Kinetics and Isotherm Studies on the removal of Methylene Blue Dye and Lead (II) Ion from Aqueous solution and Wastewater using Activated Carbon from African apple (Udara) seed.

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ABSTRACT: The *removals of Methylene blue dye and heavy metal (Pb^{2+}) from aqueous solution and waste water effluent by adsorption using activated carbon from African apple (Chrysophyllum Albidum) have been investigated. The studies were conducted at 35˚C. The adsorption data were analyzed using the Langmuir, Freundlich and Temkin Isotherm Models at different temperatures (30˚C, 40˚C and 50˚C). The Freundlich isotherm model gave the best fit of the adsorption data obtained among the three isotherm models, thereby signifying a monolayer adsorption. The Freundlich isotherm model confirmed the exothermic nature of the adsorption process. The data were also analyzed in terms of their kinetics behaviors, the R^2 value of 0.948 showed that the Pseudo-first-order kinetics fits very well the Lead (II) ion adsorption data, while the R^2 value of 0.998 showed that the Pseudo-second-order kinetics fits the adsorption of the Methylene blue dye.*

Key Words: Adsorption, Lead (II) Ion, Methylene blue dye, Activated Carbon, Udara Seed, Isotherm models.

1.0 Introduction

Environmental pollution control has been a concerned issue in many countries. The most concerned environmental pollution is air pollution and wastewater pollution. Air pollution usually comes from open burning especially the forest and vehicles combustion systems while wastewater pollution comes from the industrial effluent and also from the domestic sewage [1]. Wastewater pollution gives bad effects on public water supplies which can cause health problem such as diarrhea. Air pollution can cause lung diseases, burning eyes, and cough and chest tightness. Contamination of the environment from a variety of sources has become an increasingly serious problem in recent years. Heavy metal pollution is an environmental problem of worldwide concern [2]. The heavy metals such as lead, copper, cadmium, zinc and nickel are among the most common pollutants found in industrial effluents [3]. Even at low concentrations, these metals can be toxic to organisms, including humans.

According to the World Health Organization, the most toxic metals are aluminum, chromium, magnesium, iron, cobalt, nickel, copper, zinc, cadmium, mercury and lead [2]. The removal of heavy metals from waters and waste-waters is important in terms of protecting public health and environment owing to their accumulation in living tissues throughout the food chain as non-biodegradable pollutants. Heavy metal pollution is found to occur in various types of industrial wastewater such as these produced by metal plating facilities, mining operations, metallurgical engineering, battery manufacturing processes, the production of paints and pigments, electroplating, nuclear power plants, and ceramic and glass industries [2].

There are various methods of removing heavy metals including chemical precipitation, membrane filtration, ion exchange, liquid extraction or electro dialysis. However, these methods are not widely used due to their high cost and low feasibility for small-scale industries. In contrast, the adsorption technique is one of the preferred methods for removal of heavy metals because of its efficiency and low cost [5]. Adsorption is also recognized as an economic method to remove metal ions from aqueous solution [7]. The used economical and effective methods of removing heavy metals from waste water has resulted in the search for unconventional materials that may be useful in reducing the levels of accumulation of heavy metals in the environment [6].

Dyes have long been used in dyeing, paper and pulp, textiles, plastics, leather, cosmetics and food industries. Colour stuff discharged from these industries poses certain hazards and environmental problems. These coloured compounds are not only aesthetically displeasing but also inhibiting sunlight penetration into the stream and affecting aquatic ecosystem. Dyes usually have complex aromatic molecular structures which make them more stable and difficult to biodegrade [11]. Furthermore, many dyes are toxic to some microorganisms and may cause direct destruction or inhibition of their catalytic capabilities. Textile industry use dyes and pigments to colour their product [8]. There are more than 100,000 commercially available dyes with over 7×10^5 tonnes of dyestuff are produced annually. Many types of dye are used in textile industries such as direct, reactive, acid and basic dyes [2]. Most of these dyes represent acute problems to the ecological system as they are considered toxic and have carcinogenic properties, which make the water inhibitory to aquatic life. Due to their chemical structure, dyes possess a high potential to resist fading on exposure to light and water. The main sources of wastewater generated by the textile industry originate from the washing and bleaching of natural fibers and from the dyeing and finishing steps.

Given the great variety of fibers, dyes and process aids, these processes generate wastewater of great chemical complexity and diversity, which are not adequately treated in conventional wastewater treatment Plant [6].

There are various conventional methods of removing dyes including coagulation and flocculation, oxidation and membrane separation. However, these methods are not widely used due to their high cost and economic disadvantage [15]. Chemical and electrochemical oxidations, coagulation are generally not feasible on large scale industries. In contrast, an adsorption technique is by far the most versatile and widely used [10].

