

# Abstraction of Zinc (II) Ions from Solution unto a Nigerian Bentonite.

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## ABSTRACT

The kinetics of adsorption for the removal of Zinc (II) ions from aqueous solution unto a Nigerian bentonite was studied. The aim of the experiment was the use of the bentonite as a low-cost adsorbent for Zinc (II) ions. The experiment was carried out using batch adsorption technique to determine the effect of pH, initial metal ion concentration, contact time, and temperature. The chemical characterization of the clay showed SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> as the major constituents. The surface area of the bentonite was determined to be 29.4m<sup>2</sup>/g. pH point of zero charge of the bentonite was found to be 2.8. An optimum pH of adsorption was obtained at 5.0 and equilibrium adsorption was achieved within 60 minutes. The kinetic models applied are the Pseudo first order, Pseudo second order, Elovich, and intraparticle diffusion model. These models all gave good fits to the experimental data which indicated that physical and chemical adsorption are involved in the sorption of zinc (II) ions unto the bentonite and intraparticle diffusion is a major mechanism in the process. Among the equilibrium isotherm models tested, the Freundlich isotherm gave the best fit to the experimental data. Thermodynamic studies revealed a spontaneous and endothermic adsorption process.

(Keywords: abstraction, bentonite, kinetics, isotherms, thermodynamics, zinc (II))

## INTRODUCTION

The pollution of the environment with hazardous heavy metals is of major concern to many industrialized nations today. These metals can be very toxic, persist in the environment, and bioaccumulate in nature (Chen and Yang, 2005). The problems posed by toxic heavy metals contamination of the environment have been on the increase as a result of industrial development.

Heavy metals are very harmful to many living organisms, plants, and even humans (Ikhuoria and Omonmhenle, 2006). Zinc, for instance, when present in high concentrations in humans can cause health problems such as anaemia, nausea, stomach cramps, skin diseases, pancreas damages, and arteriosclerosis (Erdem et al., 2004).

A number of techniques have been utilized in the removal of heavy metal ions from aqueous effluents, which include evaporation, solvent extraction, reverse osmosis, ion exchange, electrochemical precipitation, electrodialysis, membrane filtration, and adsorption (Preetha and Viruthagiri, 2005). Most of the techniques, although applied for many years, have disadvantages in terms of efficiency, high capital and operational cost, or the disposal of residual sludge of metal ions (Igwe et al., 2004). However, the adsorption technique has been found to be the most efficient among the methods mentioned. In order to solve the problem of high cost involved in treating effluents contaminated with heavy metals, present day researchers have utilized different low-cost materials as adsorbents for the removal of heavy metals. Some of these materials include agricultural by-products or biomass (Iqbal and Edyvean, 2004; Niu et al., 1993; Raize et al., 2004; Sun and Shi, 1998), clay (Akpomie et al., 2012a; Akpomie et al., 2012b; Dawodu et al., 2012; Naseem and Tahir, 2001; Srivastava et al., 1989), fly ash (Okoronkwo et al., 2011), and soil (Das and Mondal, 2011; Gupta et al., 2001).

In this study, a local bentonite mineral called "Afuze bentonite" obtained from Afuze in Owan East Local Government Area, Edo State, Nigeria, was utilized as a low-cost adsorbent for the removal of zinc (II) ions from aqueous solution. The effect of solution pH, initial metal ion concentration, contact time, and temperature on

adsorption was investigated. Kinetic models were applied to explain the rate mechanism of sorption and equilibrium isotherm models were also applied to the experimental data.

## MATERIALS AND METHOD

### Sample Preparation

The bentonite was obtained from Afuze in Owan East Local Government Area of Edo State, Nigeria. Then dispersed in excess distilled water in a pre-treated container, stirred to ensure proper dissolution and then filtered to remove unwanted plant materials and suspended particles. The filtrate was allowed to settle for 24hrs after which excess water was decanted. The residue obtained was sundried for several days to get rid of water molecules, then oven dried at 105<sup>o</sup>C for 4hrs. The dried bentonite was pulverized and then passed through a 100 $\mu$ m mesh sieve. The sieved bentonite was used as the adsorbent.

### Sample Characterization

The chemical composition of the bentonite was determined by classical method by the use of the Atomic Absorption Spectrophotometer (AAS) (Buck scientific model 210VGP).

