

## OPTIMIZATION OF ACTIVATION OF KUTIGI CLAY FOR ADSORPTION OF COPPER (II) ION USING RESPONSE SURFACE METHODOLOGY

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### ABSTRACT

This research paper presented the optimization of activation Kutigi clay for the adsorption of  $\text{Cu}^{2+}$  from aqueous solution using response surface methodology. The Kutigi clay sample was activated with  $\text{H}_2\text{SO}_4$  by varying acid concentrations, activation temperature and activation time. X-ray fluorescence (XRF) analysis was carried out before activation in order to know the chemical composition of the clay sample. Response surface methodology was adopted to optimize the activation conditions, with percentage removal of  $\text{Cu}^{2+}$  set as the response. Fourier-transform infrared spectroscopy (FT-IR) and Brunauer-Emmett-Teller (BET) surface area analyses were conducted on the clay sample before and after the activation procedure. A total of twenty experimental runs were carried out and the optimal clay activation conditions obtained was 2.5 M acid concentration at 50°C and 75 minutes contact time using  $\text{Cu}^{2+}$  percentage removal as the response. At the optimum conditions, a BET surface area of 170.80  $\text{m}^2/\text{g}$  of the activated micro porous adsorbent gives good adsorption capacity of 238.095 mg  $\text{Cu}^{2+}/\text{g}$  adsorbent. The effects of contact time, initial  $\text{Cu}^{2+}$  concentration, adsorbent dosage and pH on the activated Kutigi clay adsorption capacity also examined. Freundlich isotherm and pseudo-second-order models best described adsorption of  $\text{Cu}^{2+}$  onto the activated Kutigi clay when compared to Langmuir isotherm and pseudo-first order model respectively.

**Keywords:** Adsorption, Clay, Response surface methodology, Optimization, Isotherm

### INTRODUCTION

Polluted water, most especially one with toxic substances is a major problem to humans, plants and aquatic health which can also greatly reduce the quality of the habitant environment (Erdem *et al.*, 2004). Among different toxic substances released into the environment, heavy metals are known to be one of the most dangerous to the ecosystem. This is because they are very toxic even at low concentrations in water, not susceptible to biological degradation and consequent bioaccumulation of the ion (Akpomie *et al.*, 2013). In order to regulate the uncontrollable discharge of these hazardous pollutants in wastewater, novel and recent water treatment technologies are proposed globally. Different techniques like chemical precipitation, evaporation, solvent extraction, ion exchange, electrochemical treatment, and membrane filtration technologies have been used at different times to remove these hazardous pollutants from wastewater (Khan *et al.*, 2014; Liu *et al.*, 2010; Han *et al.*, 2009). However, adsorption process is a suitable technique for the removal of various pollutant from wastewater, because of its significant advantages such as low-cost, availability, profitability, ease of operation, efficiency, flexibility of design and effectiveness (Rao *et al.*, 2014; Gupta *et al.*, 2013). Researchers have reported the use of different adsorbents for wastewater treatment which include biomass materials, clay, zeolites, silica gel, activated carbon and ash (Mikhail *et al.*, 2002). Among these adsorbents studied, attention is being drawn to natural materials capable of removing pollutants from contaminated wastewaters yet at an affordable price and readily available. Clay minerals are indicated as a suitable alternative and very good substitute for commercial activated carbon used in adsorption processes. They have many advantages over other low cost adsorbents such as availability, affordability, ion exchange capability, high adsorption capacity and surface area, mechanical and chemical stability, and different structural and surface characteristics (Rao *et al.*, 2014).

The industrial utilization of clay is closely related to its reactivity and surface properties, which depend strongly on surface modification. Several methods have been suggested in literature to improve the properties of clay materials which includes physical modification (thermal or microwave treatment) which involves alteration of chemical composition and crystalline structure by the effect of high temperature and chemical modification (by acids, bases, organic compounds) which is usually by the alteration of structure, surface functional groups and surface area (Hussin *et al.*, 2011). Acid treatment is one of the most common chemical treatments for clay minerals and has been used to increase the specific surface area and the number of acidic centres, modify the surface functional group and to obtain solids with high porosity. The various types of acids used for clay treatment includes inorganic acids such as hydrochloric, sulphuric, nitric and organic acids such as acetic, citric, oxalic and lactic. Among all of these, hydrochloric acid and sulphuric acid are probably the most widely used in clay-acid activation, because it shows strong affinity by the process parameters and superior results in specific surface area development, porosity and adsorption capacity (Kumar *et al.*, 2013). This research work seeks to optimize Kutigi clay activation for the removal of  $\text{Cu}^{2+}$  from an aqueous solution using Response surface methodology.

### MATERIALS AND METHODS

#### Materials

The raw clay was collected from Kutigi in Lavun Local Government Area of Niger state, Nigeria. All chemicals used were analytical grade. Copper (II) ions stock solution was prepared by dissolving 2.5 g of Copper Sulphate ( $\text{CuSO}_4$ ) in 1000 mL of distilled water. Freshly prepared solution was used for each experiment.

