

# Application of Kinetic Rate Equations on the Removal of Copper(II) Ions by Adsorption Unto “Aloji” Kaolinite Clay Mineral

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**Abstract**– The kinetic mechanism of sorption for the removal of Copper (II) ions from aqueous solution was determined by the use of kinetic rate equations. The experiment was performed by batch adsorption technique at a pH range, (1-8), initial metal ion concentration, (20-100mg/l), adsorbent concentration, (1-5g) and contact time, (10-120min). The kaolinite mineral was found to be composed mainly of silica and alumina, FTIR analysis revealed the presence of some functional groups on the kaolinite surface such as O-H, C=C, C-O, C-F, C-Cl and C-Br. The sorption process was found to be pH dependent as optimum pH was achieved at 6.0. The effect of contact time showed that equilibrium adsorption was achieved within 50min, after which the adsorption became negligible with further increase in time up to 120min. Six kinetic rate equations which include the first order, second order, pseudo-first order, pseudo-second order, Elovich and the Intraparticle diffusion equations were applied to investigate the mechanism of kinetics. All the rate equations applied gave good fit to the experimental data as indicated by the regression coefficient  $R^2 > 0.9$ . The results of this study indicated that both chemisorptions and physisorption participate equally in the overall adsorption process between copper(II) ions and Aloji Kaolinite clay, which involves intraparticle diffusion as a major mechanism.

**Keywords**– Adsorption, Aloji Kaolinite, Copper, First-Order, Second-Order, Elovich Equation and Intraparticle Diffusion

## I. INTRODUCTION

The problem of the environment has increased since the advancement in technology, heavy metals pollution is one of the major problems. These toxic metals when released into the environment increases continuously as a result of the industrial activities and technological developments. The release of these heavy metals to the environment poses a serious threat to public health because of their toxicity, bioaccumulation in the food chain and persistence in nature [1]. High intake of copper in humans can result in mucosal irritation, capillary and renal damages, gastrointestinal disorder, liver and kidney damages, hepatic problems and can affect the central nervous system leading to depression [2]. It can also result in lungs cancer when humans inhale sprays containing copper over a long period of time [3]. As a result of these harmful effects of copper, the need for the removal of copper and other toxic heavy metals from industrial

wastewaters is important. Presently, the main goal in the treatment involves the reduction of the concentration of heavy metals to very low levels, that is, acceptable limits not harmful to the environment and humans. Well established techniques for the removal of copper and other metals include ion exchange, membrane separation, reverse osmosis, solvent extraction, filtration, precipitation and activated carbon adsorption [4]. However, these methods are time consuming, require trained personnel, capital intensive and sometimes ineffective especially when the metal concentration in solution is in the range 1-10mg/l. Due to these reasons and especially the high cost, the search for cheaper and more effective techniques have been exploited by researchers. The adsorption of these metals on agricultural waste biomass, clay and other low cost materials have proved to be effective and can be used as cheaper alternatives. Some of the researches have reported the use of clay [5]-[10], biomass [11]-[15] and soil [16]-[18], just to mention a few. The presence of an abundance of a clay mineral called “Aloji Kaolinite clay” found in Ofu local government area, Kogi State, Nigeria was utilized as a low cost adsorbent. This paper reports the kinetics involved in the use of Aloji kaolinite clay as a cheap adsorbent for the removal of copper(II) ions from aqueous stream. Kinetic parameters were analyzed using kinetic rate equations such as First order, Second order, Pseudo-first order, Pseudo-second order, Elovich and intraparticle diffusion models.

## II. MATERIALS AND METHOD

### A. Clay Preparation and Characterization

Aloji kaolinite clay was obtained from Ofu local government area, Kogi State, Nigeria. The clay was soaked in excess distilled water and stirred vigorously to ensure proper dissolution. The dissolved clay solution was filtered in order to remove plant materials and suspended particles, after which the filtrate obtained was allowed to settle for 24hrs. Excess water was removed and the clay residue was sundried for several days. The dried clay was further dried in an oven at 105°C for 4hrs. The clay was then pulverized and sieved using a 100µm mesh sieve. The sieved clay particles were used as the adsorbent.

