

Kinetic Study of the Methylene Blue Adsorption on White Clay as a Local Adsorbent

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Abstract : The adsorption isotherm and kinetics of the sorption pigment (Methylene Blue) from aqueous solution onto Enugu White Clay as a local adsorbent was investigated. The kinetics and isotherm were carried out using batch experiments. The experimental data was analyzed in terms of intra-particle diffusion, rate of adsorption, isotherms and thermodynamics. The results showed that Methylene Blue (MB) adsorption follows second order kinetic model with adsorption rate constant of 0.2279g/(mg.min). The adsorption rate was within about 100 minutes, and 96 percent of the pigment was removed from the solution. The activation energy showed that the MB adsorption was endothermic and that the rate limiting step is surface diffusion. The results indicated that Enugu White Clay has good adsorptive potentials and can be used as a local, cheap and effective adsorbent for the removal of pigments from aqueous solutions.

Key Words: Adsorption Isotherm, Adsorption Rate. Diffusion, Kinetics Models, Local Adsorbent, Methylene Blue, White Clay,

1.0 INTRODUCTION

Adsorbents are solid substances, usually porous in nature, with a high surface area, that can adsorb chemical substances onto its surface by intermolecular forces, and the process of attracting chemical substances onto the surfaces of adsorbents is adsorption, Warren [1]. Adsorption is present in many physical, biological and chemical systems and is used extensively in industrial processes for the purposes of separation and purification. The high cost of commercial adsorbents, especially activated carbon, restricts their uses and applications Malik,[2], and hence the need to substitute them with the unconventional, locally available, cheaper and environmentally friend adsorbents. The utilization of locally available materials as a raw material in the production of adsorbents, is in line with Nigeria's economic transformation agenda.

A wide range of materials have been researched for that purpose, Nde-Age [3], Itodo[4], Kyziol [5]. Adsorption kinetic studies are important in predicting the rate of pollutant removal from aqueous systems. [Michael][6]. provides information for selecting optimum operating conditions, identifying reaction pathways, understanding rate limiting steps and, are also essential for scaling-up of laboratory studies to industrial applications.

Adsorption isotherm or equilibrium data are fundamental requirements for the design of adsorption system. The equilibrium is achieved when the capacity of the adsorbent material is reached, and the rate of adsorption equals the rate of desorption. The theoretical adsorption capacity of an adsorbent can be calculated with an adsorption isotherm.

Although, there are many adsorption isotherms, there are two basically well established types of isotherms; the Langmuir and Freundlich isotherms [Mohammed][7]. The significance of adsorption isotherm is that it shows how the adsorbate molecules (Methylene Blue in aqueous solution) is distributed

between the solution and the adsorbent (solid) at equilibrium concentration on the loading capacity at different temperatures. Langmuir adsorption isotherm is often used for the adsorption of a solute from a Liquid solution. It is best known of all isotherms describing adsorptions, process, [Nagham][8]. The adsorption isotherm may be expressed as;

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

The above equation can be rearranged to the Linear form;

$$\frac{C_e}{q_e} = \frac{1}{q_o k_l} + \frac{C_e}{q_o} \quad (2)$$

Where, q_e - Amount of adsorbate adsorbed at equilibrium mg/g, C_e - Equilibrium concentration mg/l, k_l -Langmuir adsorption constant related to energy of adsorption (L/mg), q_o - Maximum adsorption capacity corresponding to complete monolayer coverage (mg/g).

The Linear form can be used for Linearization of experimental data by plotting C_e/q_e vs C_e . The Langmuir constants q_o and k_l can be obtained from the slope and intercept of the Linear plot respectively, [Esmaeli][10].

The freundlieh isotherm is the earliest known relationship describing the adsorption equation, [8]. The work of Freundlich on Liquid solid adsorption led to the formation of the experical equation.

$$q_e = k_f C_e^{1/n} \quad (3)$$

Where, q_e = amount adsorbate adsorbed at equilibrium mg/g

C_e = equilibrium concentration mg/L, k_f and n are empirical constants depending on several environmental factors and n is greater than one. The Linerized form is obtained by taking logarithm of both sides of the equation (3).

$$\ln q_e = \ln k_f + \frac{1}{n} \ln C_e \quad (4)$$

A plot of $\ln q_e$ vs $\ln C_e$ will be a straight Line, if the data follows Freundlich adsorption isotherm. The constants can be determined from the slope and intercept of the linear plot [Erdem][11].