**Methods**

**Preparation of Adsorbent**

The Kutigi clay was handpicked to remove dirt and other foreign bodies, thereafter sieved with a 125 µm mesh sieve. The clay sample was activated using H<sub>2</sub>SO<sub>4</sub> as activating agent under the consideration of the following factors: acid concentrations of 0.5 M, 1.5 M and 2.5 M, activation temperatures of 30°C, 50°C and 70°C and activation times of 30, 75 and 120 minutes. 5 g of dried raw clay of particle sizes 125 µm was measured and mixed with 50 mL of different concentrations of H<sub>2</sub>SO<sub>4</sub> at different activation temperature and time on a magnetic stirrer which was determined by design of experiment. Then, the prepared samples were poured into a Buchner funnel to separate the acid and clay. The residual clay was washed severally with distilled water until neutral point (6.7- 7.0) was obtained with pH indicator. The clay residue was dried in an oven at 105°C for 4 hours and then stored in airtight container for further use. Central Composite Design (CCD) under RSM was used to study the individual and synergetic effect of the three factors (acid concentration, temperature and time) towards the responses. For this case, it translated to 6 axial points, 8 factorial points and 6 replicates at the center which gives a total of 20 experiments.

**Adsorption Equilibrium and Kinetic Studies**

Adsorption studies were conducted to investigate the effect of contact time, initial Cu<sup>2+</sup> concentration, pH and effect of adsorbent dosage on adsorption of Cu<sup>2+</sup> on activated Kutigi clay. Adsorption equilibrium studies were performed in a set of conical flasks (250 mL) containing 100 mL of the Cu<sup>2+</sup> solutions at different initial concentrations (50 mg/L, 100 mg/L and 150 mg/L). 0.1 g of the activated adsorbent were added, mixed and placed in water bath isothermal shaker at room temperature for 60 minutes and shaker speed of 200 rpm to attain equilibrium. Prior to equilibrium condition, the residual sorbate concentrations were measured at intervals of time and similar procedure was repeated with another set of flasks containing different initial concentrations (50, 100, 150 mg/L). The flasks were afterwards removed from the shaker for determination of final concentration of the solution using XRF analysis. The amount of the Cu<sup>2+</sup> adsorbed at time t, at equilibrium q<sub>e</sub> (mg/g) was calculated using the Equation (1).

$$q_e = \frac{(C_0 - C_e) V}{W} \tag{1}$$

Where, q<sub>e</sub> is the amount of Cu<sup>2+</sup> ions adsorbed (mg/g), C<sub>0</sub> and C<sub>e</sub> (mg/L) are the liquid-phase concentration of the Cu<sup>2+</sup> at the initial and equilibrium respectively; V (L) is the volume of the solution; and W (g) is the weight of the dry adsorbent.

In other to study the kinetics of the adsorption process, concentration of the Cu<sup>2+</sup> ions solution was determined at intervals of time. The amount of the Cu<sup>2+</sup> ions absorbed at time t, Q<sub>t</sub> (mg/g) was calculated using the Equation (2).

$$q_t = \frac{(C_0 - C_t) V}{W} \tag{2}$$

Where, C<sub>0</sub> and C<sub>t</sub> (mg/L) are the liquid-phase concentration of the Cu<sup>2+</sup> at the initial and any time t, respectively; V (L) is the volume of the solution; and W (g) is the weight of the dry adsorbent. The influence of adsorbent dosage was also investigated using a set of conical flasks (250 mL) containing 100 ml of the Cu<sup>2+</sup> solution at the same initial concentration of 100 mg/L and about 0.1 g, 0.2 g, 0.3 g, 0.4 g and 0.5 g of the

activated adsorbent were separately added, mixed and placed in a water bath isothermal shaker at room temperature under the optimized conditions of the equilibrium time.

**RESULTS AND DISCUSSION**

**Adsorbent Characterization**

**XRF Analysis**

The XRF analysis as shown in Table 1 was carried out to know the chemical compositions of the clay before acid activation. The clay sample contains alumina and silica in major quantities whereas oxides such as magnesium oxide, calcium oxide, potassium oxide, zinc oxide and titanium oxide are present in trace amounts. The loss on ignition (LOI) shows the percentage volatile content present in the sourced Kutigi clay in form of an organic material which could be traced down to the clay’s origin due to the decay of plants and animals. The high LOI value of 11% is lower than the 15 % reported by Akpomie *et al.* (2013) and could have resulted from the geographical location from where the clay samples was sourced.

