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KINETICS AND EQUILIBRIUM STUDIES OF ADSORPTION OF Pb AND Cu ON LOCAL CLAY SOIL SAMPLE

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Abstract

Kinetic studies of adsorption of Pb(II) and Cu(II) ions on local clays soil from Dan-Iyau Daddara in Jibiya Local Government Area of Katsina State have been studied using batch experimental method. The optimum parameters deployed for the equilibrium study are time of contact (50mins for both metal ions), adsorbent mass (0.6g for Pb, 0.8g for Cu) and adsorbate dosage (15mg/L for Pb, 20mg/L for Cu). The experimental data were correlated with adsorption Isotherm and kinetic equations using linear regression analysis. The plots of the amount of adsorbate adsorbed against equilibrium concentration or mass of dosage of clay or time showed two distinct segments; a straight line plot at low concentrations followed by a plateau portion at high concentration were observed. The adsorption isotherm data were adequately fitted with both Langmuir and Freundlich equations. The result of the adsorption kinetics reveals that the pseudo-second order model, appeared to be the best-fitting model for the sorption of Pb(II) and Cu(II). The investigations show that Daddara, Dan-Iyau clay could be an effective low-cost adsorbent for removal of Pb and Cu from waste water and industrial effluents.

Keywords: **kinetics, Equilibrium studies, Adsorption, Soil sample, Local clay**

1.0 Introduction

Due to its toxicological importance in the ecosystem, agriculture and human health, pollution by heavy metals has received wide spread attention in the recent years (Olaefe *et al.*, 2015). Heavy metals are naturally occurring elements that have a high atomic weight and a density at least 5 times greater than that of water (Tchounwou *et al.*, 2012). Their multiple industrial, domestic, agricultural, medical and technological applications have led to their wide distribution in the environment; raising concerns over their potential effects on human health and the environment (Vinodh *et al.*, 2011).

Lead is a heavy metal which poses serious health challenge to man in the environment. Adults absorb 35 to 50% of lead through drinking water and the absorption rate for children may be greater than 50%. In the human body, the greatest percentage of lead is taken into the kidney,

followed by the liver and the other soft tissues such as heart and brain. The nervous system is the most vulnerable target of lead poisoning. Headache, poor attention spam, irritability, loss of memory and dullness are the early symptoms of the effects of lead exposure on the central nervous system (ATSDR, 1999). Though Copper is an essential nutrient, its Short term exposure above the action level in drinking water can cause gastrointestinal distress. Long term exposure can cause liver or kidney damage.

Research on clay minerals has received considerable attention in recent times owing to their numerous industrial applications (Christian *et al.,* 2018). Due to the geometric increase in pollution indices of many towns in the developing countries, clays are being used for pollution control in engineered landfills as linings. Solid heterogeneous catalysts and adsorbents derived from clay are also becoming relevant in pollution control as they have been associated with the removal of heavy metals (Onyekuru *et al.,* 2018).

Deposits of this important raw material are widely distributed in Africa, especially, Nigeria. In spite of the extensive use and the demand for clay in industrial processes, chemical investigation of this mineral for their potentials for use in pollution control has received lesser attention (Christian *et al.,* 2018). This is important, in order to add value to this mineral resources as an industrial raw material for use in controlling hazardous chemicals been constantly released into the ecosystem, majorly from anthropogenic sources.

Adsorption is a major process responsible for accumulation of heavy metals. Therefore, the study of adsorption processes is of utmost importance for the understanding of how heavy metals are transferred from a liquid mobile phase to the surface of a solid phase (Nasrabadi *et al.,* 2017).

2.0 Materials and Methods

The adsorbents used in this study consisted of 5 clay samples collected from various points in Daddara Dan-Iyau in Jibiya Local Government Area of Katsina State. The map of local government area of sample collection is shown in fig. 1. The samples were sun dried for seven days in order to remove moisture. The particle size was reduced using a milling machine and sieved using meshes of different apertures in order to determine the mean particle size. Each of the sample sizes obtained was placed inside a clean dried container. The average particle size of 0.835mm was used.