In this work,

- The physicochemical properties of Enugu White Clay was determined
- The kinetic of MB adsorption by Enugu White Clay, which is important in predicting the rate of pollutant removal by the adsorbent was established.
- The activation energy for MB adsorption was also determined.

2.0 MATERIALS AND METHODS

2.1 Sample Collection and Characterization

The adsorbent for this research is Enugu White Clay collected from Enugu in South East providence of Nigeria. The adsorbent was collected at the peak of dry season (April) and stored in a polyethylene bag. It was characterized for moisture and volatile matter contents, fixed carbon, specific gravity, p^H value, and bulk density, using standard methods, and the results are shown in tables I to V

2.2 Acid Activation of the Adsorbent

The dry sample of the raw clay was treated with 1.5m H_2SO_4 at acid to adsorbent ratio of 1:1. The activation was carried out in a around bottom flesk. The slurry was continuously stirred at a temperature of 90°C for 3 hours. When activation was completed, the slurry was filtered and washed several times with distilled water until neutral P^H was obtained. The sample was dried at 105°C to reduce moisture content. The dry sample was stored in an air tight container.

2.3 Methylene Blue Solution Preparation

A stock solution of 100 mg/L was prepared by dissolving 1g of methylene blue in 1000cm³ (Litre) of distilled water. The desired concentrations for adsorption were made by dilution of the stock solution.

2.4 Methylene Blue Adsorption

The adsorption was carried out using batch adsorption method of [7]. A fixed amount of adsorbent (2g) was mixed with 50ml of MB solution with initial concentrations of 50 mg/L, 90 mg/L, 110mg/L and 150 mg/L at 30°C. The system was agitated for 2hours, and the resultant solution filtered. The filtrate was analyzed with UV-spectrophotometer for the residual MB. The uptake of MB was calculated from the relationship, as given by, [Volesky] [12].

$$q_e = \frac{V}{m}(C_0 - C_e) \quad (5)$$

Where, q_e - Amount of methylene blue adsorbed at equilibrium mg/g, V -Initial volume of MB (litre), m–Mass of adsorbent (2g), C_0 -Initial concentration of MB mg/L, C_e –

Equilibrium concentration of MB mg/L, The experiment was repeated at 40, 50 and 60°C.

2.5 Residence Time Distribution

The effect of contact time on the uptake of MB by Enugu White Clay was investigated at MB concentration of 50mg/L at adsorbent dosage of 2g per 50ML of the MB solution. The experiment was carried out by shaking the adsorbent suspension in the methlene blue solution for 20,40,60,80,100 and 120 minutes. The suspension was filtered and the filtrate analyzed for the residual methylene blue using UV-spectrophotometer at 661nm wave length, a length corresponding to maximum absorbance, and the MB removal efficiency determined.

$$\% \text{ MB removal efficiency } q_e = \frac{(C_0 - C_t) \times 100}{C} \quad (6)$$

The uptake of MB was calculated from [6], with the relationship given by;

$$q_t = v (C_0 - C_t) \quad (7)$$

Where q_t = MB adsorbed at time t (mg/g), v = Initial volume of MB (Litre), m = Mass of adsorbent used (2g), C_0 =Initial concentration of MB mg/L, C_t = Concentration of MB at time t > 0 mg/L

3.0 RESULTS AND DISCUSSION

The physicochemical properties of an adsorbent usually affects its adsorptive capacity, since they have profound influence on the specific surface area. The physicochemical properties of white clay is shown in table I.

Table I The physicochemical properties of white clay, Egbuna et al[13].