Table 1: Composition percentage of Kutigi clay

Composition	Weight (%)
SiO <sub>2</sub>	53.61
Al <sub>2</sub> O <sub>3</sub>	32.67
Fe <sub>2</sub> O <sub>3</sub>	0.67
K <sub>2</sub> O	0.005
TiO <sub>2</sub>	0.81
CaO	0.008
MgO	0.027
MnO	0.2
ZnO	0.0063
LOI	11.0

**BET Surface Area Analysis**

The Brunauer Emmett Teller analysis of raw and activated Kutigi clay as shown in Table 2 gave BET surface area of 137.70 and 170.80 m<sup>2</sup>/g, average pore diameter of 0.73 and 0.84 nm and a cumulative pore volume of 0.0590 and 0.0731 cm<sup>3</sup>/g respectively. The relatively increase in surface area of the activated clay maybe attributed to the acid treatment of the clay with H<sub>2</sub>SO<sub>4</sub>. Acid leaching of the Kutigi clay created more number of pores with diameter 0.84 nm (<2 nm) of which is micro pores. The high adsorption capacity of the acid activated clay on Cu<sup>2+</sup> is strongly believed to be due creation of more pores after acid treatment (Kumar *et al.*, 2013).

**Fourier-Transform Infrared Spectroscopy Analysis**

The FTIR spectrums of raw and treated Kutigi clay are shown in Figures 2 and 3 respectively and the corresponding band assignments are shown in Table 3. A number of absorption peaks were displayed which reflect the complex nature of clay with some peaks observed to have shifted or disappeared and new ones detected on comparison of the FTIR analysis of raw and activated clay sample. These changes observed in the spectra of both clay samples confirmed that activation process modified the clay sample (Afolabi *et al.*, 2016).

Table 2: BET analysis result for raw and acids activated Kutigi clay

	Surface area ( $\text{m}^2/\text{g}$ )	Pore volume ( $\text{cm}^3/\text{g}$ )	Pore size (nm)
Raw Kutigi clay	137.70	0.0590	0.73
Activated Kutigi clay at optimum condition	170.80	0.0731	0.84

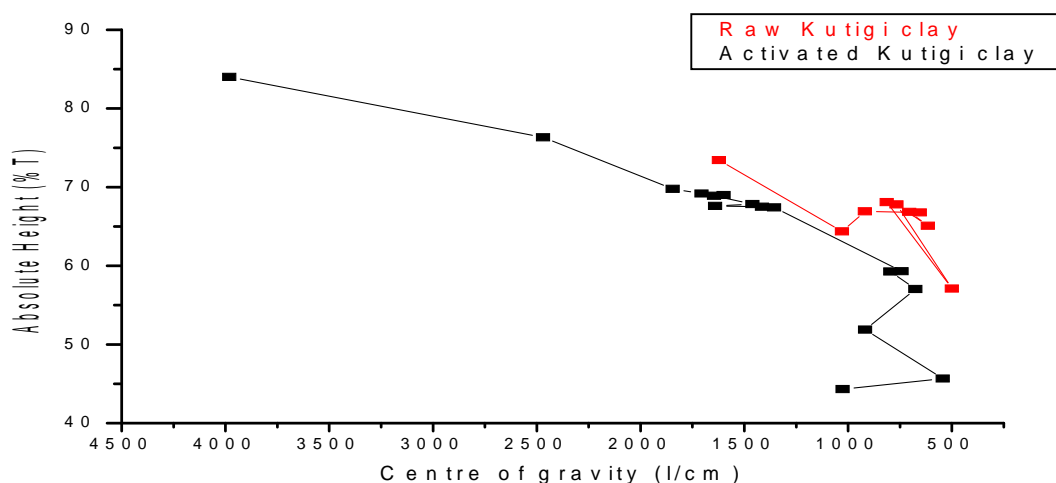


Figure 1: Fourier-transform infrared spectroscopy analysis on raw and activated Kutigi clay

Table 3: FT-IR assignments of raw and activated Kutigi clay

Band ( $\text{cm}^{-1}$ )	Peak Assignments
3988	Al-O-H <sub>str</sub> (Physisorbed and interlayer water)
1620, 1651 and 1674	H-O-H <sub>bending</sub> (Physisorbed)
1744 and 2376	Al-O-H <sub>str</sub> (Structural hydroxyl groups, octahedral)
1034, 1366, 1458 and 1520	Si-O <sub>str</sub>
918	Si-O <sub>str</sub>
787 and 795	Al-Mg-OH <sub>str</sub>
756	Si-O-Al <sub>str</sub>
687, 648 and 602	Si-O <sub>str</sub> , Si-O-Al <sub>str</sub>
525 and 548	Si-O <sub>str</sub> , Si-O-Al <sub>str</sub>

(De Sales *et al.*, 2013)