In this study, the use of waste biomass of activated carbon as low-cost adsorbents, impregnated with two activation agents (phosphoric acid and sodium chloride salt) for the removal of heavy metal (Pb^{2+}) and Methylene blue dye from wastewater were investigated.

2.1 Materials and Method

2.1.1. Preparation of Raw Materials

The African apple/Udara (*chrysophyllum Albidum)* seeds fiber were sourced locally and then processed as follows; they were cut into definite smaller sizes and then carefully sorted out to remove every debris and contaminants. They were sun dried and kept inside a polythene bag ready for further analysis.

2.1.2. Waste Water Effluent for Heavy Metal and Aqueous Methylene blue dye solution.

The waste water effluent was collected from United Textile Industry Oshodi in Lagos State western province of Nigeria. It was then analyzed to establish the presence of any heavy metal and the presence of Lead (Pb^{2+}) was confirmed**.** Also aqueous solution of Methylene blue dye was prepared by contaminating clean water with Methylene blue dye in the laboratory to a known concentration. Then

adsorption experiments were carried out using the activated carbons from Udara seeds.

2.1.3. Production and Treatment of Activated Carbon

The dried fibers were washed thoroughly with distilled water to remove dirts. They were then dried in the oven at 105˚C for 2 hours. The samples were then removed, crushed properly using the mortar and pestle to obtain a uniform grain particle size of about 10mm/mg and 2mm wide, sieved and properly stored in a container. The samples were soaked in 60 % H_3PO_4 acid in weight ratio of 1:1 for 24 hours at room temperatures washed with distilled water until a pH of 7, dried in the oven at 105˚C for 24 hours. The samples were allowed to cool to room temperatures sieved to different particle sizes and stored in air tight container

2.2. Batch Adsorption Studies

The adsorption experiments were performed by taking 100 ml stock solution of the wastewater effluent and dye (10 mg/l) and treated with 0.2g of adsorbent dosage. After the desire time of treatments, samples were filtered to remove the adsorbent and progress of adsorption was determined spectrophometrically at the absorbance of 498nm. The experiment was conducted at room temperature (25˚C). The samples were equilibrated for about 2 hours and then withdrawn, filtered using the Wattman filter paper and then analyzed. Each of the parameters were singled out and varied while the other was kept constant and their results taken.

The amount of dye adsorbed was calculated based on mass balance equation as given by the equation;

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

Where;

q_e = The equilibrium adsorption capacity per gram dry weight of the adsorbent (mg/g).

C_o = Initial concentration of dye in the solution (mg/l).

C_e = Final or equilibrium concentration of dye in the solution (mg/l).

V = Volume of the solution (L)

W = The dry weight of adsorbent (g)

The percentage removal (%) was calculated for each equilibrium state as:

$$\text{Percentage removal (\%)} = \frac{C_o - C_e}{C_o} \times \frac{100}{1}$$

3.1 Results and Discussion

3.2 Isotherm Studies

Adsorption isotherm is a relationship between the amount of a substance removed from liquid phase by unit mass of adsorbent and its concentration at constant temperature. They are useful in the evaluation of the adsorption capacity and to determine the characteristics of an adsorbent if suitable for application. Isotherms are often used as empirical models which do not make statements about the underlying mechanisms and measured variables. They are obtained from measured data by means of regression analysis. The most frequently used isotherms are the Langmuir isotherm, Freundlich isotherm, Temkin isotherm, etc.

3.2.1 Langmuir isotherm model

The Langmuir isotherm is based on the theoretical principle that only a single adsorption layer (monolayer) exist on an adsorbent. It assumes that all active sites on the adsorbent are homogenous and there is no interaction between active sites [8][20].

The linear form of Langmuir equation is given as;

$$\frac{C_e}{q_e} = \frac{1}{ab} + \frac{1}{a} C_e$$

Where;

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

q_e= The adsorption capacity at equilibrium (mg/g).

The constant '**a**' signifies the maximum adsorption capacity (mg/g) when monolayer is complete and '**b'** is related to the affinity of the binding sites. When C_e/q_e was plotted against C_e, a straight line graph with slope of 1/a is obtained. The Langmuir constants **b** and **a** are calculated using the slope and intercept (constant) from the graph.

The essential feature of the Langmuir isotherm to identify the feasibility and the favorability of the adsorption process expressed by a dimensionless constant called Separation factor **(RL)** was adopted. The separation factor (RL) was calculated in each case using the equation below:

$$RL = \frac{1}{1+bC_o}$$

Where, C_o is the initial dye concentration (mg L^{-1}).