Moisture content %	7.95 ± 0.51
Volatile metter %	2.46 ± 0.04
Fixed carbon %	0.84 ± 0.08
Specific gravity g/cm ³	2.57
Bulk density g/cm ³	1.57
pH	5.7
Non clay residue %	3.55
Ignation loss %	11.26
Titration loss %	0.78
SiO ₂	63.39
Al ₂ O ₃	4.42
CaO	1.62
MgO	2.33
Na ₂ O	4.10
K ₂ O	3.48

It was observed that natural white clay was ideal in terms of non-clay residue, moisture content, ignition loss and titrable acidity, but low in bulk density.[13], also noted that physical properties of clay influence their ability to adsorb carotenoids. Nutting,[14], Richardson,[15], indicated that low moisture content is an indication of good adsorptive capacity. Low ignition loss and non clay residue of the white clay, indicate that the clay is free from inorganic substances which would naturally hinder its adsorptive properties. Soon,[16], in his experiment on natural clays observed that high level of SiO₂ (about 65%), in a clay sample proves it to be montmorillonite, and hence, the chemical properties of the clay presented here as analyzed, proved it to be montmorillonite.

3.1 Resident Time

The residence time is presented in table II as a function of concentration, and removal efficiency.

Table II, Residence Time

Time (Minutes)	Ct (mg/L)	Removal Efficiency %
20	5.7913	88.42
40	4.9656	91.07
60	4.8434	93.31
80	3.2726	93.48
100	1.9433	96.11
120	1.9360	96.07

From table II it was observed that the rate of MB adsorption was faster at the residence time of 20 to 60 min. and becomes slower towards equilibrium. This is obvious from the fact that large number of recent surfaces were available for adsorption at the initial stage. After some time, the remaining vacant sites become difficult to be occupied due to repulsive forces between the adsorbate molecules on the adsorbent and the bulk phase. Table II, also indicates an increase in the percentage removal efficiency of the methylene blue. This may be attributed to the fact that longer residence time means time until about 100 minutes when, the adsorptive removal of MB reached equilibrium.

According [10], a long contact time is necessary to reach equilibrium indicating that the predominant mechanism is physical adsorption, and hence, the relatively long contact time observed for the MB removal by Enugu White Clay. more complete adsorption. The data showed a rapid drop in the amount of initial MB concentration remaining after each

3.2 Kinetic Treatment of the Sorption Process

The kinetic treatment of the experimental data was discussed in terms of intra-particle diffusion and the rate of adsorption.

3.3 Intra-Particle Diffusion

Besides adsorption on the outer surface, there is also possibility of intra-particle diffusion from the outer surface into the pores of the adsorbent. The possibility of intra-particle diffusion was explored based on the weber-morris model equation [Michael][6].

$$q_t = K_d t^{1/2} + C \quad (8)$$

According to Weber, [17], if the weber-morris plot of q_t vs $t^{1/2}$ gives a straight line, then the adsorption process is controlled by surface diffusion only. However, if the data exhibit multi-linear plots, two or more steps influence the adsorption process. The mathematical dependence of the adsorbate uptake on $t^{1/2}$ is shown in figure 1.

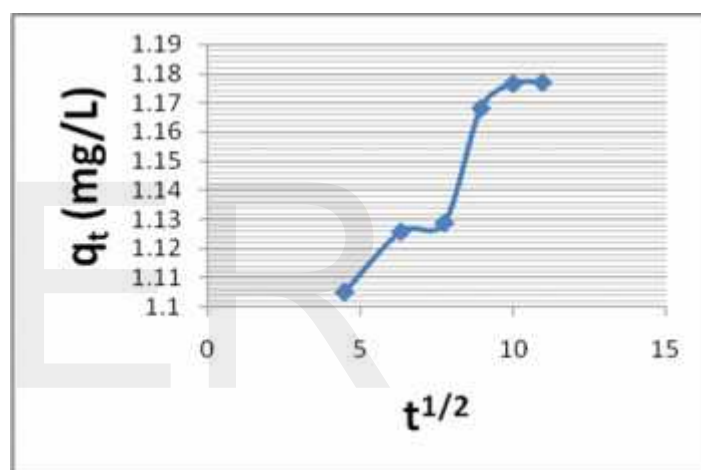


Fig. 1 Plot of adsorbate uptake q_t against $t^{1/2}$

The plot shows a curvature for the initial period, usually attributed to boundary layer diffusion effects [McKey[18] and Strivastave, [19]. The multilinearity of the plots indicates the presence of two or more steps taking place. The first sharper portion is the instantaneous adsorption stage (External adsorption), the second portion is the gradual adsorption stage where intra particle diffusion is the rate limiting, and the third portion is the final equilibrium stage, where intra-particle diffusion starts to slow down due to extremely low MB left in the solution. [Michael][6], carefully examination of the plot observed that the third stage is the limiting step. Extrapolation of the plot, gives the intercept, which provides the measure of the boundary layer thickness. Kannan [20], noted that the larger the value of Ct, the greater the boundary effect.