During activation of the clay sample, protons from the acid medium penetrate into the clay structures and attack the OH-groups thereby causing the alteration in the adsorptive bands attributed to the OH vibrations and octahedral cations (Temunjin *et al.*, 2004). As shown in Figure 1, it is clear that there were some structural modifications on the clay sample as a result of acid activation. The untreated clay sample shows adsorption bands at 525, 602, 648, 756, 795, 918, 1034, and 1512  $\text{cm}^{-1}$ . After treatment with  $\text{H}_2\text{SO}_4$ , the bands at 525, 602 and 648  $\text{cm}^{-1}$  attributed to the Si-O-Al stretching of the Kutigi clay were modified to 548 and 787 respectively while bands at 687, 756, 918 and 1034  $\text{cm}^{-1}$  associated with Si-O-Al, Al-Al-OH and Si-O stretching remained after acid leaching. The band at 795 attributed to the Al-Mg-OH stretching was completely absent after acid treatment and the vibrational band at 1512  $\text{cm}^{-1}$  related to the H-O-H bending (physisorbed) was also modified to 1520, 1620, 1651, 1674, 1744 and 2376  $\text{cm}^{-1}$  while new band formed at 3988 was associated with Al-O-H stretching (structural hydroxyl group and octahedral). The result obtained shows that the peaks are due to the formation of free amorphous silica and is also in

clear agreement with the XRF study (De Sales *et al.*, 2013; Temunjin *et al.*, 2004).

#### Analysis using Response Surface Methodology Response obtained from the Experiment

The percentage  $\text{Cu}^{2+}$  removal was in the range of 86.01– 98.45 %; these can be found on the total experimental design matrix and the values of the responses obtained presented in Table 4. The quadratic model was selected based on the highest order polynomials where the additional terms were significant and the models were not aliased, according to the sequential model sum of squares. The six replicate variables at the centre points, run 15–20 were conducted to determine the experimental error and the reproducibility of the data. The high percentage removal of 98.45% maybe attributed to the increase in specific surface area, number of acidic centres, modified surface functional group and high porosity of the Kutigi clay which is as a result of acid activation with  $\text{H}_2\text{SO}_4$  by showing strong affection by the process parameters and superior results in specific area, porosity and adsorption capacity (Korichi *et al.*, 2009).

Table 4: Result of experimental design matrix for acid activated Kutigi clay

Runs	Point Type	Concentration (M)	Temperature (°C)	Time (min)	Cu <sup>2+</sup> Removal (%)
1	Factorial	0.50	30.00	30.00	86.11
2	Factorial	2.50	30.00	30.00	91.57
3	Factorial	0.50	70.00	30.00	86.77
4	Factorial	2.50	70.00	30.00	95.80
5	Factorial	0.50	30.00	120.00	88.13
6	Factorial	2.50	30.00	120.00	86.01
7	Factorial	0.50	70.00	120.00	89.13
8	Factorial	2.50	70.00	120.00	93.79
9	Axial	0.50	50.00	75.00	89.02
10	Axial	2.50	50.00	75.00	98.45
11	Axial	1.50	30.00	75.00	90.64
12	Axial	1.50	70.00	75.00	91.67
13	Axial	1.50	50.00	30.00	87.82
14	Axial	1.50	50.00	120.00	88.56
15	Centre	1.50	50.00	75.00	91.91
16	Centre	1.50	50.00	75.00	90.66
17	Centre	1.50	50.00	75.00	92.11
18	Centre	1.50	50.00	75.00	93.22
19	Centre	1.50	50.00	75.00	92.99
20	Centre	1.50	50.00	75.00	91.94

**Development of Regression Model Equation**

Correlation between the response surface and factors were developed using central composite design (CCD) of the design expert software as shown in Table 5. Correlation coefficient and standard deviation were used to evaluate the fitness of the model developed. The closer the R<sup>2</sup> value to unity and the smaller the standard deviation, the better the model in predicting the response (Alam *et al.*, 2009). Table 5 shows that the quadratic model for percentage Cu<sup>2+</sup> by the Sulphuric acid activated Kutigi clay has relatively small standard deviation of 1.4 and relatively high R<sup>2</sup> value of 0.9806 which is in agreement with adjusted R<sup>2</sup> of 0.9612. The result implies that the quadratic model for response on percentage Cu<sup>2+</sup> removal can be employed to describe the relationship between response on the percentage removal and the interacting variables. The R<sup>2</sup> values of 0.9806 implies that 98.06% of the variation on Cu<sup>2+</sup> removal efficiency for the acid activated clay can be attributed to the qualitative agreement between the experimental and the predicted value of the variables under study (A- acid concentration, B- activation temperature and C- activation temperature). Therefore, the quadratic model used for optimization in this work gives the response surface model equation in their actual value as:

$$\% \text{ Cu}^{2+} \text{ Removal} = 92.01 + 2.65A + 1.47B - 0.25C + 1.29AB - 1.49AC + 0.49BC + 1.91A^2 - 0.67B^2 - 3.64C^2 \quad (3)$$