Classical technique was used to determine the chemical composition of the clay by the use of the Atomic Absorption Spectrophotometer (AAS) (Buck Scientific model 210VGP). The Fourier Transform Infrared spectra was determined by the use of the FTIR Spectrophotometer (Shimadzu FT-IR 8400s). The Specific surface area was determined by the methylene blue absorption test method [19], while the pH point of zero charge was determined as described [20].

### B. Preparation of Copper(II) ion Solution

The adsorbate was prepared by dissolving appropriate amounts of analytical grade of  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  in de-ionized water in order to obtain a concentration of 1000mg/l. This solution was diluted to lower concentrations of 20, 40, 60, 80 and 100mg/l. The pH of each solution was adjusted to the required value by the drop wise addition 0.1M  $\text{H}_2\text{SO}_4$  or 0.1M NaOH when required by the use of a pH meter. Each experiment was conducted using freshly prepared solution.

### C. Adsorption Procedure

The adsorption was carried out by the use of batch method. This was performed at pH values (1-8), metal ion concentration (20-100mg/l), contact time (10-120 min) and sorbent dose (1-5g). In order to investigate the effect of a particular parameter, that parameter was varied while others were kept constant. 2g of the adsorbent was added to 20mls of the adsorbate at a room temperature of  $27^\circ\text{C}$ , agitated and left for a given contact time. At the end of the contact time, the solution was filtered and the filtrate was analyzed for residual copper(II) ion concentration using the Atomic Absorption Spectrophotometer (AAS). The experiment was repeated and the mean value calculated. The uptake capacity of the clay for copper(II) ions was calculated using the mass balance equation

$$qe = v[Co-Ce]/m \quad (1)$$

Where  $qe(\text{mg/g})$  is the equilibrium uptake capacity,  $Co$  (mg/l) and  $Ce$  (mg/l) are the initial and equilibrium copper(II) ion concentrations respectively,  $v$ (litres) is the volume of the solution and  $m$ (g) is the mass of adsorbent.

## III. RESULTS AND DISCUSSION

### A. Characterization of Clay Mineral

The chemical composition, specific surface area and pH point of zero charge of Aloji kaolinite clay is presented in Table 1. It is observed that the major compositions are silica and alumina. The specific surface area of the clay is not large, most kaolinite minerals are found to have a low surface area, usually less than  $20\text{m}^2/\text{g}$ . Also, the determination of the pH point of zero charge (pHpzc) of an adsorbent is important as it helps us to have an idea about the optimum pH of adsorption of a material. It has been reported that the adsorption of anion is favored at a pH value less than the pHpzc while that of a cation is favored at a value greater than the pHpzc [21]. The FTIR spectra of Aloji kaolinite clay is shown in Fig. 1, it is observed that certain functional groups are present on the clay surface which could influence the adsorption capacity of the

material. The broad adsorption at  $3440\text{cm}^{-1}$  indicates the presence of O-H groups, the peak at  $1640.93\text{cm}^{-1}$  shows the presence of C=C, also, C-O stretching vibration was indicated by the band at  $1102.33\text{cm}^{-1}$ , the presence of C-F, C-Cl and C-Br groups were suggested by the bands at  $1026.58\text{cm}^{-1}$ ,  $694.81\text{cm}^{-1}$  and  $542.20\text{cm}^{-1}$  respectively.

### B. Influence of pH

The influence of initial solution pH on the removal of copper(II) ions by Aloji kaolinite clay is presented in Fig. 2. An increase in adsorption with increase in pH was observed from pH 1 to 6. Optimum adsorption was obtained at a pH of 6.0 greater than the pHpzc of 5.5 for the adsorbent. Subsequent experiments were performed at this pH value for optimum removal. The increase in adsorption with pH is simply due to decrease in the acidity of the solution as pH increases which reduces the number of protons competing with copper(II) ions for the active sites on the clay surface.