3.4 Adsorption Rate Constants

The sorption kinetic of the experimental data was evaluated in terms of the rate of adsorption. The adsorption constants were evaluated using the following kinetic models.

3.5 Kinetic Model

First Order Models: The sorption kinetic may be described by a simple first order equation. The change in bulk concentration of the system was done using the simple first order rate equation.

$$C_t = C_o e^{kt} \quad (9)$$

This can be re-arranged to obtain the linear form

$$\text{Log} C_t = \frac{K_1 t}{2.303} + \text{Log} C_o \quad (10)$$

Where, C_o and C_t are the initial and final concentrations of the solute at time t in (mg/t), K_1 = first order rate constant (mm-In order to obtain the rate constant, a straight line plot of $\log C_t$ vs t at 30°C was made as shown in figure 2.

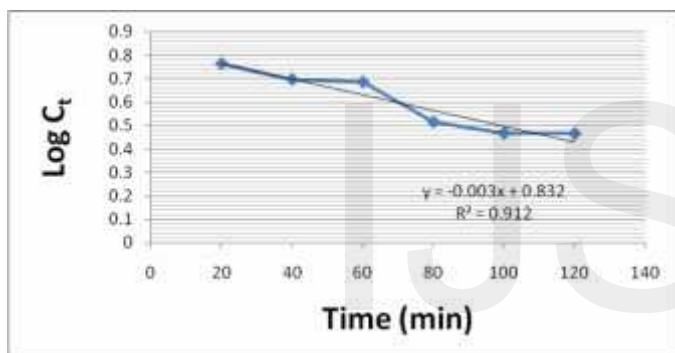


Fig. 2 Plot of $\log c_t$ vs t at 30°C

Near linear fit was observed, indicating that the kinetic model may be approximated by first order kinetic mode. The rate constant and co-efficient of determination are presented in table III.

Table III, Rate law constants and activation energy for the adsorption of MB by Enugu White Clay

1 st Order		Pseudo 1 st order		2 nd order		Pseudo second order	
K_1	-0.00678	K_p	-0.0576	K_2 (L/(mg.mm))	0.0021	K_{p2} (g/(mg.mm))	0.2279
C_o	6.531	q_e (mg/g)	0.5012	C_e (mg/L)	7.4174	q_e (mg/g)	1.2093
R^2	0.912	R^2	0.787	R^2	0.893	R^2	0.999
						E (J/Mil.k)	303.49

Pseudo-First order kinetic model

The pseudo first order kinetic was examined by the differential equation of [6]

$$\frac{d^2 t}{dt} = k_p (q_e - q_t) \quad (11)$$

Understanding the above equation for the boundary condition $t = 0$ and $q_t = q_e$

$$\text{Log}(q_e - q_t) = \text{Log} q_e - K_p \frac{t}{2.303} \quad (12)$$

Where, q_1 = amount of solute adsorbed at equilibrium (mg/g), q_t = amount of solute adsorbed at time t (mg/g)
 k_p = pseudo first order equilibrium adsorption constant (min^{-1}), t = time

In order to obtain the rate constant, linear plot of $\log (q_e - q_t)$ vs t was made, (Fig. 3).

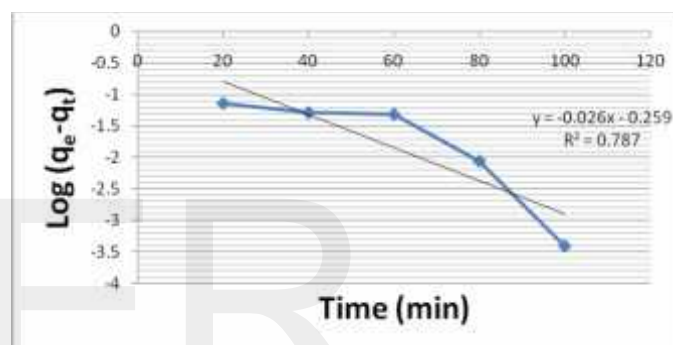


Figure 3 Pseudo – 1st order kinetic model.