Table 5: Analysis of variance (ANOVA) on percentage Cu<sup>2+</sup> removal

Source	Sum of square	Degree of freedom	Mean square	F- Value	Probability> F
Model	177.21	9	19.69	9.99	0.0006
A	70.01	1	70.01	35.52	0.0001
B	21.61	1	21.61	10.96	0.0079
C	0.60	1	0.60	0.30	0.5932
AB	13.39	1	13.39	6.79	0.0262
AC	17.85	1	17.85	9.06	0.0131
BC	1.89	1	1.89	0.96	0.3504
A <sup>2</sup>	10.03	1	10.03	5.09	0.0477
B <sup>2</sup>	1.24	1	1.24	0.63	0.4463
C <sup>2</sup>	36.35	1	36.35	18.44	0.0016
Residual	19.71	10	1.97	-	-
Lack of fit	15.54	5	3.11	3.72	0.0877
Pure error	4.17	5	0.83	-	-
Correlation Total	195.92	19			

**Analysis of Variance (ANOVA)**

The model equation selected were further evaluated using ANOVA component of the software as shown on Table 5. The response surface quadratic model for the percentage Cu<sup>2+</sup> removal by the acid activated Kutigi clay had F-value of 9.99 which implied that the model was significant and had only a 0.06 % chance that its magnitude could occur due to noise (induced variation under normal operating conditions by uncontrollable factors). As expected, non-significant lack of fit was obtained with lack of fit F-value of 3.72 implying that it is not significant relative to the pure error and the chances that 8.77% of its value also occurred due to noise. Values of Probability> F less than 0.05 indicates that the model terms are significant and largest F- value signifies the model term having the most significant effect on the response (Emman and Abeer, 2012). In this case significant model terms are A, B, AB, AC, A<sup>2</sup> and C<sup>2</sup> and while C, BC and B<sup>2</sup> are the insignificant model terms for the quadratic percentage Cu<sup>2+</sup> removal model developed as shown on Table 5. Therefore, removing the insignificant model terms, the quadratic model equation becomes:

$$\% \text{ Cu}^{2+} \text{ Removal} = 92.01 + 2.65A + 1.47B + 1.29AB - 1.49AC + 1.91A^2 - 3.64C^2 \quad (4)$$

**Adsorption Study**

*Effect of Contact Time*

The time required to reach equilibrium between the activated Kutigi clay and aqueous solution of Cu<sup>2+</sup> was studied as shown in Figure 2. From the graph, it was observed that at initial concentration of 50 mg/L Cu<sup>2+</sup> equilibrium condition was attained after 45 minutes while at 100 and 150 mg/L Cu<sup>2+</sup> concentration, it took 60 minutes before equilibrium was established. The fast uptake observed at the initial stages was as a result of abundant availability of active sites on the surface of the clay for binding to the positive Cu<sup>2+</sup> in the solution, which becomes saturated as time progressed and later became less active after 45 min for 50 mg/L and 60 min for 100 and 150 mg/L. Taking into account these observations, the metal- acid activated Kutigi clay contact time of 60 min was used for further studies (Akpomie *et al.*, 2013; Sdiri *et al.*, 2016).