Table 1: Chemical Characterization of Aloji Kaolinite

Composition	% by weight
$\text{SiO}_2$	53.9
$\text{Al}_2\text{O}_3$	27.2
$\text{CaO}$	0.6
$\text{MgO}$	0.4
$\text{Na}_2\text{O}$	0.5
$\text{Fe}_2\text{O}_3$	0.9
$\text{K}_2\text{O}$	1.2
$\text{TiO}_2$	0.2
$\text{MnO}$	0.1
Loss on Ignition	15.0
Surface Area ( $\text{m}^2/\text{g}$ )	19.8
pHpzc	5.5

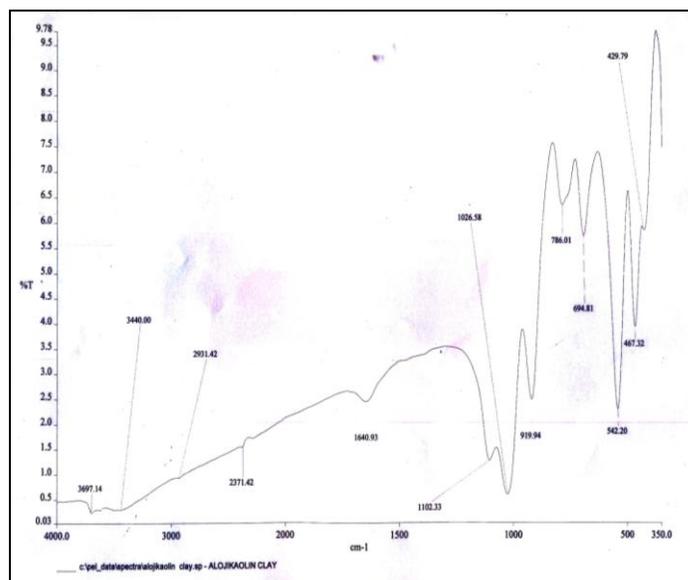


Fig. 1: FTIR Spectra of Aloji Kaolinite

### C. Influence of metal Ion Concentration

The result on the effect of initial metal ion concentration on the adsorption of copper(II) ions unto Aloji kaolinite clay is shown in Fig.3. Looking at the graph, an increase in sorption uptake capacity with increase in initial metal ion concentration was obtained. This is simply as a result of more metal ions in solution available for binding unto the active sites of the adsorbent [6].

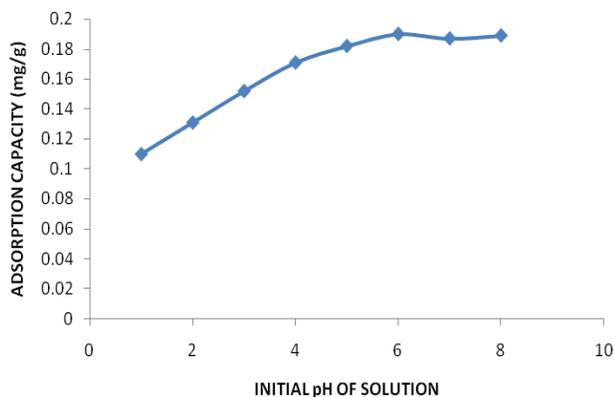


Fig. 2: Influence of pH on copper(II) ion sorption (conc, 20mg/l, temp, 300K, time, 2hrs, sorbent dose, 2g)

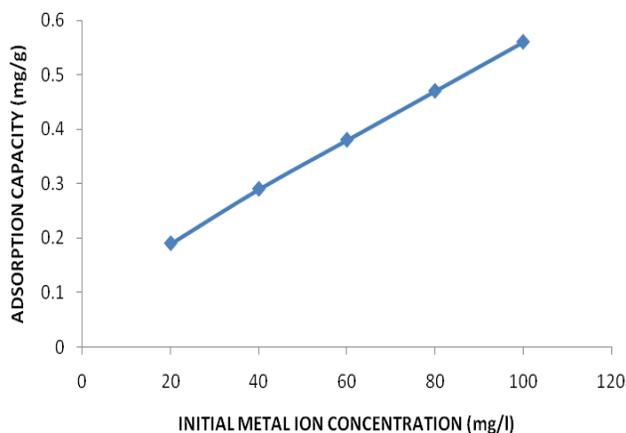


Fig. 3: Influence of initial metal ion concentration on copper(II) ion sorption (pH, 6.0, time, 2hrs, temp, 300K, sorbent dose, 2g)