Second Order Kinetic Model:

The typical second order rate equation [Octave][21], was used.

$$\frac{dC_t}{dt} = k_2 C_t^2 \quad (13)$$

Integrating when $C_t = 0$, $t = 0$ and $C_t = C_t$ at $t = t$

$$\text{Implies that } \frac{1}{C_t} = k_2 t + \frac{1}{C_D} \quad (14)$$

C_o and C_t (mg/L) are initial and final concentration of solute.

In order to obtain the rate constant K_2 , linear plot of $1/C_t$ vs t was made as shown in figure 4.

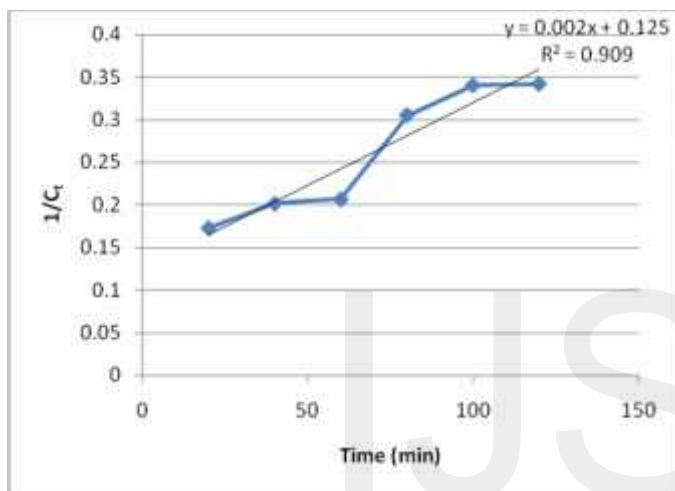


Fig. 4 Linear plot of $1/C_t$ vs t

Near Linear fit was observed indicating that the kinetic model may be approximated by the second order kinetic model. The adsorption rate constant and coefficient of determination are presented in table III.

Pseudo-Second Order Kinetic Model

Here, it is assured that the adsorption capacity is proportional to the number of binding sites occupied on the adsorbent, [Horsfall][22], and the kinetic model becomes,

$$\frac{dq_t}{dt} = k_{p2}(q_e - q_t)^2 \quad (15)$$

Integrating for boundary conditions $t = 0$, $q_t = 0$, and $t = t$, when $q_t = q_t$ and re-arranging,

$$\frac{t}{q_t} = \frac{1}{k_{p2} q_e^2} + \frac{t}{q_e} \quad (16)$$

Where, t = time (minutes), q_t amount adsorbed at time t , in (mg/g), k_{p2} pseudo 2nd order rate constant [mg/(g.min)], q_e amount adsorbed at equilibrium (mg/g). The initial

absorption rate as $t \rightarrow 0$ can be defined by the Ho-constant (h_o) (H_o)[23] as

$$h_o = k_{p2} q_e^2 \quad (17)$$

The Linear plot of t/q_t vs t is shown in figure 5.

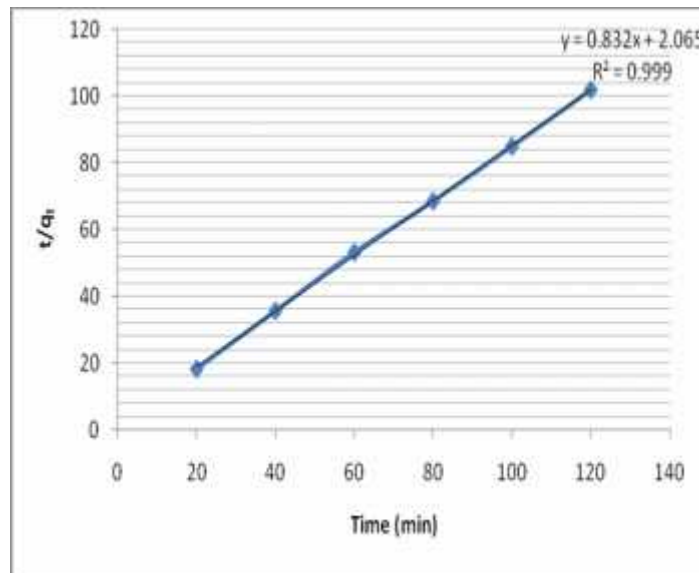


Fig. 5 Linear plot of t/q_t vs t

The initial adsorption rate, h_o , the equilibrium amount adsorbed, q_e , the pseudo-second order rate kinetic k_{p2} and the coefficient of determination r^2 were determined and presented in table III.