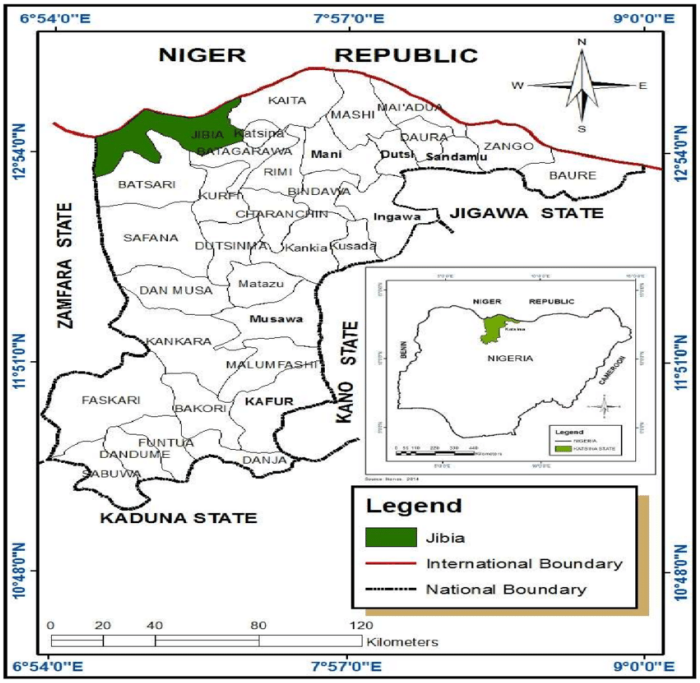

Fig. 1: Map of Local Government Area of Sample Collection.

Heavy metals chosen as the adsorbed materials in this study were Pb and Cu. The lab grades of Copper(II) nitrate, $Cu(NO_3)_2$ lead(II) nitrate, $Pb(NO_3)_2$ were all used in this experiment. The stock solutions of Pb and Cu were prepared by completely dissolving appropriate masses of each of their salts in 1 litre of distilled water each. The stocks were then serially diluted using (C_1V_1=C_2V_2) to obtain solutions between 5-35mg/L. The experimental technique was carried out in a batch adsorption.

1g of the adsorbent was added to each concentration between 5.0 to 35 mg/L, the resulting solutions were shaken continuously and left till the next day. It was filtered into a clean dried empty conical flask and labelled accordingly. The filtrates were taken for analysis of the metals (adsorbate concentrations) using already calibrated Atomic Absorption Spectrophotometer (AAS). AAS was well calibrated using standard solutions for each of the heavy metals.

50 ml solution was pipette from 35 mg/L solution into a conical flask followed by the dosage of different masses of the adsorbent between 0.2g to 1.2g and labeled accordingly. The resulting solutions were shaken continuously and left till the next day. Solutions were filtered into clean dried empty conical flasks and labeled accordingly. The filtrates collected in sample bottles were analyzed by the use of AAS. The effect of time was studied by following the aforementioned procedure using constant mass adsorbent and 35 ppm solution of adsorbate. Minimum of five sets were set up and each experiment terminated at a specific time between 10-70 minutes. The clear filtrate obtained in each case was analyzed by using AAS.

The amount of adsorbate adsorbed was calculated using the equation;

$$q_e = \frac{(C_o - C_{eq})V_{sol}}{M_s} \quad \text{(1)}$$

where q_e is the amount of adsorption of heavy metals per unit weight within soil (mg/g), C_n is the initial concentration of heavy metal solution (mg/l), C_{eq} is the equilibrium concentration of the solutions (mg/l), V_{sol} is the volume of solution (cm^3) and Ms is the mass of soil (g).

The adsorption isotherms were used to investigate the relationship between the concentration of sorbed species and sorption capacity of sorbing species (Sadia *et al.,* 2012). The data between *Ceq* and *q* were graphically plotted to obtain the adsorption isotherms. Though many mathematical models bound to represent the adsorption isotherm, the Freundlich and Langmuir isotherms were deployed in this work. Equations 2 and 3 gives the linear forms of Freundlich and Langmuir isotherm models, respectively

$$logq_e = logk_f + \frac{1}{n} logC_e \quad ---------(2)$$

$$\frac{1}{q_e} = \frac{1}{Q_{max}} + \frac{1}{b.Q_{max}} \frac{1}{C_e} \quad ----------(3)$$

Where,

qe is the equilibrium metal concentration sorbed in sorbent (mg/g), "*Ce*" is the metal equilibrium concentration in solution (mg L^{-1}). *Kf* is Freundlich constant related to the sorption capacity, and *I/n* is an empirical parameter related to sorption intensity, which varies with heterogeneity of the material. Q_{max} is the maximum possible amount of metal that can be adsorbed per unit dry weight of sorbent, *b:* Empirical constant, indicating the affinity of sorbent towards the sorbate.