The specific surface area of the bentonite was determined by the use of the methylene blue absorption test method (Santamarina et al., 2002).

The pH point of zero charge of the bentonite was determined by the method described (Onyango et al., 2004). 50ml of 0.01M NaCl was put into different Erlenmeyer flask and then corked tightly. The solutions were adjusted to different pH values ranging from 2-12 by the addition of 0.1M HCl or 0.1M NaOH drop by drop. 0.5g of the bentonite was added to the solutions and agitated in a shaker for 1hr after which it was allowed to settle for 48hrs at a room temperature of 27<sup>o</sup>C. The zeta potential of each solution was then determined. The plot of the zeta potential (mV) against the initial pH of the solution (not shown) was used to determine the pH point of zero charge (pHpzc) of the bentonite. The point at which the plot touches the x-axis is the pHpzc of the adsorbent.

### Batch Adsorption Method

The reagents used in this study were of analytical grade, 100mg/l of zinc (II) ion solution was prepared from ZnSO<sub>4</sub>.7H<sub>2</sub>O by appropriate dilution in de-ionized water. Lower concentrations were prepared from the stock by serial dilution. The pH of each solution was adjusted to the required value by the addition of 0.1M NaOH and 0.1M H<sub>2</sub>SO<sub>4</sub> drop by drop. Batch adsorption was performed at pH (1-8), initial metal ion concentration (20-100mg/l) and contact time (10-120 minutes). This was performed by adding 2g of the bentonite to 20ml of a given solution at a room temperature of 27<sup>o</sup>C. At the end of a given contact time, the solution was filtered and the filtrate was analyzed for residual metal ion concentration using the AAS. Each experiment was performed twice and the mean value calculated. The amount of zinc (II) ions adsorbed by the clay was calculated using (1) and (2).

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

$$\% \text{ Removal} = 100[Co - Ce]/Co \quad (2)$$

where  $q_e$  (mg/g) is the adsorption capacity,  $Co$  (mg/l) and  $Ce$  (mg/l) are the initial and equilibrium zinc (II) ions concentrations respectively,  $v$  (litres) is the volume of solution and  $m$  (g) is the mass of adsorbent.

## RESULTS AND DISCUSSION

### Characterization of Bentonite

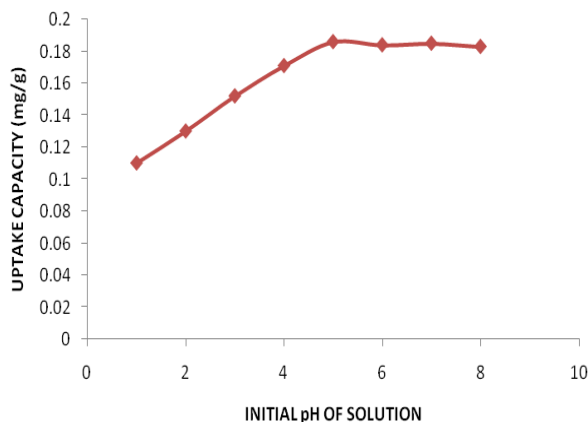
The chemical composition of the bentonite as determined by classical method is presented in Table 1. Also, the mechanism of adsorption is better understood if the point of zero charge (pHpzc) of the adsorbent is determined. This is because it has been reported that the adsorption of cations is favored at pH values greater than the pHpzc while the adsorption of anion is favored at a pH lower than the pHpzc (Mondal, 2009). The pHpzc of the bentonite is recorded in Table 1. Also, the specific surface area of an adsorbent which is the ratio of its surface area to its mass is very important in determining its adsorption capacity. The specific surface area of the bentonite is also presented in Table 1.