B = the Langmuir constant

The value of RL indicates the type of the isotherm to be either

a. Unfavorable = (RL >1)

b. Favorable = (O< RL <1)

c. Linear = (RL =1)

d. Irreversible = (RL < 1)

Equally, the regression coefficient $\boldsymbol{R^2}$ was used to further analyze and determine the suitability and conformity of the isotherms on how they fit into the models. The closeness of the $\boldsymbol{R^2}$ value to 1.0 determines its level of fit. As calculated, the RL values and the R^2 values of the Langmuir isotherm at the different temperatures are shown below;

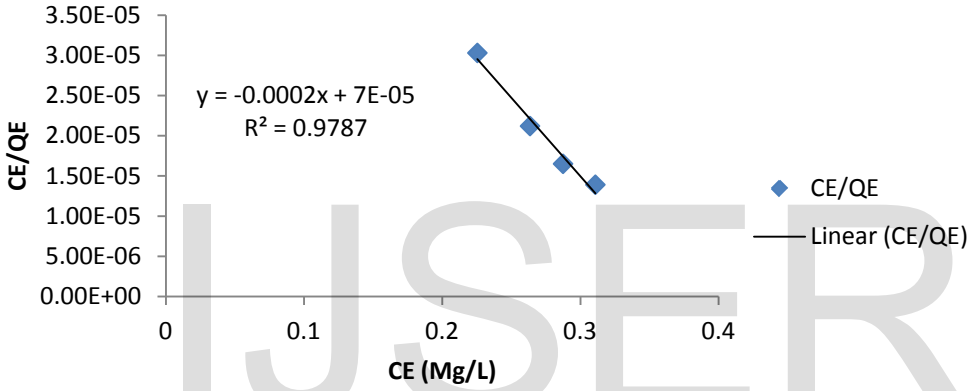

Fig. 3.1: Langmuir isotherm at 30˚C for Methylene blue dye adsorption.

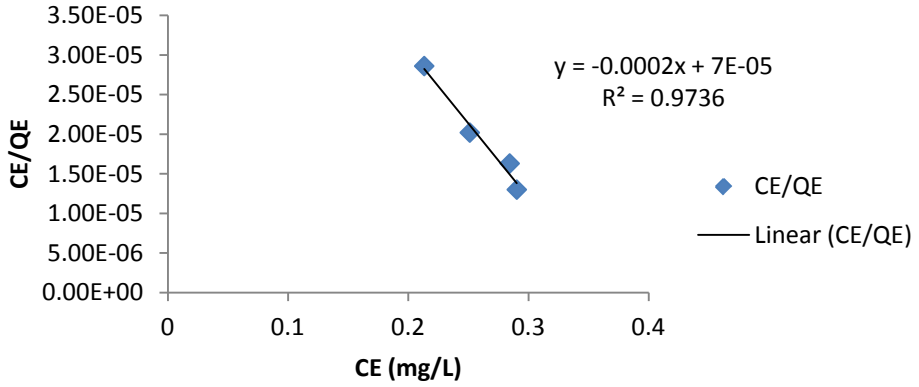

Fig. 3.2: Langmuir isotherm at 40°C for Methylene blue dye adsorption.

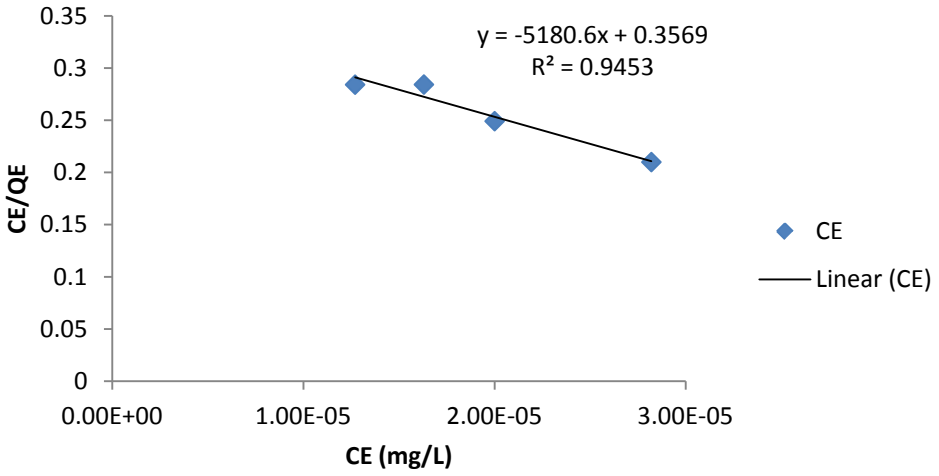

Fig. 3.3: Langmuir isotherm at 50˚C for Methylene blue dye adsorption.