2.1 Kinetic Parameters. The Lagergren's kinetics equation has been most widely used for the adsorption of an adsorbate from an aqueous solution. The Lagergren model may not reflect the true nature of kinetic study. It was applied due to its simplicity and good fit (Ho, 2004). The model is based on the assumption that rate is directly proportional to the number of free sites according to Lagergren equation:

$$\log (q_e - q_t) = \log q_e - \frac{k_t}{2.303} \quad ----------(4)$$

The pseudo-second-order model is based on the bio sorption followed by second-order mechanism nearby the rate of sorption is proportional to the square of number of unoccupied sites and can be represented as:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad ----------(5)$$

3.0 RESULTS AND DISCUSSION

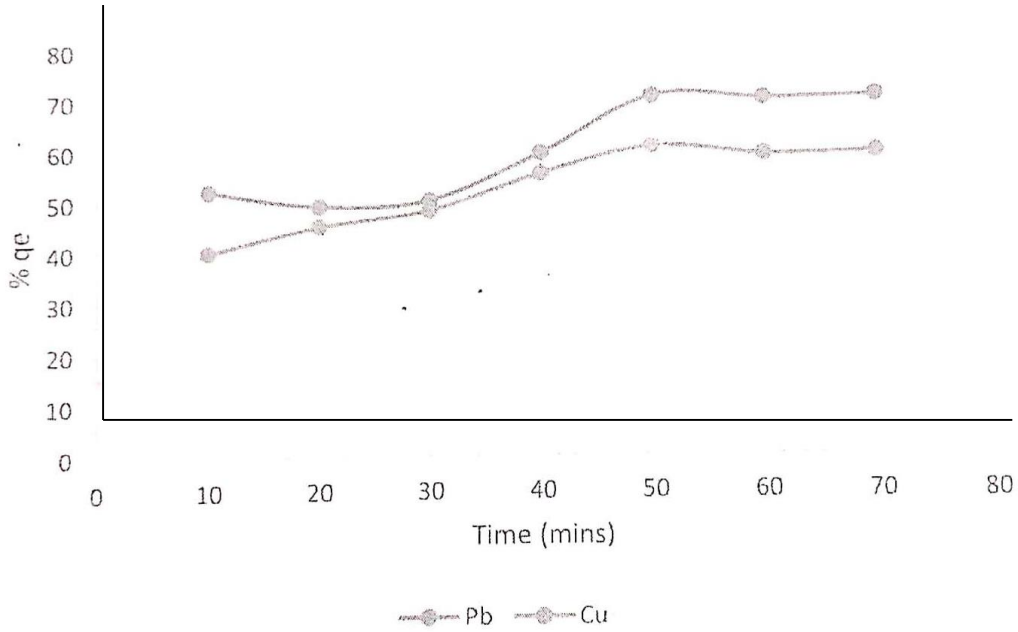

Figure 2: Effect of contact time on adsorption of metals by clay sample

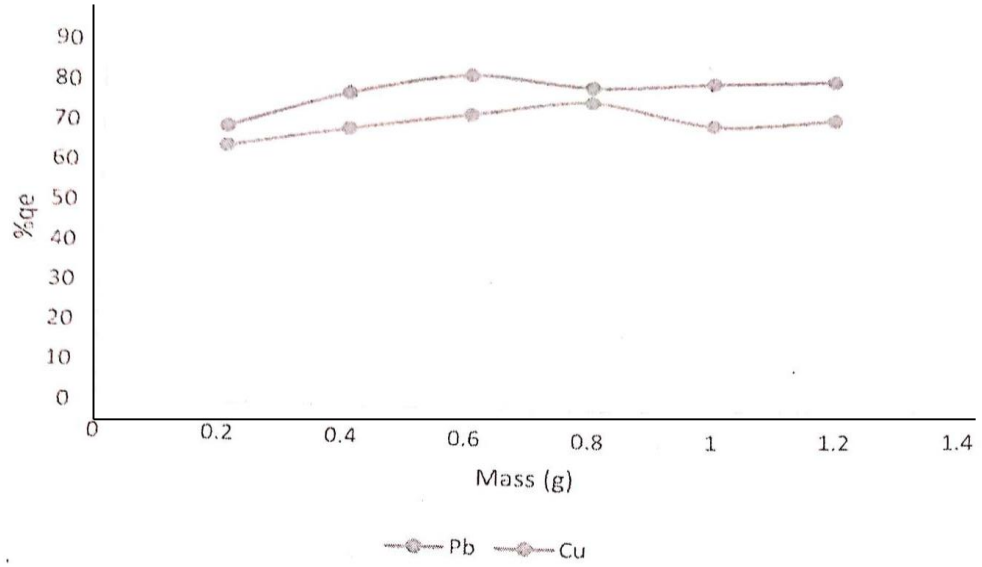

Figure 3: The effect of varied mass on the adsorption of the metal ions at constant adsorbate concentration