**Table 1:** Chemical Characterization of the Bentonite.

Composition	% by Weight
SiO <sub>2</sub>	53.12
Al <sub>2</sub> O <sub>3</sub>	22.81
CaO	4.01
MgO	1.87
Na <sub>2</sub> O	1.02
Fe <sub>2</sub> O <sub>3</sub>	2.65
K <sub>2</sub> O	1.27
TiO <sub>2</sub>	0.51
MnO	0.42
LOI	12.32
pHpzc	2.8
SSA (m <sup>2</sup> /g)	29.4

### Effect of Solution pH

The initial pH of a solution is important in most adsorption studies because it determines the surface charge of an adsorbent material and the degree of ionization and specification of an adsorbate (Imamoglu and Tekir, 2008). The result on the effect of solution pH on zinc (II) ion adsorption is shown in Figure 1. Optimum pH of adsorption was recorded at 5.0. The optimum pH of 5.0 was maintained in this study in subsequent parameters determination.

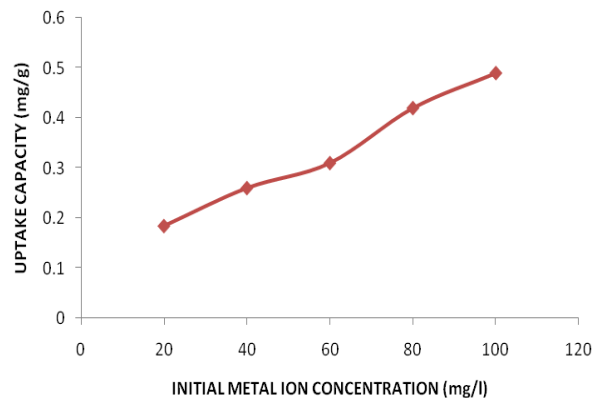


**Figure 1:** Effect of initial pH of solution on the uptake of zinc(II) unto the bentonite (conc, 20mg/l, time, 2hrs, Temp, 300K).

### Effect of Initial Zinc (II) Ion Concentration

The effect of different initial zinc (II) ion concentration on the adsorption of zinc (II) ion by

the bentonite is shown in Figure 2. There was an observed increase in the adsorption capacity of the bentonite with increase in initial concentration of zinc. This is simply due to an increase in concentration gradient which acts as increasing driving force to overcome resistances to mass transfer between the adsorbent and adsorbate (Das and Mondal, 2011).

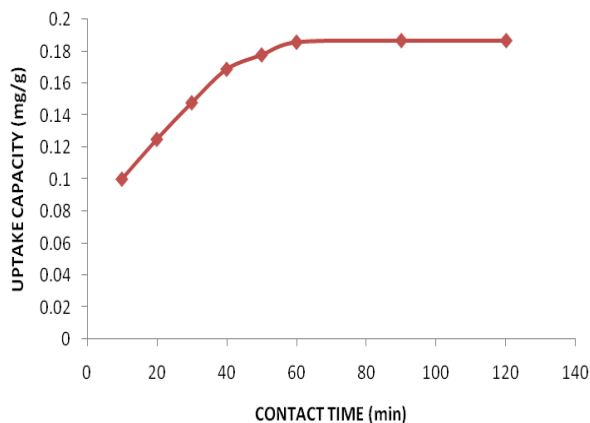


**Figure 2:** Effect of initial metal ion concentration on the uptake of zinc (II) unto the bentonite (pH,5.0, time, 2hrs, Temp, 300K).

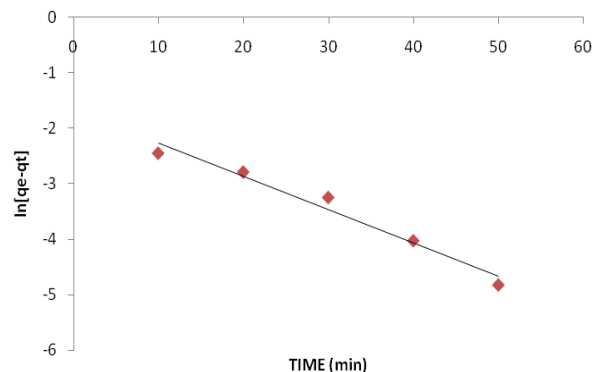
### Effect of Contact Time

In order to obtain comprehensive information on the kinetics of adsorption, the effect of contact time on adsorption was determined. The effect of contact time on the removal of zinc (II) ions from aqueous solution unto the bentonite is shown in Figure 3.

The rate of adsorption was rapid initially after which it became insignificant with time. Equilibrium sorption was achieved within 60 minutes of the process. The fast adsorption at the initial stage is due to the availability of abundant active sites on the clay surface which became saturated as time progresses. In the initial stages the fast adsorption is controlled by diffusion process from the bulk to the surface of the bentonite, while the slow adsorption in the later stages is due to an attachment controlled process (Badmus et al, 2007).