Table 3.1: For Methylene blue adsorbed with *chrysophyllum Albidum (Udara)*:

Langmuir isotherm	RL	R^2
30˚C	0.9965	0.978
40˚C	0.9950	0.973
50˚C	0.8931	0.945

Table 3.2: For Heavy metal (Pb^{2+}) adsorbed with *chrysophyllum Albidum (Udara)*:

Langmuir isotherm	RL	R^2
30˚C	0.999	0.972
50˚C	0.999	0.9733

From the results shown above, Langmuir isotherm at 30˚C and 40˚C gave very good fits for Methylene blue dye; 30˚C and 50˚C for Lead (II) ion adsorption respectively. This is basically owing to the fact that its R^2 value was the closest to

1.0. Equally the RL values fitted into the favourable correlation range (0<RL<1) 0< 0.9965 < 1 except for 50˚C.

3.2.2 Freundlich Isotherm

This isotherm is an empirical equation employed to describe heterogeneous system. Freundlich isotherm is also applied to plot the equilibrium of the adsorption.

The linear form of Freundlich equation can be expressed as;

$$\text{Ln } qe = \text{In}k_f + (I/n)\ \text{In } Ce$$

Where;

q_e=the amount of adsorbate adsorbed per unit mass of adsorbent (mg/g)

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

$\boldsymbol{k_f}$ and **n** are isotherm constants; where k_f indicates the adsorption capacity of the adsorbent which can be defined as the adsorption or distribution coefficient, **n** represents the quantity of the adsorbate adsorbed onto the activated carbon for a unit equilibrium concentration.

The Freundlich isotherm is determined by plotting the graph of **In** q_e against **In** C_e. Linearising the Freundlich isotherm model, Ink_f and 1/n are determined as the Freundlich constant and slope respectively. The slope 1/n ranges between 0 and 1; it is a measure of the adsorption intensity or surface heterogeneity. The k_f, n and R^2 values of the Freundlich isotherm at the 3 temperature values are shown below;

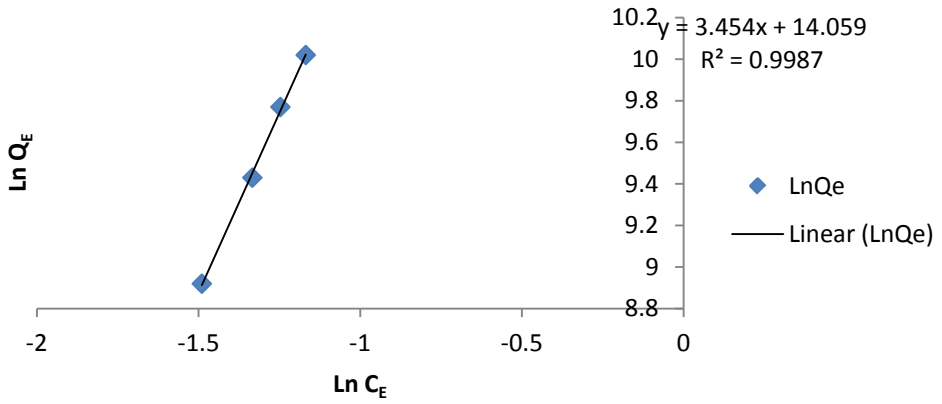

Fig. 3.4: Freundlich isotherm at 30˚C for Methylene blue dye adsorption.

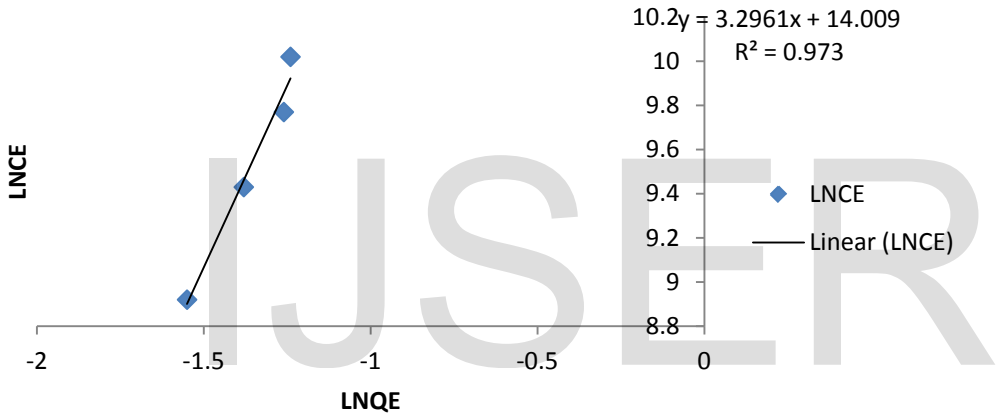

Fig. 3.5: Freundlich isotherm at 40˚C for Methylene blue dye adsorption.