Figure 5 shows that the MB absorption by Enugu White Clay can be appropriately approximated by the pseudo - 2nd order kinetic model.

Elovic Kinetic Model: In Liquid phase adsorption reaction, the rate decreases with time due to an increase in surface coverage. One of the most useful models for describing such condition is the elovic model, [6],

$$\frac{dq_t}{dt} = \alpha \beta \exp(-\beta q_t) \quad (18)$$

Integrating and rearranging at $q_t = 0$, $t = 0$,

$$q_t = \frac{1}{\beta} \ln(\alpha) + \frac{1}{\beta} \ln t \quad (19)$$

The applicability of the Elovic model to the experimental data was tested by the linear plot of q_t vs $\ln t$, (Fig.6)

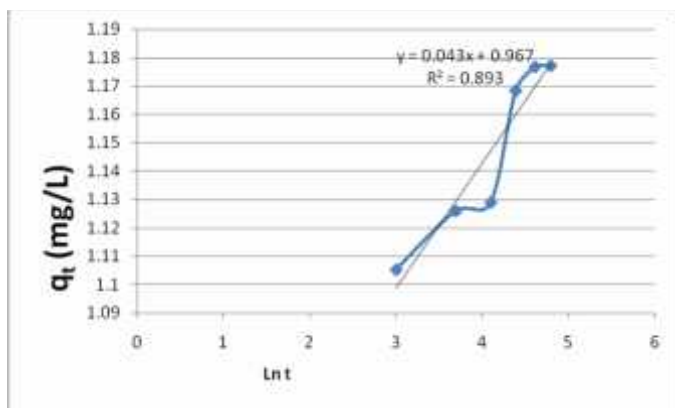


Fig. 6 linear plot of q_t vs $\ln t$

None linear fit was observed, indicating that the MB adsorption cannot be approximated by elovic kinetic model.

3.6 Evaluation of Activation Energy

The pseudo second order adsorption rate constant was used to evaluate the activation energy using an Arrhenius form equation [6],

$$K_{p2} = h_0 \exp (-\Sigma/RT) \quad (20)$$

K_{p2} pseudo second order rate constant, h_0 initial pseudo second order rate constant, Σ activation energy, R gas constant (8.314 J/K.Mol) T absolute temperature (303K or 30°C).

The value of E , was computed from the above equation and presented in table III. The activation energy is positive indicating endothermic reaction. That is, the adsorption of Methylene Blue by Enugu White Clay is favoured, Octave,[20] noted that the reactions with high activation energies are more temperature sensitive than those with lower activation energies. Therefore, the lower activation energy observed for MB adsorption by Enugu White Clay means that its sensitivity to temperature may not be too high.

3.7 Sorption Isotherms for Mb Adsorption By Enugu White Clay

The adsorption isotherms were studied at different temperatures of 30, 40, 50 and 60°C. The experimental data were investigated using Langmuir and Freundlich, adsorption isotherms, Fig 7

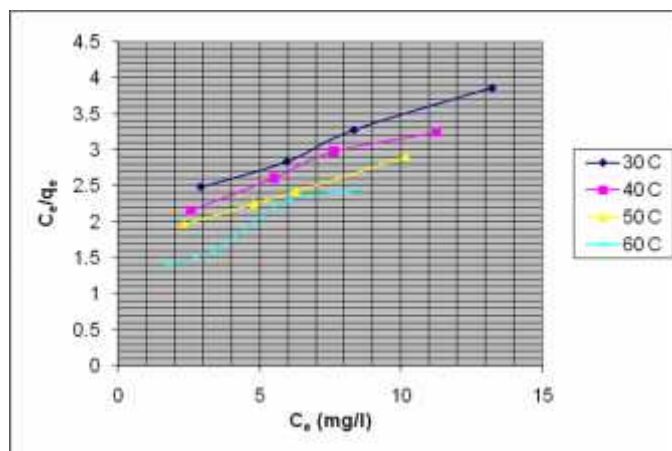


Figure 7, The Langmuir adsorption isotherms.