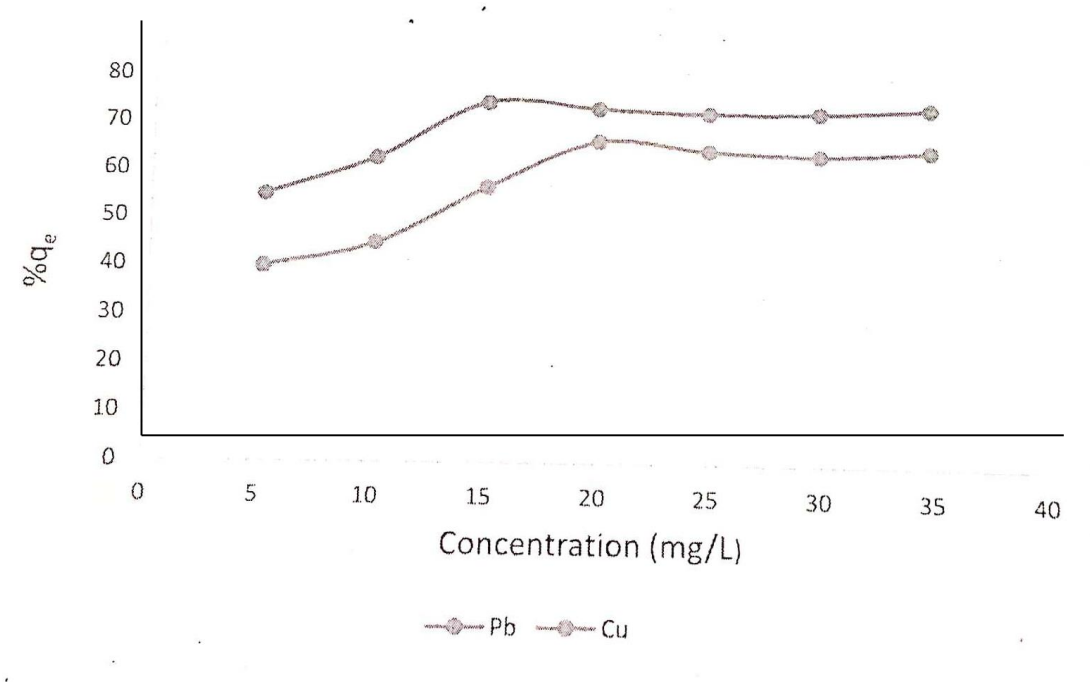

Fig. 4: Effect of concentration of the adsorbates on their adsorption by the adsorbent.