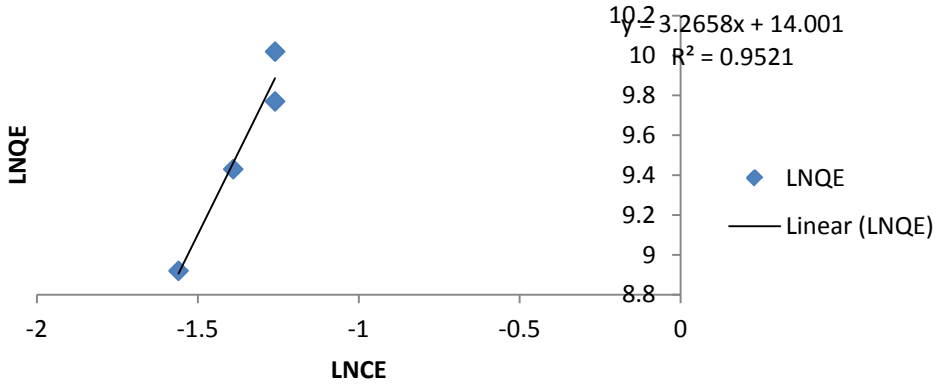

Fig. 3.6: Freundlich isotherm at 50˚C for Methylene blue dye adsorption.

Table 3.3: For Methylene blue dye adsorption with chrysophyllum Albidum (Udara):

Freundlich isotherm	K_f	n	R^2
30˚C	1.28×10^7	0.2895	0.998
40˚C	1.21×10^7	0.3034	0.973
50˚C	1.20×10^7	0.3062	0.952

Table 3.4: For heavy metal adsorption with *chrysophyllum Albidum (Udara)*:

Freundlich isotherm	K_f	n	R^2
30˚C	4.95×10^6	0.60	0.994
50˚C	2.46×10^6	0.81	0.996

From Table 3.3 and 3.4 respectively, the k_f values decreased with increasing temperature which indicates an exothermic process. The values of the correlation coefficient also lie in the acceptable range of $R^2 > 0.90$, showing that the Freundlich isotherm can be used to fit this experimental data. Equally the value of $n > 1$ represents favourable adsorption. The values of **n** (adsorption intensity) obtained were between 0 and 1; further indicating favourable and beneficial adsorption.

3.2.3The Temkin Isotherm Model

The Temkin isotherm equation suggests a linear decrease of sorption energy as the degree of completion of the sorptional center of an adsorbent is increased. This model takes into account the presence of indirect adsorbate/adsorbent interaction

and suggests that because of these interactions, the heat of adsorption of all molecules in the layer would decrease linearly with coverage [12]

The Temkin isotherm has been used in the form

$$q_e = \left(\frac{RT}{bt}\right) L_n K_T C_e$$

Where $BT = \left(\frac{RT}{bt}\right)$

R = Universal gas constant (8.314 J/mol.K)

T =Absolute temperature (K) (25˚C+273K)

To linearise the Temkin isotherm model, a graph of q_e versus Inc_e gives a straight line which enable the determination of the isotherm constants K_T and B_T. K_T is the equilibrium binding constant (L/mg) corresponding to the maximum binding energy, the value increased with increase in temperature for the adsorption system, suggesting a corresponding increase of maximum binding energy. B_T is related to the heat of adsorption.

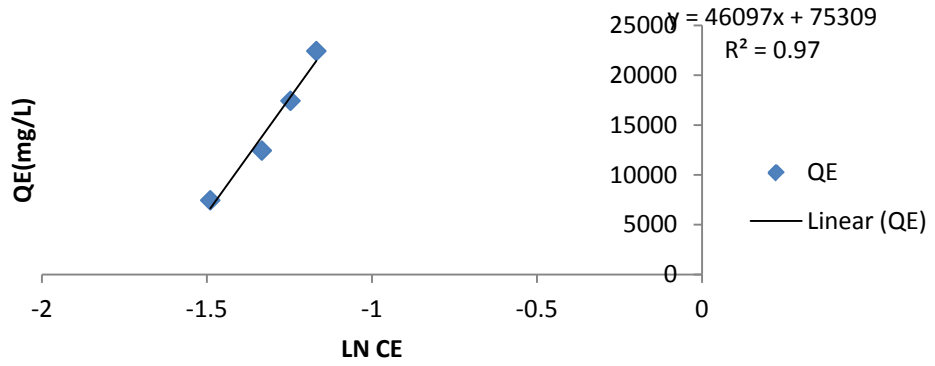

Fig. 3.7: Temkin isotherm at 30˚C for Methylene blue dye adsorption.

