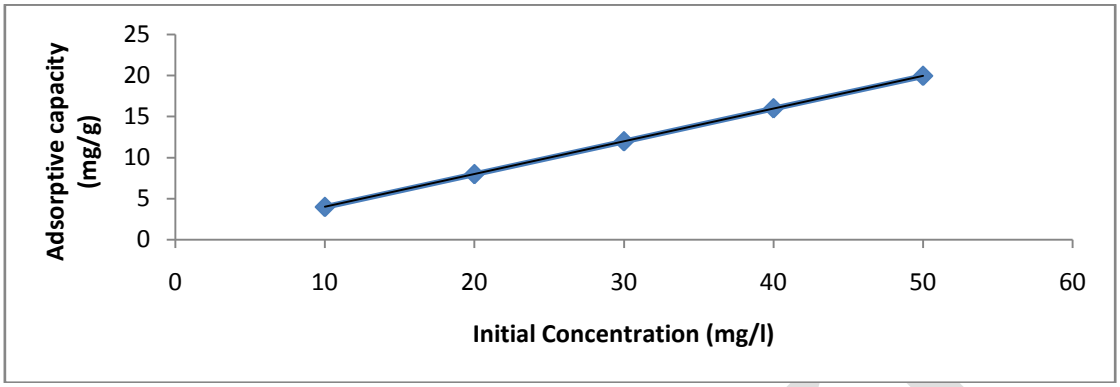

(b)

Fig.4: Effect of Initial concentration of MB dye on (a) removal efficiency (b) Adsorptive capacity

F. KINETIC MODELS

1. PSEUDO-FIRST- ORDER MODEL

The pseudo-first-order equation is written as follows

$\ln (q_e - q_t) = \ln q_e - k_1 t$ 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 respectively (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 = 0.8053, it can be said that the model fitted the data well.

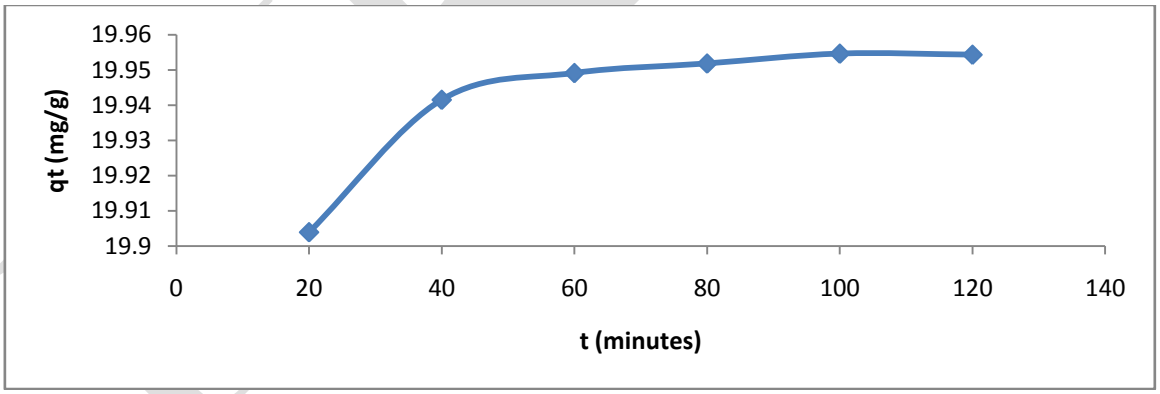

Fig. 5: Effect of contact time on the adsorptive capacity of the adsorbent.

1. INTRA PARTICLE DIFFUSION

The intra particle diffusion model was proposed to identify the adsorption mechanism and to predict the rate controlling step. The intra particle diffusion model usually includes three steps. The first portion is the external surface adsorption or boundary layer diffusion. The second portion is the gradual stage of adsorption which is the intra particle diffusion. If the plot of qt versus $t^{1/2}$ is linear and passed through the origin, then the intra particle diffusion is the rate-controlling step [17]. The third portion is the final equilibrium stage in which the intra particle diffusion starts to slow down due to the extremely low dye concentration left in the solution [18].

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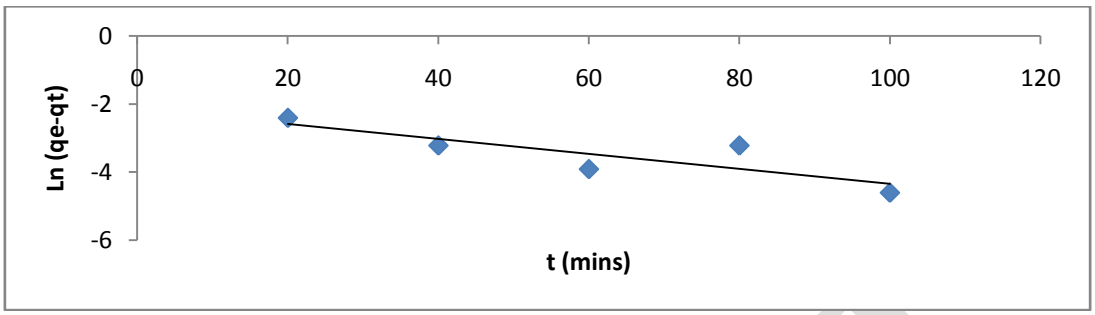

Fig. 6: Pseudo-first order plot

The plot in fig. 7 shows that the linear plot did not pass through the origin which indicated that the intra particle diffusion was not only the rate controlling step and the boundary layer diffusion controlled the adsorption to some extent [18].