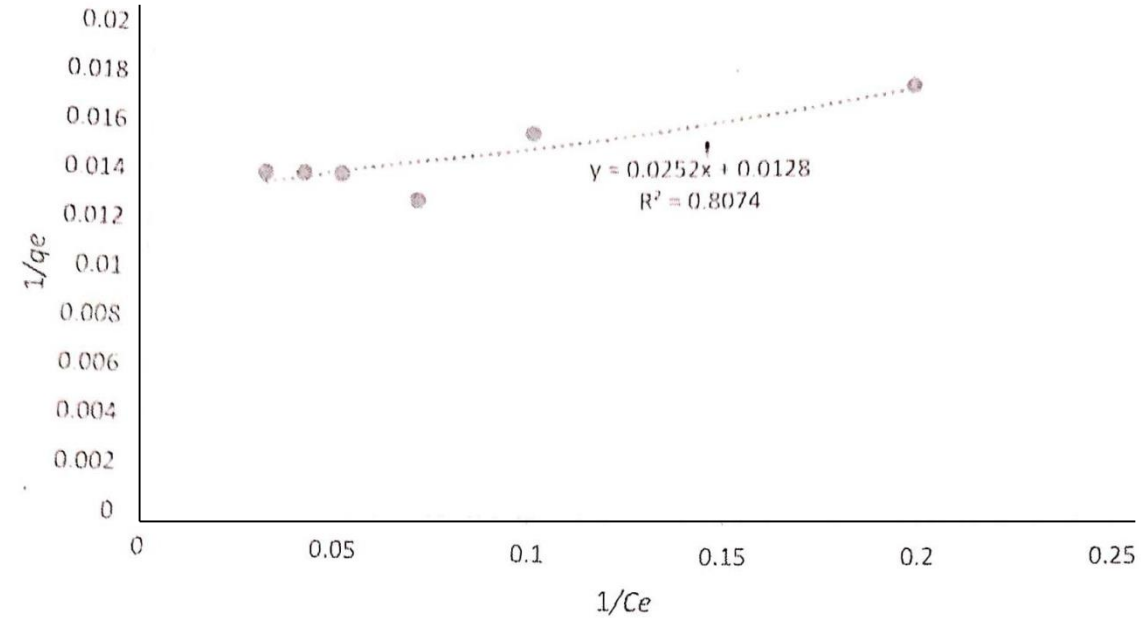

Figure 5: Langmuir Adsorption Isotherm plot for Pb

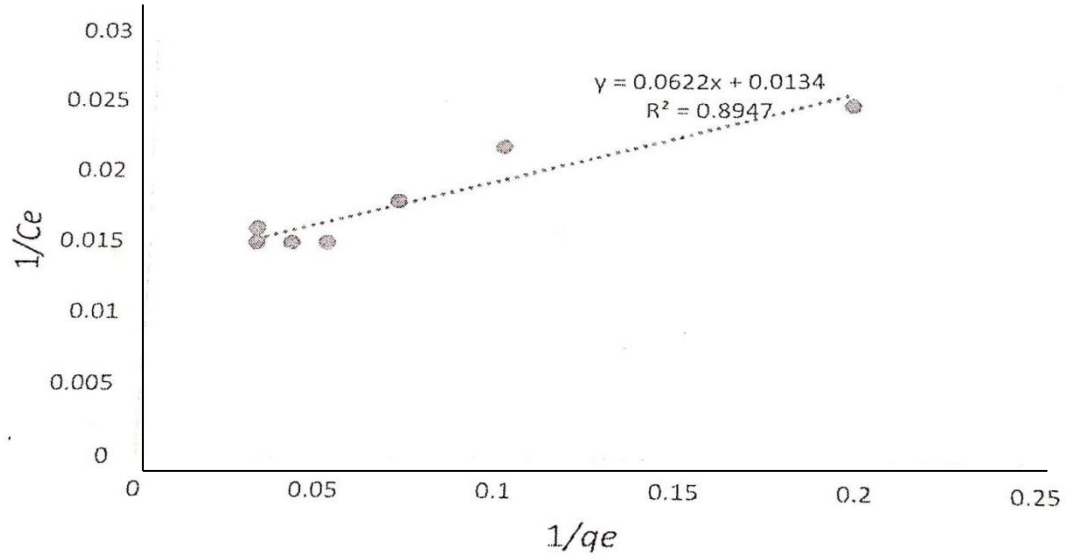

Figure 6: Langmuir Adsorption Isotherm plot for Cu

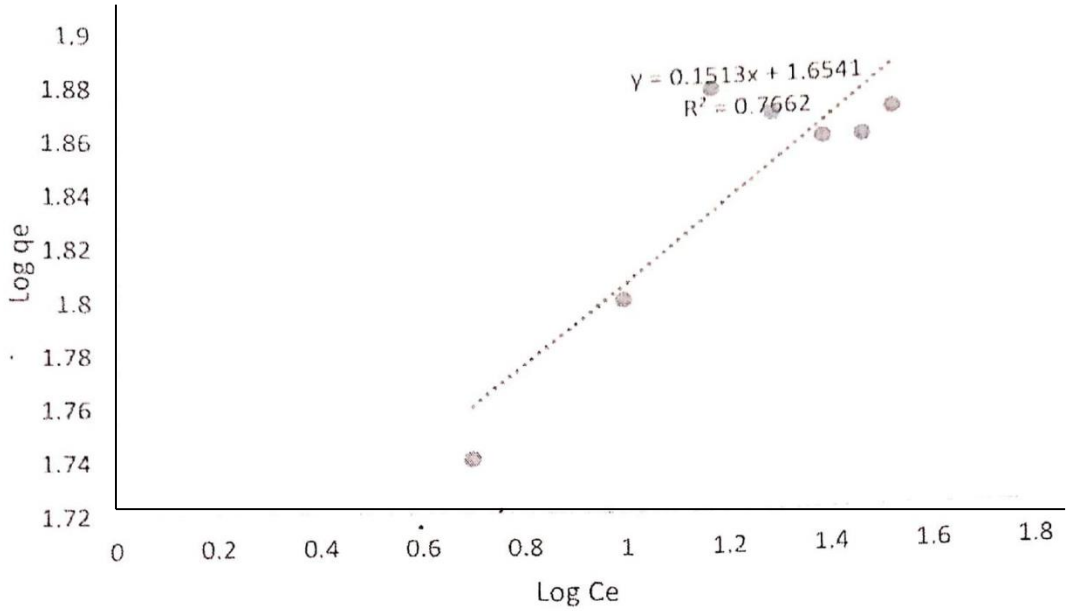

Fig. 7: Freundlich Absorption Isotherm Plot for Pb

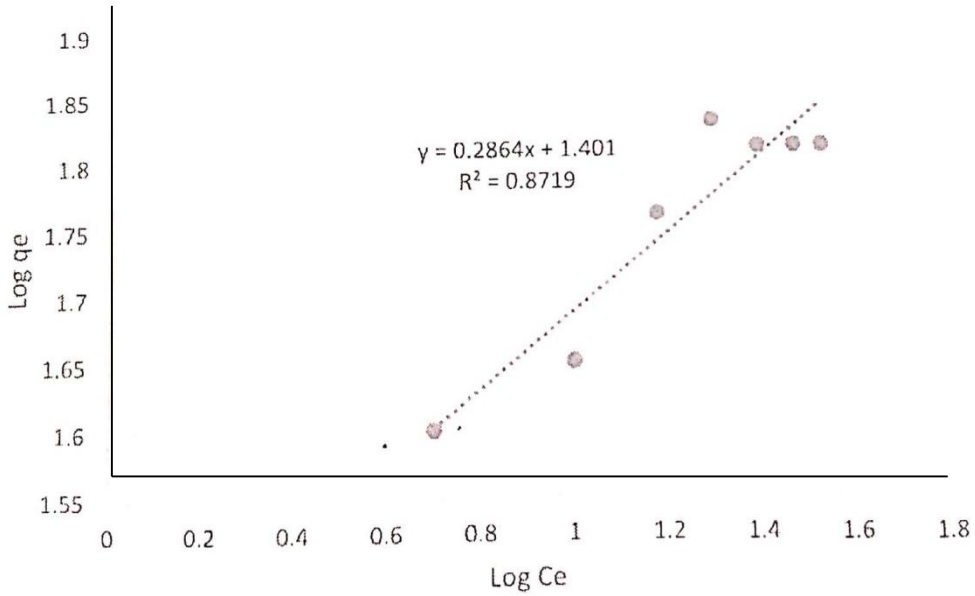

Fig. 8: Freundlich Absorption Isotherm Plot for Cu

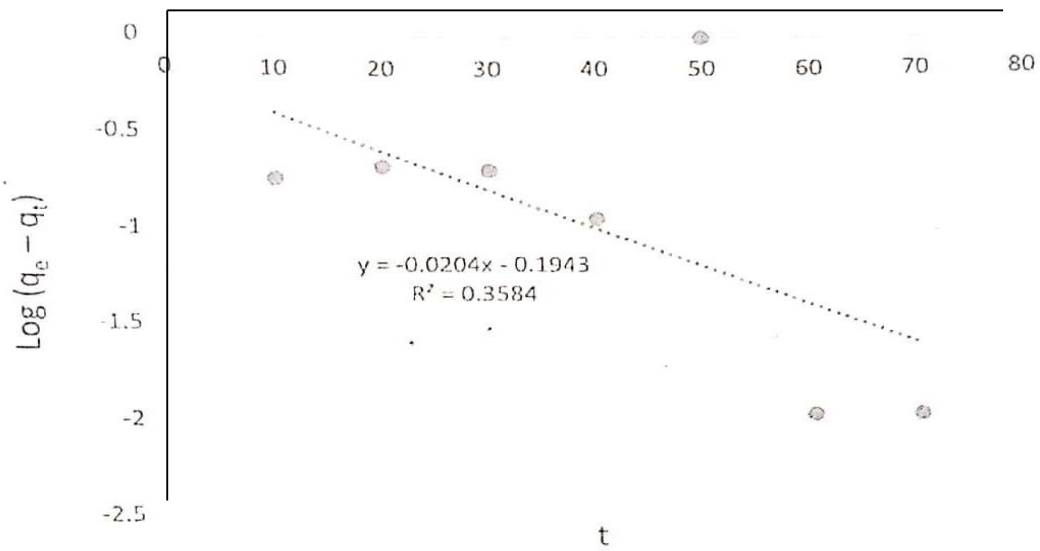

Figure 9: First-order adsorption kinetics of Pb on Clay

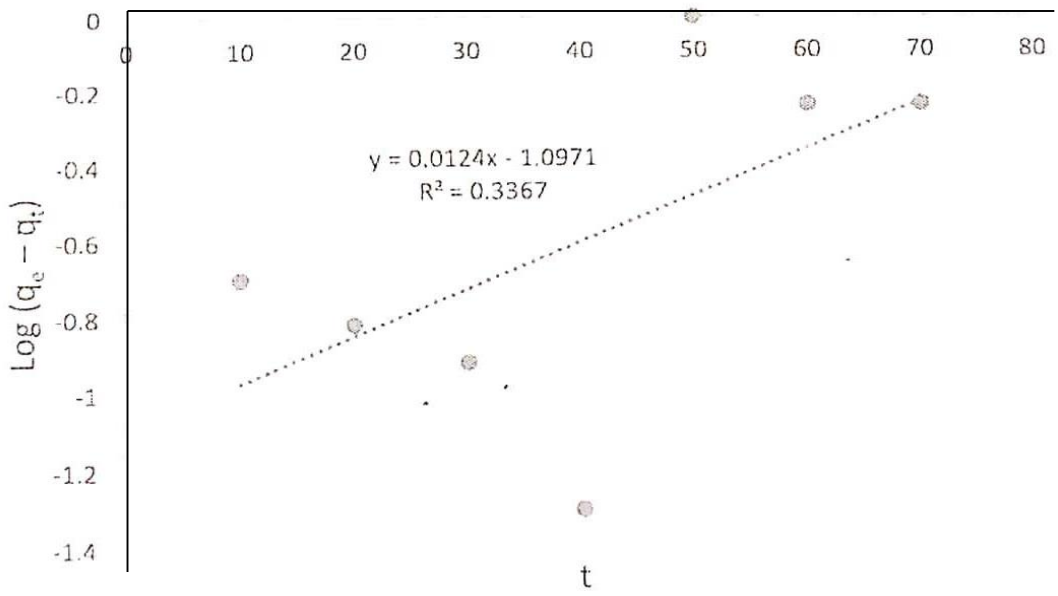

Figure 10: First-order adsorption kinetics of Cu on Clay

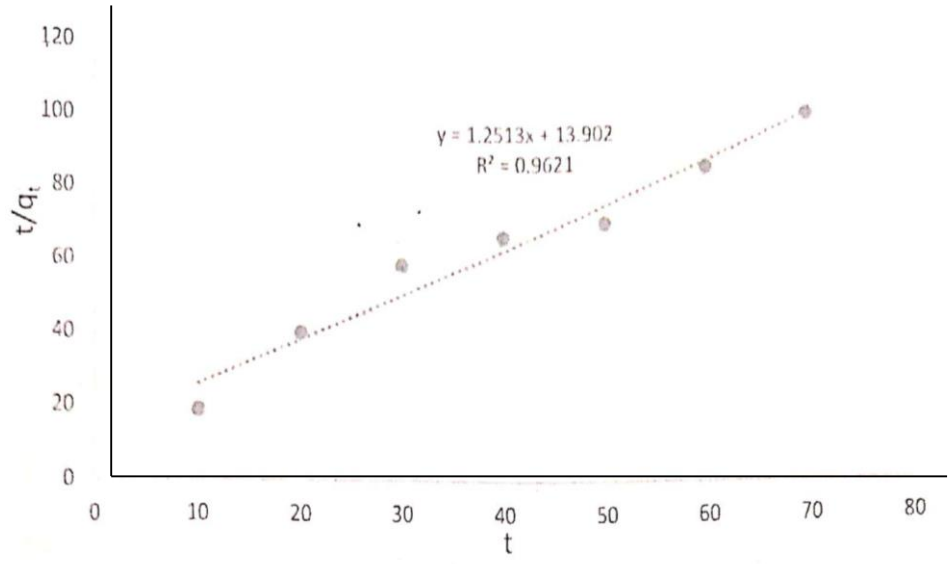

Figure 11: Pseudo-second-order adsorption kinetics of Pb on Clay

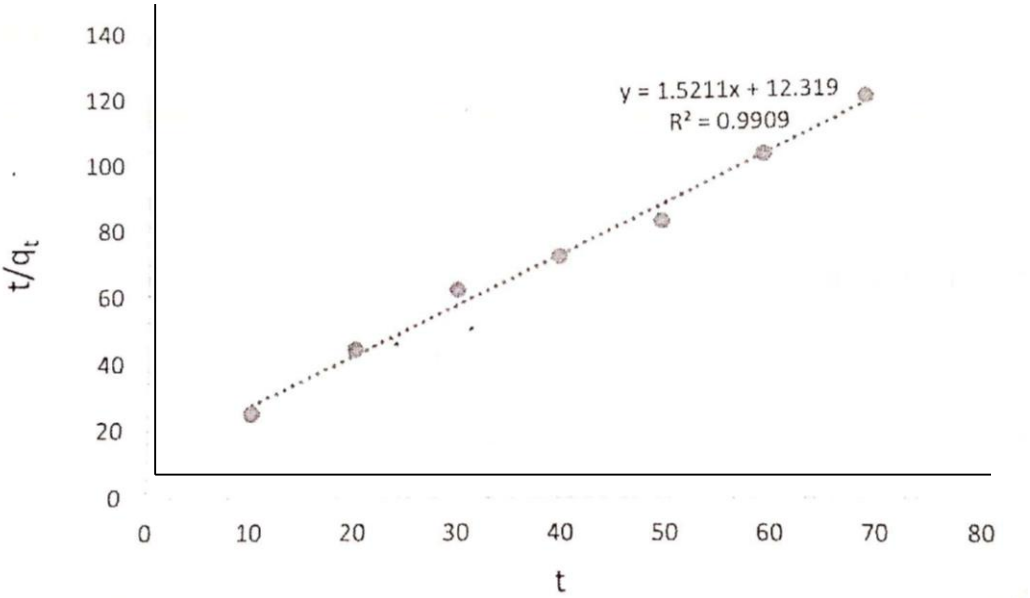

Figure 12 Pseudo-second-order adsorption kinetics of Cu on Clay

Fig 2 shows graphically the relationship between percentage adsorption, q_e and time. The curves show that adsorption of metal ions on local clays is symmetrically time dependent as percentage q_e increases with time. The adsorption of Pb and Cu increase gradually on the clay for the first 50 minutes after which a decline was observed. Thus, adsorption equilibrium time for Pb and Cu is 50 minutes. The increase in adsorption with time at the onset of the reaction could be as a result of the increased in number of sites of the adsorbent filled by the adsorbates as time increases. The increase in adsorption potentials with increase in contact time may be attributed to increase in mass transfer within the pores of the particles (Olaoefe *et al.