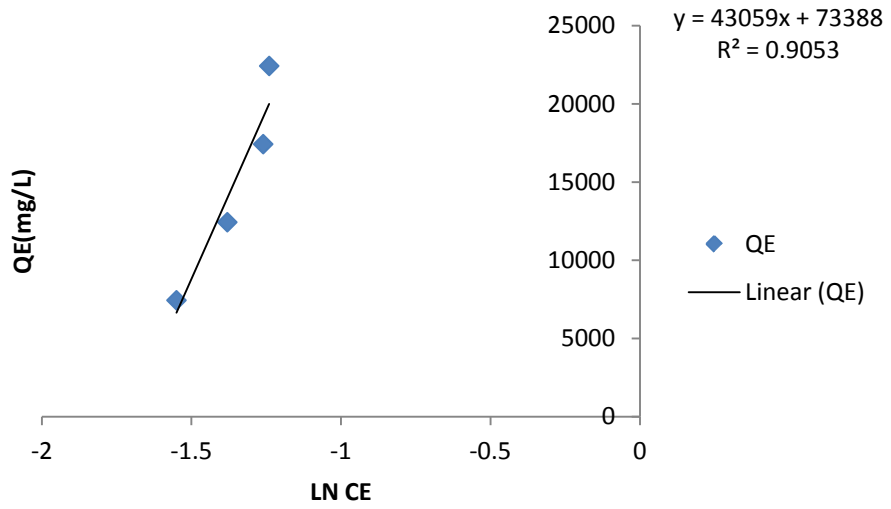

Fig.3.8: Temkin isotherm at 40˚C for Methylene blue dye adsorption.

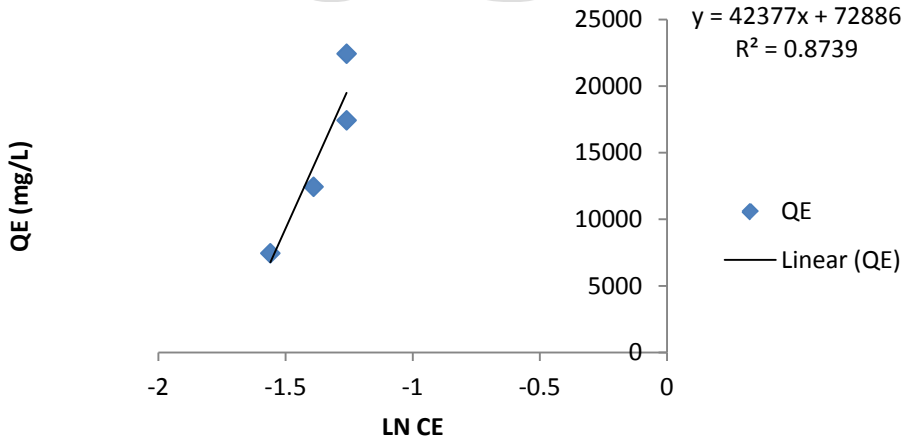

Fig. 3.9: Temkin isotherm at 50˚C for Methylene blue dye adsorption.

The correlation coefficients R^2 of about 0.873 and 0.905 indicate that adsorption did not fit best into Temkin isotherm. The correlation coefficient, R^2 from this work confirms that the Temkin isotherm does not fit into this work.

3.3 Batch Adsorption Kinetics Studies

In order to analyze the controlling mechanisms of the adsorption of Methylene blue dye and Lead (II) ion onto African apple seed activated carbon, a first-order, pseudo-first-order equation, pseudo- second order equation were used to study the adsorption data as discussed below;

3.3.1. First-Order Kinetics

The first -order kinetics model equation is given by:

$$I_n \frac{C_t}{C_o} = k_{it}$$

The plot of ln (c_t/c_o) versus t gave a linear relationship from which k_i was determined. From the correlation coefficient R^2 value, the first-order kinetics didn't fit this model.