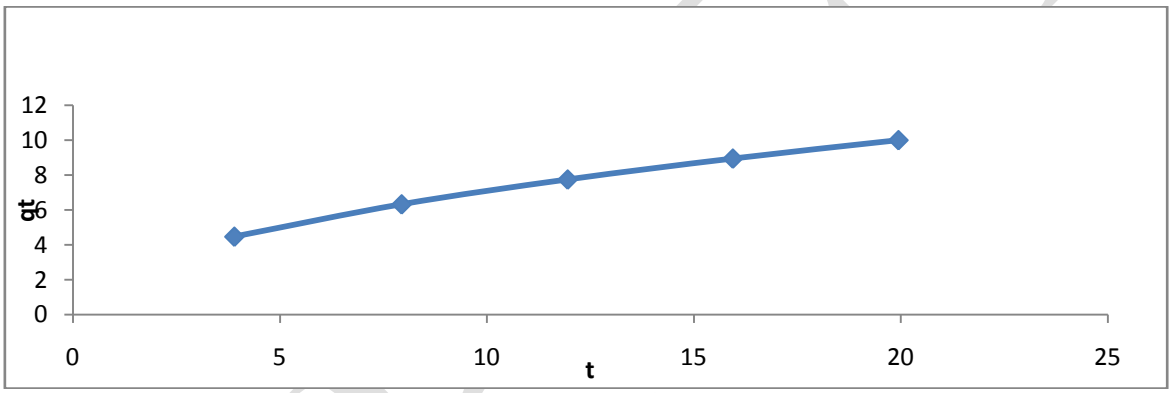

Fig. 7: Intra particle diffusion model plot

This deviation may be due to the difference in mass transfer rate in the initial and final stage of adsorption [17], [19]. Equally, its R^2 value of 0.9876, which is very close to 1.0 further confirm that the data fit well with the model.

G. EQUILIBRIUM STUDIES

An adsorption isotherm describes the relationship between the amount of adsorbate up taken by the adsorbent and the adsorbate concentration remained in the solution [20], [21].. The equation parameter and the underlying thermodynamic assumptions of these equilibrium models often provide some insight into the

TABLE 1: ISOTHERM PARAMETERS

Temperature	Langmuir constants			Freundlich constants		
(^{0}C)	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	0.7221	-1.4	0.8951
50	9.0	0.002	0.3093	0.7521	1.3	0.4017

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From the results shown, Langmuir Isotherm at 40^0c 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.

For freundlich isotherm, 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.

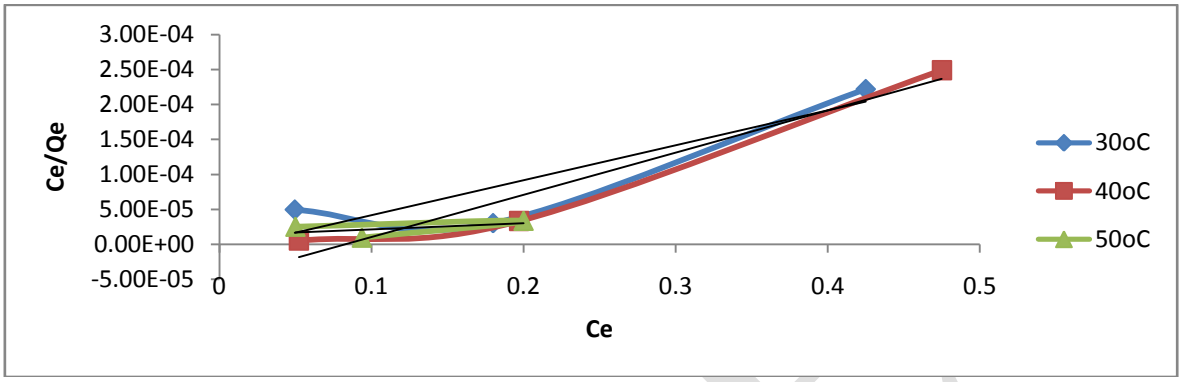

Fig. 8: Langmuir Isotherm model

adsorption mechanism, the surface properties of an adsorbent and affinity of the adsorbent for an adsorbate [22], ,[21], [23], [24]. In this study, the experimental results were fitted to langmuir, and freudlich Isotherms. The R_L values (dimensionless equilibrium parameter) which indicates the type of Isotherm to be either; Unfavorable, Linear, favorable, or irreversible and the R^2 values of the Langmuir Isotherm at three different temperatures are shown on table 1.