*, 2015). Since adsorption and desorption occur side by side, after an appropriate time, equilibrium takes place. At equilibrium time, the maximum adsorption is observed due to the attractive forces developed between the clay and the metals. Initial adsorption of the metal is on exterior surface of clay. After complete adsorption on outer surface, the metals enter to the inner surface via pores. After equilibrium time desorption takes place.

The effect of varied masses of the clay on the rate of adsorption of the metal ions at constant adsorbate concentration is depicted in fig. 3. The curves obtained have shown that the adsorption of Pb and Cu increases with increasing masses to 0.6g and 0.8g, respectively before a plateau is observed. The plateau might be as result of exhaustion of the available active sites of the clay leading to the attainment of monolayer coverage. Also, it was observed that the metal ions concentration left in solution decreases with increasing amount of adsorbent for a given initial metal concentration. This could be explained thus; increase in the amount of adsorbent provides greater surface areas or active sites for the adsorbate. The slower adsorption rate at the end of the curve is probably due to the saturation of active sites and attainment of equilibrium. Similar conclusions have been drawn by Asrari et al, 2010).

Figure 4 shows the variation of percentage adsorption with different adsorbate concentrations. The results reveal that adsorption of the clays steadily increases with increasing concentration of the metal ions. However, a peak was observed at 15mg/L and