### D. Influence of Adsorbent Concentration

The result of the experiment with varying adsorbent concentration is illustrated in fig.4. With increase in adsorbent dose from 1 to 5g the adsorption uptake capacity of the adsorbent for copper(II) ions decreased. Certain reasons have been recommended to explain the decrease in adsorption capacity with increase in adsorbent concentration which include electrostatic interactions, interferences between binding sites and the availability of solute [15].

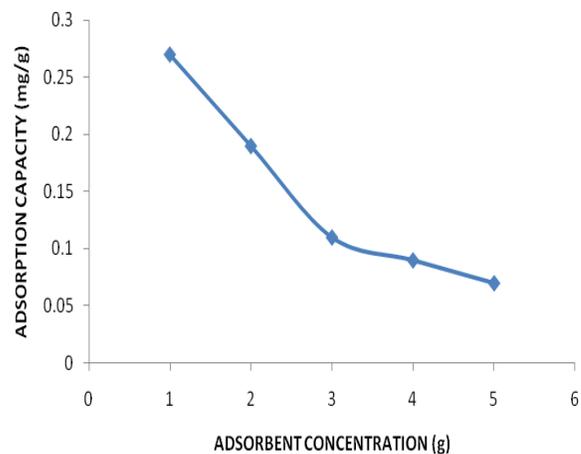


Fig. 4: Influence of adsorbent concentration on copper(II) ion sorption (pH, 6.0, conc, 20mg/l, time, 2hrs, temp, 300K)

### E. Influence of Time

The result for the effect of contact time on the removal of copper(II) ion is shown in Fig.5. As observed, the adsorption of copper(II) ion on Aloji kaolinite clay was rapid initially, until about 40 minutes. However, the adsorption rate became slower and reached a constant with passage of time up to 120 minutes. Equilibrium removal was achieved within 50minutes. The initial rapid rate of removal may be due to the availability of uncovered active sites on the surface of the clay, as sorption kinetics is largely controlled by the surface area of an adsorbent available for sorption. However, as the time progresses the active sites became used up, which resulted in the negligible uptake capacity observed from 40 to 120 minutes. This fast metal uptake is important in practical uses during process design and operations.

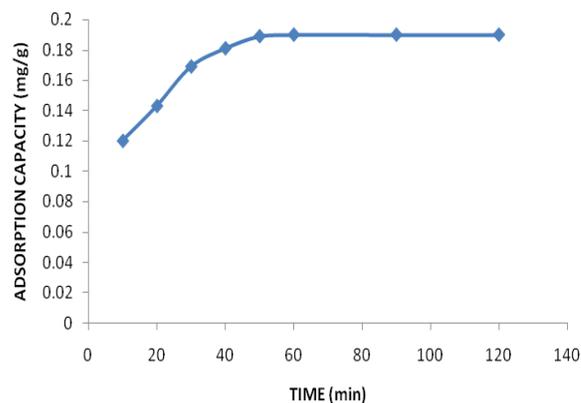


Fig. 5: Influence of contact time on copper(II) ion sorption (pH, 6.0, conc, 20mg/l, temp, 300K, sorbent dose, 2g)

### F. Kinetic modeling

The kinetics of the adsorption of an adsorbate on an adsorbent governs the rate, which determines the residence time and helps in defining the efficiency of an adsorbent. This

can be controlled by several independent processes which could act in series or parallel such as bulk diffusion, chemisorptions, intraparticle diffusion, physisorption and mass transfer. In order to investigate the kinetics of sorption, six models were applied in this study which include the first order, second order, pseudo-first order, pseudo-second order, Elovich and the intraparticle diffusion model. These models were assessed based on their regression parameters  $R^2$  to indicate if applicable or not to the adsorption process.