**Figure 3:** Effect of contact time on the uptake of zinc(II) unto the bentonite (pH,5.0, conc, 20mg/l, Temp, 300K).



**Figure 4:** Pseudo first order model on the uptake of zinc (II) unto the bentonite (pH,5.0, conc, 20mg/l, Temp, 300K).

### Kinetic Modelling

The time dependent experimental data was used for kinetic modelling. The kinetics of adsorption is required for selecting optimum operating conditions for the full scale batch process. Kinetic parameters reveal very useful information about sorbent design, with sorbent time and reactor dimension. The adsorption kinetics also revealed useful information about the physico-chemical characteristics of an adsorbent which greatly influences sorption (Ho et al., 1995). In this study the Pseudo first order, Pseudo second order, Elovich and Intraparticle diffusion models were applied in the analysis of kinetic parameters.

The Pseudo-first order equation (Lagergren, 1898) was applied to the experimental data in its linear form given in (3).

$$\ln[qe-qt] = \ln qe - K_1 t \quad (3)$$

Where  $q_e$  (mg/g) and  $q_t$  (mg/g) is the amount of the adsorbate adsorbed by the adsorbent at equilibrium and time,  $t$  respectively.  $K_1$  ( $\text{min}^{-1}$ ) is the pseudo first order rate constant. This model equation was applied by a linear plot of  $\ln[qe-qt]$  versus  $t$  shown in Figure 4. The constants  $K_1$  and  $q_e$  were calculated from the slope and intercept respectively. The pseudo first order kinetic parameters  $K_1$ ,  $q_e$  and the regression  $R^2$  are presented in Table 2. The value of the regression  $R^2$  of 0.9692 showed the applicability of the pseudo first order model and implies that the rate of adsorption is dependent on the concentration of zinc (II) ions in solution.

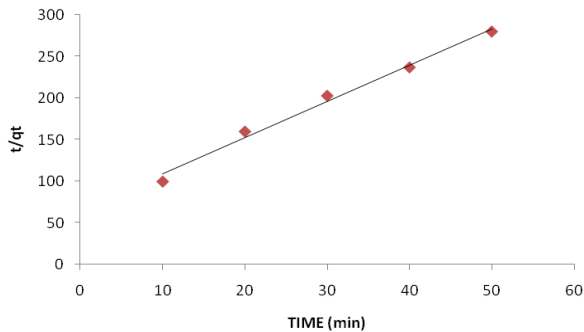
The pseudo second order model is based on the assumption that the rate of occupation of adsorption sites is proportional to the square of the number of unoccupied sites (Zafar et al, 2006) and that chemisorptions is the rate determining step (Ho and McKay, 2000). The linear form of the pseudo first order equation is given in (4).

$$t/qt = t/qt + 1/K_2 qe^2 \quad (4)$$

where  $q_e$  (mg/g) is the calculated equilibrium uptake capacity,  $K_2$  (g/mg/min) is the pseudo second order rate constant. The pseudo second order model can be determined experimentally by plotting  $t/qt$  against  $t$  as shown in Figure 5 and the constants  $q_e$  and  $K_2$  obtained from the slope and intercept. The initial sorption rate,  $h$  was calculated from (5).

$$h = K_2 qe^2 \quad (5)$$

The pseudo second order kinetic parameters and the  $R^2$  value obtained are given in Table 2. This model can thus be applied to the adsorption data as indicated by the good  $R^2$  value (0.9896) obtained. This implies that the rate limiting step is a chemisorption involving valency forces caused by sharing or exchange of electrons between sorbent and sorbate species in solution (Unlu and Ersoz, 2006). The pseudo second order model have been reported to give very good fits to experimental data by many researchers (Malkoc and Nuhoglu, 2007; Sari et al, 2007).



**Figure 5:** Pseudo second order model on the uptake of zinc (II) onto the bentonite (pH,5.0, conc, 20mg/l, Temp, 300K).