20mg/L for Pb and Cu, respectively. After these points, a flat profile was observed on the clay sample, indicating that monolayer coverage of the clays has been achieved. It is likely that adsorption sites took up the available metal ions more quickly at lower concentrations due to more active sites than adsorbates. At higher metal ions concentrations, there would be likely greater adsorption in order to occupy the available adsorption sites.

Figures 5 and 6 give the Langmuir isotherms plot for Pb and Cu, respectively. Straight lines were obtained for both plots. The higher values of R^2 (0.8074 for Pb and 0.8947 for Cu) show that the models could be accurately described the adsorption processes. Hence, it could be inferred that there exists a high chance of the adsorbates forming a unimolecular adsorbed layer on the adsorbent. In the same vain, the results of the Freundlich adsorption isotherm are presented by fig. 7 and 8 for Pb ($R^2 = 0.7662$) and Cu($R^2 = 0.8719$), respectively. Juxtaposing the results of the two adsorption isotherms, it was observed that the Freundlich isotherm can describe the adsorption as competently as the Langmuir isotherm. i.e., there could possible incidence of formation of multimolecular layer of adsorbate on the surface of adsorbent. Though the Langmuir model still described best the adsorption process owing to its higher coefficient of determination, R^2 compared to the Freundlich isotherm model.