Table 2: Kinetic Rate Parameters

First Order			Second Order		
$K_1$	$R^2$		$K_2$	$R^2$	
0.05	0.995		0.019	0.906	
Pseudo-first Order			Pseudo-Second Order		
$K_1^1$	$q_e$	$R^2$	$K_2^1$	$q_e$	$R^2$
0.101	0.302	0.905	0.475	0.22	0.996
Elovich Equation			Intraparticle Diffusion		
$\beta$	$\alpha$	$R^2$	Kd	I	$R^2$
22.7	0.062	0.987	0.018	0.063	0.983

### G. First Order Equation

The first order equation was applied in the analysis of kinetic data. The linear form of the first order equation [22] is given in (2)

$$-\ln[Ct/Co] = K_1 t \quad (2)$$

Where  $Ct$  (mg/l) is the concentration of copper(II) ions in solution at a given time  $t$ ,  $Co$  (mg/l) is the initial copper ion concentration in solution,  $K_1$  ( $\text{min}^{-1}$ ) is the first order rate constant of adsorption. The applicability of this equation was tested by a linear plot of  $-\ln[Ct/Co]$  against  $t$ , illustrated in Fig. 6. The first order kinetic parameters are presented in Table 2. The value of the linear regression coefficient ( $R^2$ ) obtained suggested the applicability of this equation in the description of the kinetics of sorption.

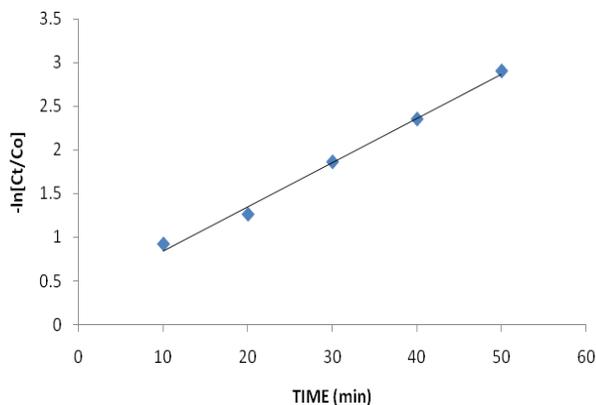


Fig. 6: First- order rate equation plot for the sorption of copper(II) ions unto Aloji Kaolinite

### H. Second Order Equation

The second order equation was also used to analyze kinetic parameters [22], this equation in its linear form is given below:

$$[1/Ct-1/Co] = K_2 t \quad (3)$$

Where  $K_2$  ( $\text{Lmg}^{-1}\text{min}^{-1}$ ) is the second order rate constant for the adsorption process. This isotherm was tested by a linear plot of  $[1/Ct-1/Co]$  versus  $t$ , shown in Fig. 7. The rate equation  $K_2$  was obtained from the slope of the plot. The value of  $K_2$  and the regression  $R^2$  are presented in Table 2. The  $R^2$  obtained is greater than 0.9, which indicated a good fit to the experimental data.

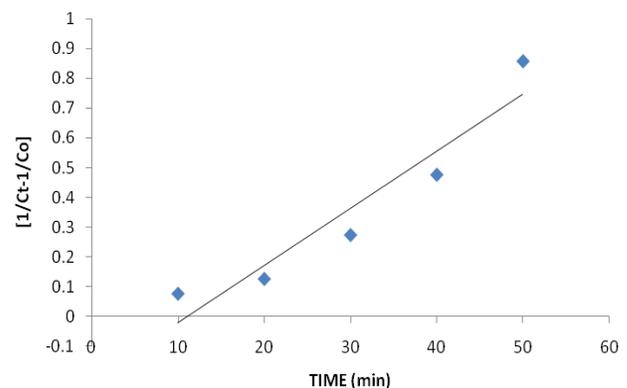


Fig. 7: Second- order rate equation plot for the sorption of copper(II) ions unto Aloji Kaolinite

### I. Pseudo-First Order Rate Equation

The Pseudo-first order model described by Lagergren was adopted to investigate the kinetics [23]. The linearized form of the equation is given in (4).