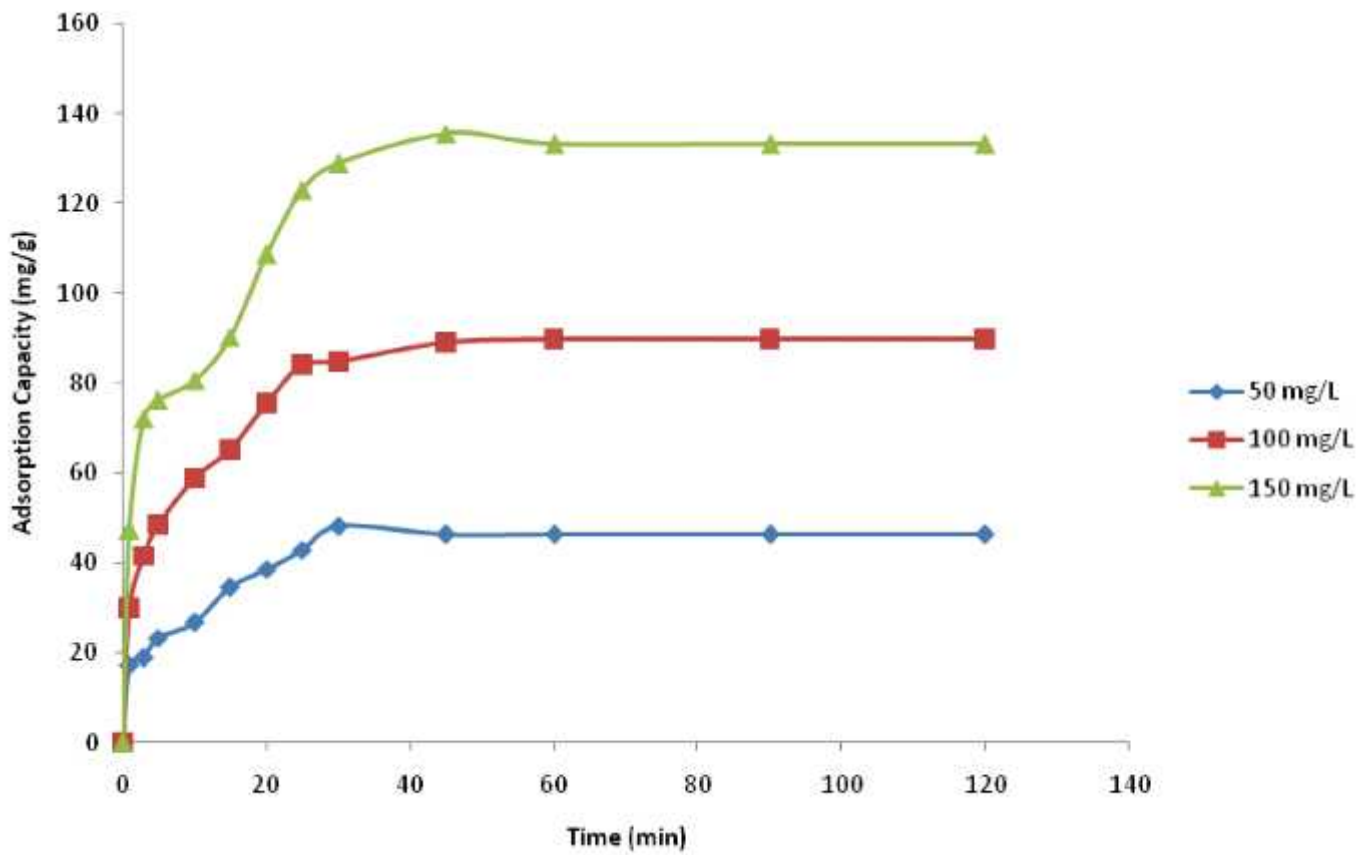


Figure 2: Effect of contact time on the adsorption of Cu<sup>2+</sup> by the activated Kutigi clay

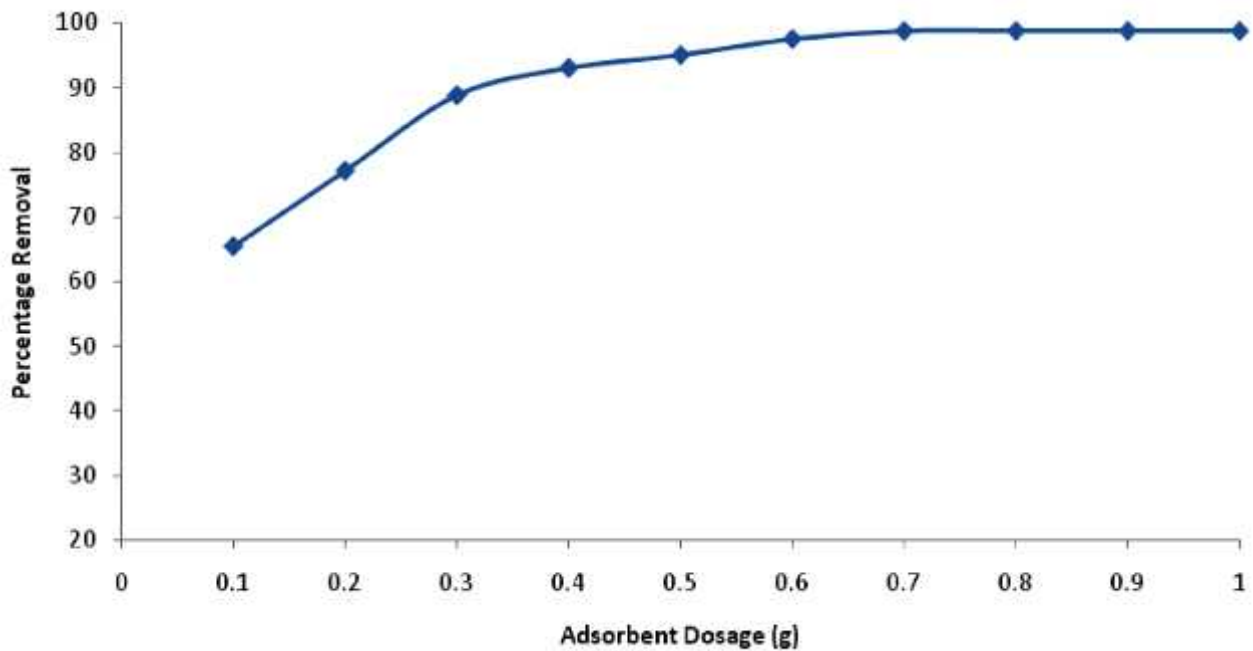


Figure 3: Effect of adsorbent dosage on the adsorption of Cu<sup>2+</sup> by the activated Kutigi clay