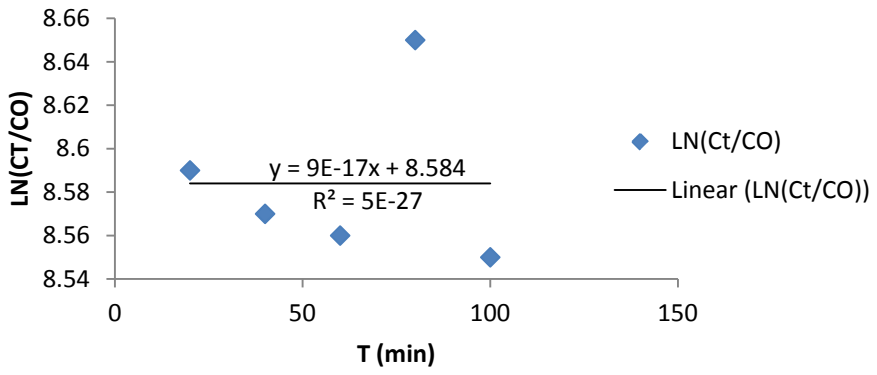

Fig. 3.10: First order kinetics for Methylene blue adsorption

3.3.2 Pseudo – First Order Kinetics

The pseudo-first-order kinetics equation is written as;

$I_n(q_e - q_t) = \ln q_e - K_{it}$

K_J = The rate constant of the pseudo-first order adsorption (1/min).

q_t and q_e = The adsorption amount at time, t_1 and at equilibrium (mg/g).

Values of the quantities k_1 and q_e were obtained from the slope and the intercepts of the plot of the graph of ln $(q_e - q_t)$ versus t. From the values of the correlation coefficient R^2, the pseudo-first-order fits better in the adsorption model for Lead (II) ion adsorption than in the Methylene blue dye adsorption process. Equally, the equilibrium adsorption capacity, q_e decrease with increase in temperature, confirming that the process was exothermic.

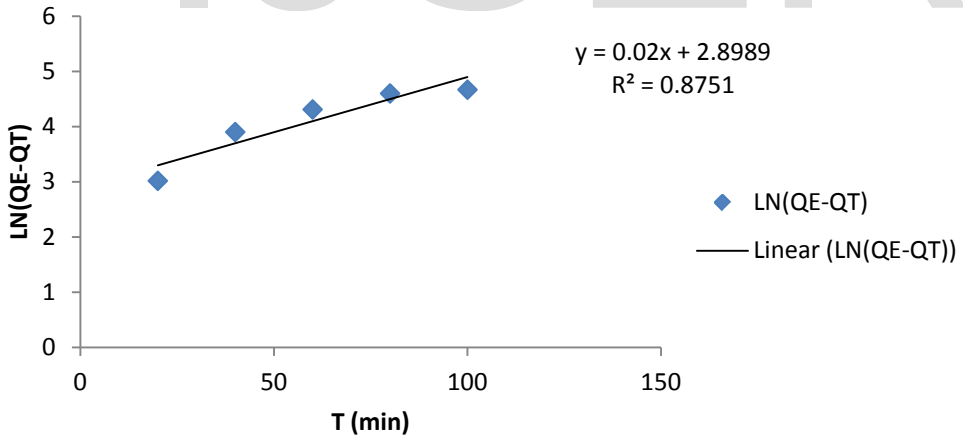

Fig. 3.11: Pseudo-first order kinetics for Methylene blue dye adsorption.

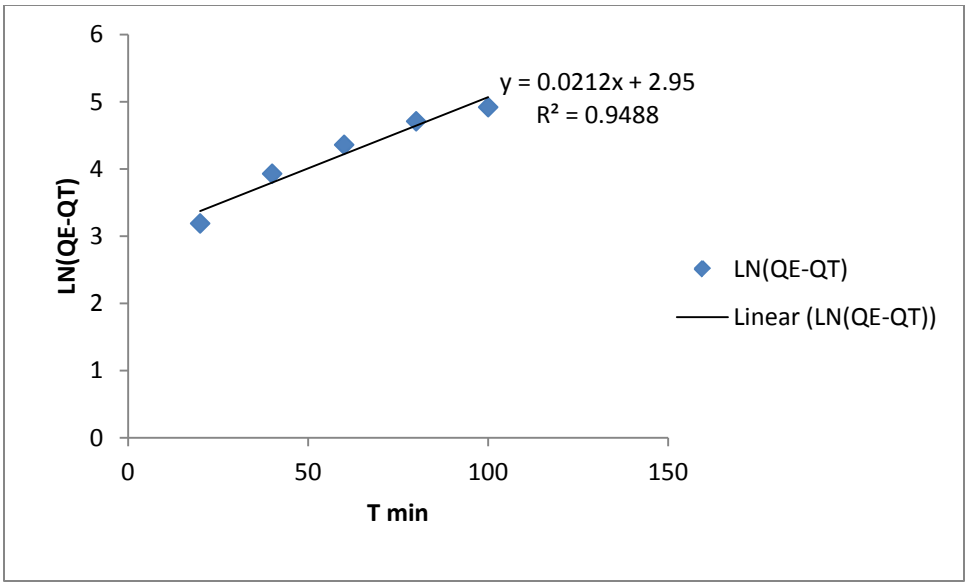

Fig. 3.12: Pseudo-first order kinetics for Lead (II) ion adsorption.