$$\ln[qe-qt] = \ln qe - K_1^1 t \quad (4)$$

where  $qt$  (mg/g) represents copper (II) ion uptake at a given time,  $t$ ,  $qe$  (mg/g) is the equilibrium adsorption capacity and  $K_1^1$  ( $\text{min}^{-1}$ ) is the Pseudo-first order rate constant.  $\ln(qe-qt)$  was plotted against  $t$  as shown in Fig.8 and the constants  $qe$  and  $K_1^1$  were calculated from the intercept and slope respectively. The pseudo first order parameters obtained are given in Table 2. As obtained also, the value of the regression coefficient ( $R^2$ ) obtained confirmed the applicability of this model equation.

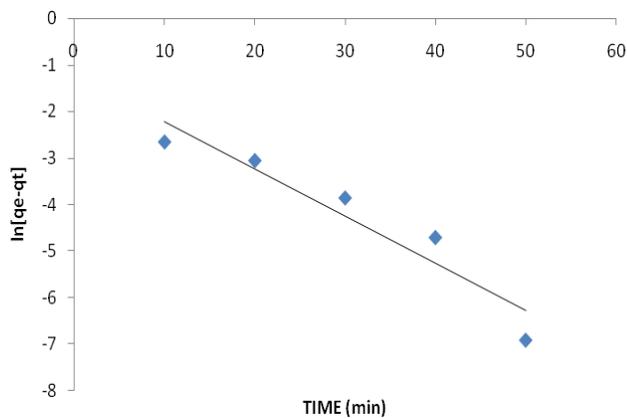


Fig. 8: Pseudo- first- order rate equation plot for the sorption of copper(II) ions unto Aloji Kaolinite

### J. Pseudo-Second Order Rate Equation

The Pseudo-second order equation for the sorption of divalent metal ions was applied [13]. This model is simply based on the assumption that adsorption follows a second order mechanism and implies that the rate of occupation of the active sites is proportional to the square of the number of unoccupied sites. The linearized form of the equation is given in (5).

$$t/qt = 1/K_2^1 qe^2 + t/qe \quad (5)$$

where  $K_2$ (g/mg/min) is the Pseudo-second order rate constant. The values  $t/qt$  was plotted against  $t$  as shown in Fig.9 and the constants  $qe$  and  $K_2^1$  were calculated from the slope and intercept respectively, these values and the regression ( $R^2$ ) are given in Table 2. It is seen from the regression obtained that this model provided a good and better fit to the adsorption data than the second order and Pseudo-first order equations, but a negligible difference from the first order equation. This rate equation indicates chemisorptions between Aloji kaolinite clay and copper(II) ions in solution.

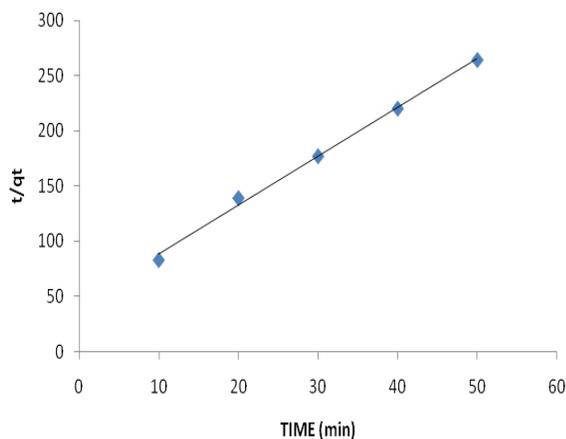


Fig. 9: Pseudo-second order rate equation plot for the sorption of copper(II) ions unto Aloji Kaolinite

### K. Elovich Rate Equation

The Elovich rate equation was first applied in the description of the kinetics of chemisorptions of gas molecules on a solid surface [24]. This equation has been applied presently by many scientist in the description of the kinetics of metal ions adsorption unto different adsorbents [25]. The linear form of the Elovich equation is given in (6).

$$qt = [1/\beta] \ln[\alpha\beta] + [1/\beta] \ln t \quad (6)$$

where  $\beta$ (g/mg) and  $\alpha$ (mg/g/min) are the Elovich constants corresponding to the extent of surface coverage and rate of sorption at zero coverage respectively. This equation was applied by a linear plot of  $qt$  versus  $\ln t$ , illustrated in Fig.10. The constants were calculated from the intercept and slope of the plot and presented in Table 2. The value of  $R^2$  shown in Table 2 showed a very good fit to the experimental data, better than the previous rate equations applied.