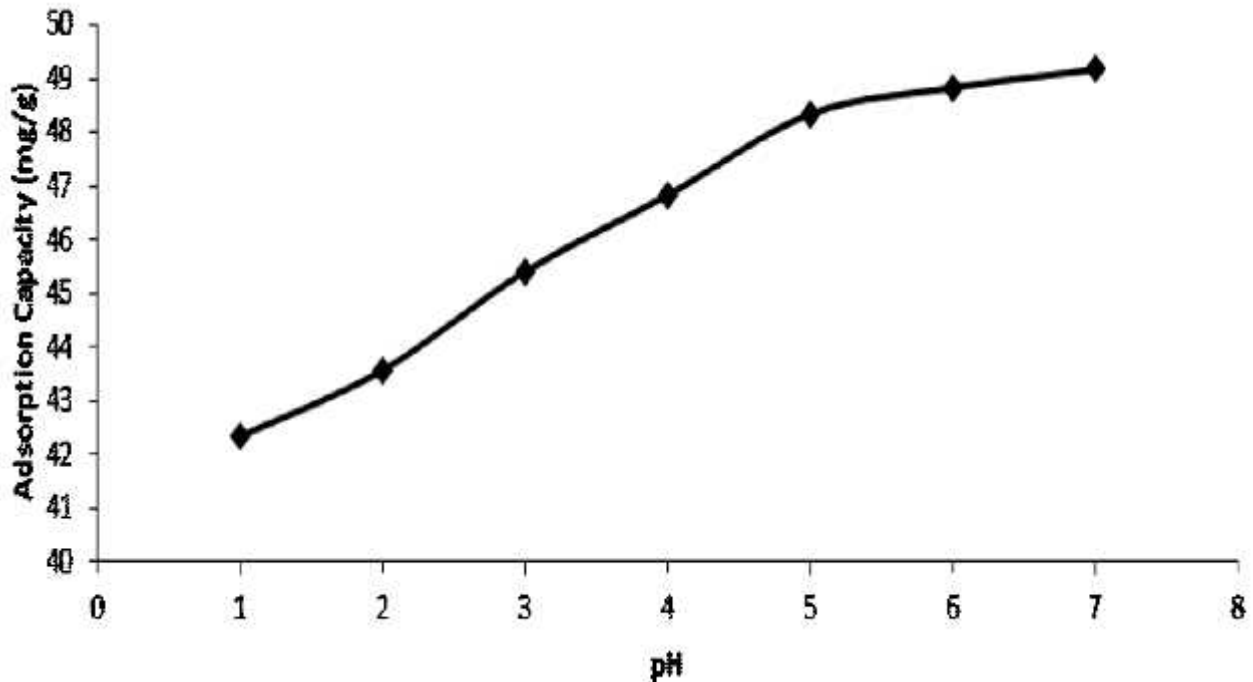


Figure 4: Effect of pH on the adsorption of  $\text{Cu}^{2+}$  by the activated Kutigi clay

#### Effect of Adsorbent Dosage

The acid activated Kutigi clay dosage was varied from 0.1 to 1g with a constant initial  $\text{Cu}^{2+}$  concentration of 100 mg/L and agitation time of 60 minutes at 30°C. Figure 3 shows the effect of adsorbent dosage on the percentage metal ions removal at equilibrium conditions. It was observed that the amount of metal ions adsorbed varied with varying adsorbent dosage. An increase in the adsorbent dosage from 0.1 to 0.7 g resulted in a rapid increase in the uptake of  $\text{Cu}^{2+}$ . Further increase in the adsorbent dosage, however, did not result in a sufficient increase in the percentage removal of the metal ion. The increase in the percentage adsorption of metal ion is related to the adsorption sites available on the activated Kutigi clay. This result is in agreement with Olgun and Atar, (2012) findings who stated that, at lower adsorption dosage, the metal ions compete for adsorption at limited adsorption sites but as the adsorbent is increased, the availability of adsorption sites promotes adsorption resulting in a greater percentage removal of the metal ion.

#### Effect of pH

Figure 4 shows the effect of pH on the removal of  $\text{Cu}^{2+}$  onto activated Kutigi clay from aqueous solution. The result shows that the uptake levels of the metal ions increased significantly with increasing pH. The increase in the metal ion adsorption and pH values can be explained on the basis of a competition between the proton and metal ions for the same terminal binding site on the activated Kutigi clay. At low pH values, concentrations of  $\text{H}^+$  far exceeds that of the metal ions and hence  $\text{H}^+$  ions compete with  $\text{Cu}^{2+}$  for the surface of the

adsorbent which would hinder the metal ions from reaching the binding sites of the adsorbent caused by repulsive forces. This is in agreement with the result obtained by Auta and Hameed (2013) who studied acid modified local clay beads as effective low cost adsorbent for dynamic adsorption of methylene blue.