Figure 7, shows the Langmuir adsorption isotherms. The values of q_0 and k_L at different temperatures were obtained for the linear plot of C_e/q_e vs C_e and tabulated in table IV. The plot of $\ln q_e$ vs $\ln C_e$ is shown in figure 8.

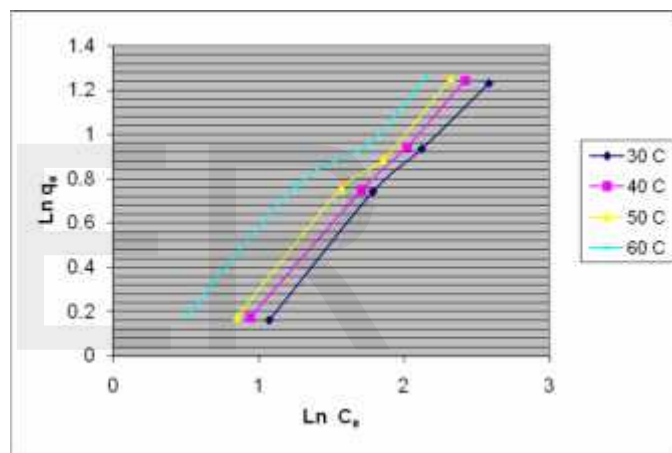


Fig. 8 The plot of $\ln q_e$ vs $\ln C_e$

The Freundlich constants k_f and n , which indicate the adsorption capacity and intensity were calculated from the slope and intercept of the plot as shown in table IV.

Table IV: Langmuir and Fredindlich adsorption Isotherms constants with their correlation coefficients.

T°C	Lensmuir			Freundlich		
	K_L	q_0	R^2	k_f	$1/n$	R^2
30	0.067	6.800	0.993	0.5599	0.7273	0.993
40	0.085	8.571	0.964	0.6188	0.8800	0.999
50	0.072	8.571	0.999	0.7261	0.9714	0.993
60	0.125	6.667	0.934	0.7711	0.6617	0.985

It was observed that k_f increases with temperature. The increase in the values of k_f with increases in temperature confirm, that the MB adsorption was favoured by

temperature. From table IV, it can be seen that the correlation factor r^2 is close to unity for both models, indicating that the experimental results can be approximated by Langmuir or Freundlich Isotherm.

In order to understand the nature of the adsorption of MB by Enugu White Clay very well, thermodynamic parameters such as free energy change, (ΔG) enthalpy change (ΔH) and entropy change (ΔS) were evaluated. These parameters for the adsorption were evaluated by considering the equilibrium constants under different experimental conditions. They were calculated using the following equations [Sirichote][24]

$$\Delta G = -R \ln K_d (T) \quad (21)$$

$$\Delta G = \Delta H - T\Delta S \quad (22)$$

Combining the two equations and rearranging,

$$\ln K_d = \frac{S}{R} - \frac{H}{RT} \quad (23)$$

k_d is the ratio of the amount adsorbed (mg/g) to the adsorptive concentration (mg/L).

R is the universal gas constant, T is absolute temperature.

The linear plot of $\ln K_d$ vs $1/T$ is shown in figure 9.



Fig. 9: Graph of $\ln K_d$ Vs $1/T$

The enthalpy change (ΔH) and entropy change (ΔS) were calculated from the slope and intercept of the linear plot and presented in table V. The entropy change at different temperatures was evaluated from equation 21 and presented in table V. The negative value for entropy change indicate decrease in the degree of freedom. The positive value of the free energy indicate non-spontaneous process.

Table V

Temp °C	$-\Delta G$ (kJ/mol.K)	ΔH (J/Mol)	ΔS (J/mol. K)
30	8.656		
40	9.694	748.26	30.9697
50	10.003		
60	10.313		

4.0 CONCLUSION

The results show that Enugu White Clay could be used as an effective adsorbent for the removal of pigments like methylene blue from aqueous solution. The removal efficiency was very high and fast. The kinetic of methylene blue adsorption can be best approximated to pseudo second order kinetic model. The equilibrium isotherm for the MB adsorption agrees with both langmuir and Freundlich isotherm and the adsorption was favoured by increase in temperature.

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