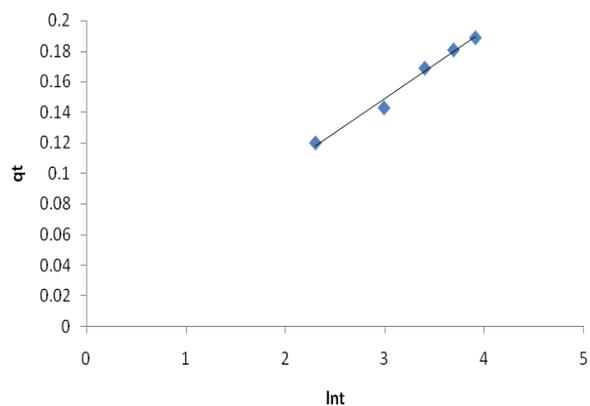


Fig. 10: Elovich rate equation plot for the sorption of copper(II) ions unto Aloji Kaolinite

### L. Intraparticle Diffusion Rate Equation

The mechanism of sorption using the intraparticle diffusion rate equation was adopted [26]. The intraparticle diffusion rate equation is given in (7)

$$qt = K_d t^{1/2} + I \quad (7)$$

where  $K_d$  (mg/g/min<sup>0.5</sup>) is the intraparticle diffusion rate constant and  $I$  represents the intercept which reflects the boundary layer effect. The plot of  $qt$  against  $t^{1/2}$  is shown in Fig. 11. Intraparticle diffusion is the sole rate determining step of adsorption if the plot passes through the origin, but if not, the larger the value of  $I$  the greater is the contribution of surface sorption mechanism in the rate determining step. The intraparticle rate equation parameters and the  $R^2$  value obtained are given in Table 2. The very good value of  $R^2$  obtained showed that the adsorption of copper(II) ions on Aloji kaolinite clay is mainly particle diffusion controlled. However, since the plot did not pass through the origin it indicated that intraparticle diffusion is not the only mechanism involved in the sorption process, and indicates the

contribution of other surface phenomenon on the adsorption process.

### M. Analysis of the Rate Equations

The good regression coefficient  $R^2$  provided by all the rate equations showed that the mechanism of sorption of copper(II) ions onto Aloji kaolinite clay is complex, this made it difficult to state clearly and precisely which equation fits better. As a result the only clear conclusion that can be made is that both physisorption and chemisorptions are involved in the overall sorption process and intraparticle diffusion is one of the major mechanism.

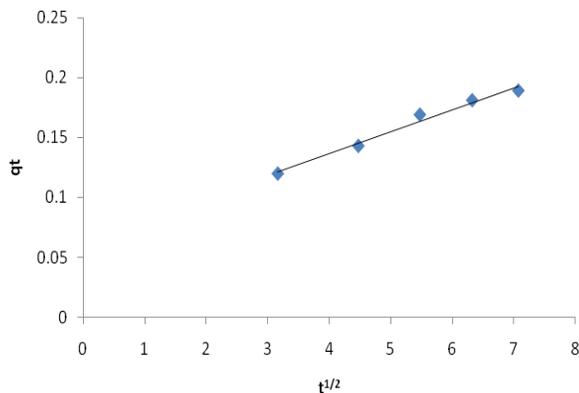


Fig. 11: Intraparticle Diffusion rate equation plot for the sorption of copper(II) ions onto Aloji Kaolinite

## IV. CONCLUSION

The results suggested that Aloji kaolinite clay can be used as a low-cost adsorbent for the removal of Copper (II) ions from solution. The first order, second order, pseudo-first order, Pseudo-second order, Elovich and intraparticle diffusion rate equations all proved to be useful in the description of the kinetic of the sorption process.

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