#### Adsorption Isotherms

The models parameters which were obtained from the plots of equilibrium adsorption against their corresponding concentration are presented in Table 6. Assessment of the models fitness revealed that Freundlich model was the best fit for adsorption of  $\text{Cu}^{2+}$  on acid activated Kutigi clay as seen by the larger values of  $R^2$  (>0.90) and was closely followed by the Langmuir isotherm model. Thus adsorption of  $\text{Cu}^{2+}$  on acid activated Kutigi clay occurred heterogeneously in majority while homogeneous surface adsorption occurred but in minority (Nanganoa *et al.*, 2014). The maximum adsorption capacity was found to be 238.095 mg/g. Freundlich constants,  $K_F$  and  $1/n$  were 30.810 and 0.6143 respectively. The Freundlich exponent  $1/n$  indicates favourable condition of adsorption of  $\text{Cu}^{2+}$  onto acid activated clay since  $0 < 1/n < 1$ . To affirm the fitness of Langmuir model to the experimental data, an equilibrium parameter expressed as dimensionless constant  $R_L$  was evaluated. The  $R_L$  values obtained as shown on Table 4.7 is interpreted as follows: adsorption systems with  $R_L > 1$  (unfavorable),  $0 < R_L < 1$  (favorable),  $R_L = 1$  (linear) or  $R_L = 0$  (irreversible). Langmuir model favourable fitness to the experimental data was ascertained as the characteristics values were all within the range (0.0177, 0.00894 and 0.00591) of favourability (Auta and Hameed, 2014).

Table 6: Langmuir and Freundlich Isotherm model parameters for the adsorption of Cu<sup>2+</sup> onto acid activated Kutigi clay at 25°C

Isot her ms	Parameter
<b>Langmuir</b>	
Q <sub>m</sub> (mg/g)	238.095
K <sub>L</sub> (L/mg)	0.115
R <sup>2</sup>	0.8121
<b>Freundlich</b>	
K <sub>F</sub>	30.810
1/n	0.6143
R <sup>2</sup>	0.9746

Table 7: Pseudo-First and second order kinetics for Cu<sup>2+</sup> adsorption on acid activated Kutigi clay at 25°C

Adsorbents	Pseudo- first order		Pseudo- second order			q <sub>e</sub> cal (mg/g)	K <sub>2</sub> (min <sup>-1</sup> )	R <sup>2</sup>
	Cu <sup>2+</sup> conc. (mg/L)	q <sub>e</sub> exp (mg/g)	q <sub>e</sub> cal (mg/g)	k <sub>1</sub> (min <sup>-1</sup> )	R <sup>2</sup>			
Activated Kutigi clay at optimum condition	50	46.36	14.733	0.0336	0.499	48.309	0.00559	0.9964
	100	89.70	34.498	0.0412	0.7434	92.592	0.00320	0.9978
	150	136.25	57.122	0.0463	0.7523	140.845	0.00184	0.9960

### Adsorption Kinetics

The results of the two kinetic models tested as shown in Table 7, indicated that pseudo-second model described adequately the adsorption process Cu<sup>2+</sup> on acid activated Kutigi clay. This is confirmed by its model's rate adsorption constant observed to be higher when compared with the adsorption constant values for first order. Similarly, the calculated adsorption capacity values for second-order model were equally in close agreement with the experimental adsorption capacity values than those of the pseudo-first-order adsorption capacity. However, the correlation coefficient R<sup>2</sup> values were more tending towards unity for the pseudo-second-order model than for first order model which further showed none preference for first order model fit for description of the adsorption process (Auta and Hameed, 2011). This implies, the high kinetic rate associated with pseudo second order model will facilitate adsorption of high concentration of Cu<sup>2+</sup> and equilibrium attain within a short period of time (Nanganoa *et al.*, 2014).

### CONCLUSION

By using response surface methodology, Kutigi clay sample was activated and used for adsorptive removal of Cu<sup>2+</sup> from aqueous solution. At an optimum activation condition of 2.5 M, 50 °C, 75 minutes, an increase in surface area of the raw clay sample by 33.10 m<sup>2</sup>/g was recorded and 98.45% of Cu<sup>2+</sup> removal obtained with adsorbents' surface area of 170.80 m<sup>2</sup>/g and adsorption capacity of 238.095 mg/g of Cu<sup>2+</sup>. The adsorption capacity of activated Kutigi clay increases with time and then after, reaches a constant value where no more

metal ions can be removed from the solution. The adsorption isotherm obtained affirm the fitness of Langmuir and Freundlich models to the experimental data, while pseudo-second-order model gave the best adsorption of Cu<sup>2+</sup> on acid activated Kutigi clay in term adsorption kinetic study.

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