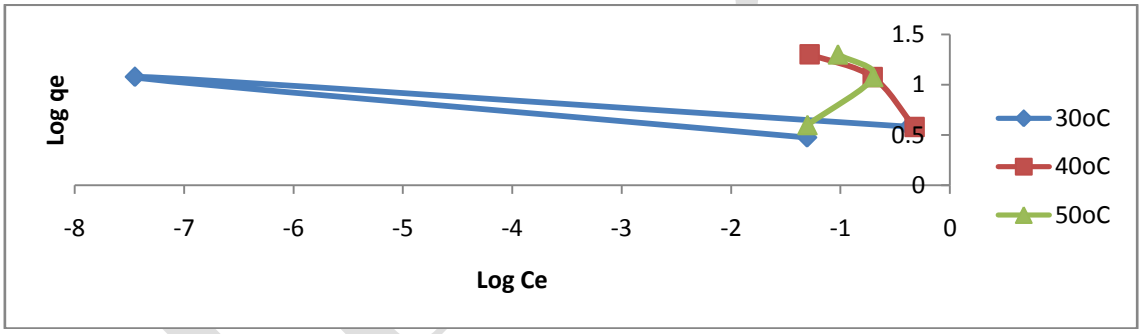

Fig. 9: Freundlich Isotherm model

From the freundlich parameters listed in table 1, the values of 1/n for all the temperatures studied were less than 1, indicating normal langmuir isotherm model.

H. THERMODYNAMIC STUDIES

From the thermodynamics study (table 2), the negative value of ΔG° 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 condition, it equally indicates a physical adsorption process [25].

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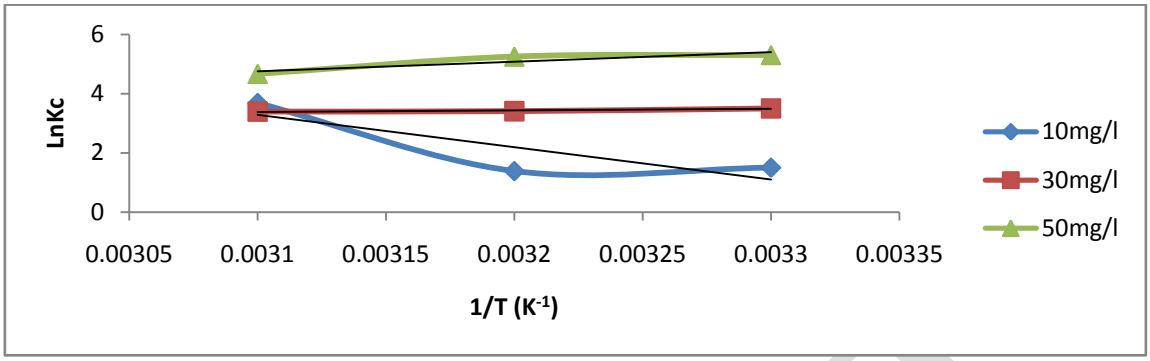

Fig. 10 Thermodynamic Plot

The positive value of ΔS° at lower concentrations shows that an increase in randomness occurs at the interface during the sorption process. ΔH° was positive at 10mg/l initial concentration signifying endothermic reaction but was negative at 30 and 50mg/l initial concentration thereby signifying exothermic in nature.

Table 2: Thermodynamic parameters

Concentrations (mg/l)	$\Delta HX10^{-7}$			$\Delta GX10^{-7}$			ΔS
	30^{0C}	40^{0C}	50^{0C}	30^{0C}	40^{0C}	50^{0C}	
10	2.7	2.8	2.9	2.7	2.8	2.9	321.3
30	-1.5	-1.6	1.5	1.5	1.6	-1.6	-105.0
50	-.0.8	-0.8	0.8	0.8	0.8	0.9	- 29.5

IV. CONCLUSION

Adenia lobata fiber is an effective adsorbent for the removal of MB dye from its aqueous solution.

- The scanning Electron microscopy revealed well pronounced pores that are responsible for the trapping and adsorption of the MB dye on the adsorbent.
- P^H does not strongly affect the rate of adsorption of the dye on the adsorbent. Percentage removal efficiency increased from 99.66 to 99.82% as pH was increased from 2 to 10.
- Dosage which determines the capacity of the adsorbent for a particular initial concentration affected the adsorption. Increase in adsorbent dosage increased the removal efficiency but decreased the adsorptive capacity.
- Increase in initial MB dye concentration decreased the removal efficiency but increased the adsorptive capacity.
- Contact was seen to have strong effect on the adsorption process, it was found that the adsorption occurred in three phases; the rapid, slow and steady phases.
- The kinetic data were fitted to pseudo- first order and intraparticle diffusion model. Intraparticle diffusion model fitted the data well but was not the only the rate controlling step, boundary layer diffusion equally controls the process to some extent.
- The equilibrium adsorption data were fitted to Langmuir and Freundlich models. It was confirmed that the data fitted well with Langmuir model.
- The Gibb's free energy (ΔG^o), and entropy (ΔS^o) parameters confirmed the process to be feasible and spontaneous in nature, while the enthalpy (ΔH^o) confirmed the process to be endothermic at lower initial concentration and exothermic at higher initial concentration.

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