3.3.3 Pseudo-Second Order Kinetics

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

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e}$$

Where, k_2 is the rate constant of the pseudo-second order kinetics (g/mg.min). The slope and the intercept of the plots of the graph of t/q_e versus t were obtained to calculate k_2 and q_e. The R^2 value of the second-order kinetics was close to unity for Methylene blue dye adsorption, but did not fit well for heavy metal adsorption. Therefore, the pseudo-second order kinetics model fitted the Methylene blue dye adsorption than the heavy metal adsorption for both initial concentrations.

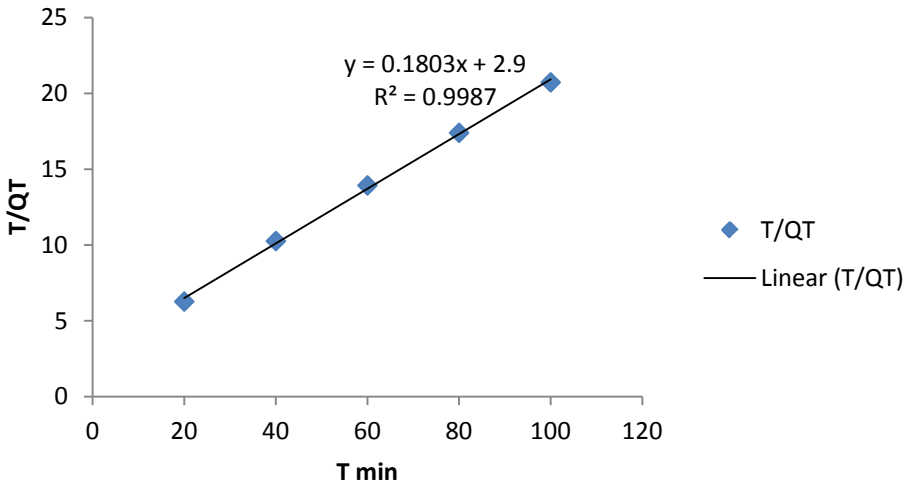

Fig. 3.13: Pseudo-Second Order kinetics for Methylene blue dye adsorption.

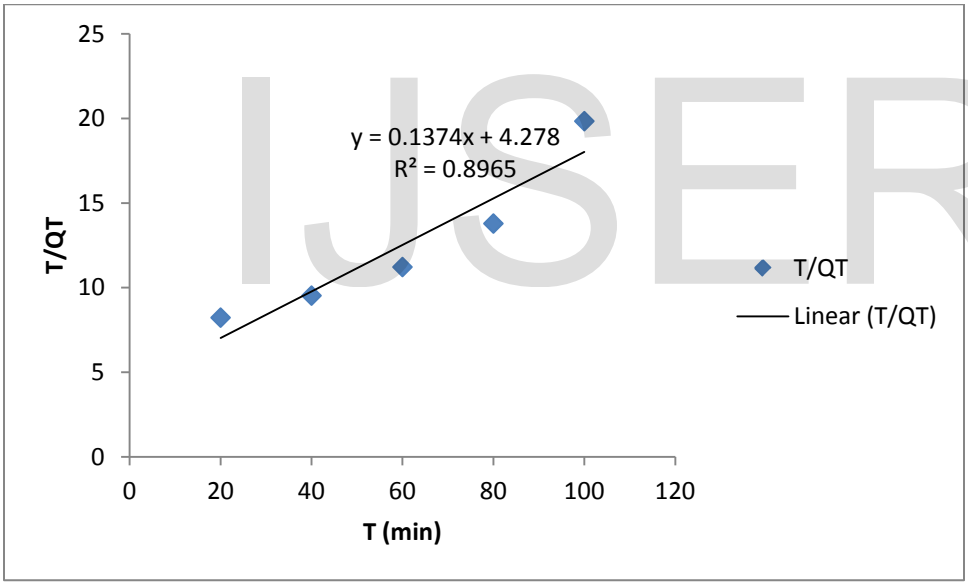

Fig. 3.14: Pseudo-Second Order kinetics for Lead (II) ion adsorption.

3.7 Conclusion

The present study showed that activated carbon prepared from *chrysophyllum Albidum (Udara)* seed is a promising adsorbent for the removal of Methylene blue dye and Lead (II) ion from aqueous solution over a wide range of concentrations.

The Freundlich isotherm model gave the best fit amongst the three isotherm models selected for this study at different temperatures as its R^2 values were the closet to 1.0. The pseudo-first-order kinetics fits better the adsorption model for heavy metal (Pb^{2+}) adsorption while the pseudo-second order kinetics fits the adsorption model for Methylene blue dye.

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