Figures 9 and 10 give the linear plots of log ($qe - qt$) versus t for Pb ($R^2 = 0.3584$; $k = 0.047 min^{-1}$) and Cu ($R^2 = 0.3367$; $k=0.029 min^{-1}$), respectively. Obviously, the Lagergren model is not fitted in the adsorption of both metals on the clay sample owing to the very low pseudo-first-order coefficient of determination and rate constants values recorded.

The pseudo-second-order kinetic model for Pb ($R^2 = 0.9621$: $k = 0.1126\ M^{-1}\ min^{-1}$) and Cu ($R^2 =$ 09009, $k = 0.1880\ M^{-1}\ min^{-1}$) are depicted by figures 11 and 12. respectively. Evidently, the adsorption of both metals on the clay sample aligns with the pseudo-second-order kinetic model.

4.0 Conclusion

The result of this study indicates that Dan-Iyau , Clay sample is an effective adsorbent for the uptake of toxic heavy metals from aqueous solution. The adsorption of Pb and Cu ions by the clay has been shown to increase with increasing adsorbate concentration/dosage, adsorbent mass and contact time at low values and reached a plateau at high values. The optimum parameters for equilibrium study are time of contact (50mins for both metals), adsorbent mass (0.6g for Pb, 0.8g for Cu) and adsorbate dosage (15mg L for Pb, 20mg/L for Cu). The adsorption isotherm data were adequately fitted with both Langmuir and Freundlich equations. The result of the adsorption kinetics reveals that the pseudo-second order model, appeared to be the best-fitting model for the sorption of Pb(II) and Cu(II). This present work has demonstrated that Dan-Iyau clay in Daddara Jibiya, Katsina State Nigeria have the potential to be used as cost effective sorbent for Pb and Cu sorption.

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