**Table 2:** Kinetic Model Parameters.

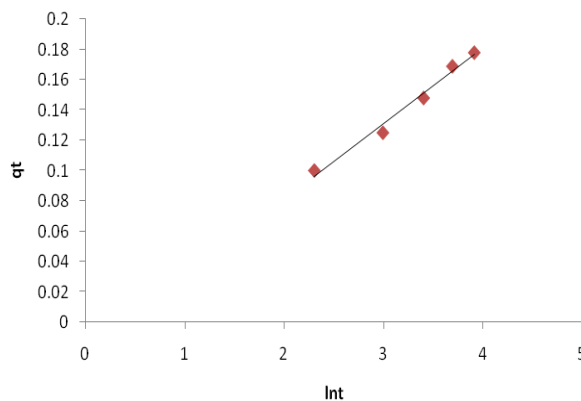
Pseudo First Order			
qe	K <sub>1</sub>	R <sup>2</sup>	
0.19	0.06	0.9692	
Pseudo Second Order			
qe	K <sub>2</sub>	h	R <sup>2</sup>
0.23	0.29	0.015	0.9896
Elovich Equation			
β	α	R <sup>2</sup>	
20.1	0.034	0.983	
Intraparticle Diffusion			
K <sub>d</sub>	C	R <sup>2</sup>	
0021	0.034	0.9937	

The Elovich equation was first used to describe the kinetics of chemisorptions of a gas onto solid surfaces (Low, 1960). However, many researchers presently have successfully applied this equation in the kinetics of sorption of metal ions by adsorbents (Chien and Clayton, 1980). The simplified form of the Elovich equation is given in (6).

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

where  $\beta$  (g/mg) and  $\alpha$  (mg/g/min) are Elovich constants related to the extent of surface coverage and the rate of chemisorptions at zero coverage respectively. The applicability of the Elovich equation was tested by the linear plot of  $qt$  against  $Int$  as shown in Figure 6. The constants  $\beta$  and  $\alpha$  were calculated from the slope and intercept and recorded in Table 2. The good value of the regression  $R^2$  (0.983) obtained clearly suggest the applicability of the Elovich equation. This further supports the assumption of the pseudo second order model that a chemical

adsorption mechanism exist between the bentonite and zinc (II) ions in solution.



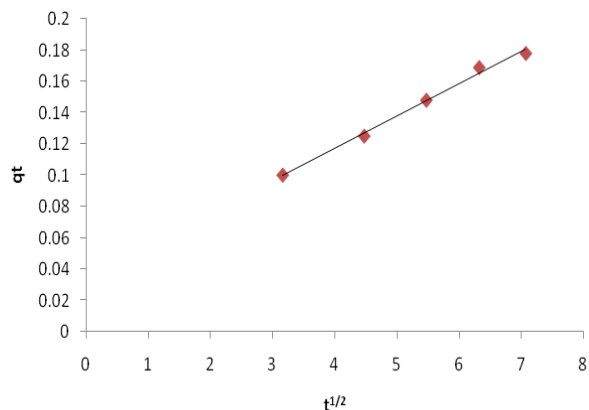
**Figure 6:** Elovich Equation model on the uptake of zinc (II) onto the bentonite (pH,5.0, conc, 20mg/l, Temp, 300K).

The intraparticle diffusion model (Weber and Morris,1963), was applied to analyze kinetic parameter. The intraparticle diffusion model is given in (7).

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

where  $K_d$  (mg/g/min) is the intraparticle diffusion rate constant and  $C$  is the intercept which reflects the boundary layer effect. This model was applied by the linear plot of  $qt$  against  $t^{1/2}$  as shown in Figure 7, and the constants  $K_d$  and  $C$  were obtained from the slope and intercept. The larger the value of the intercept  $C$ , the greater is the contribution of surface adsorption in the rate determining step. Also, intraparticle diffusion is the sole rate determining step if a linear plot of  $qt$  against  $t^{1/2}$  passes through the origin. The intraparticle diffusion parameters are presented in Table 2. The value of  $R^2$  obtained (0.9937) and the small value of  $C$  (0.034) showed that the sorption of zinc (II) ions onto the bentonite is mainly particle diffusion controlled.

The high value of  $R^2$  obtained in all the models applied makes it difficult to distinguish between the various models. The conclusion that can be drawn is that physical and chemical adsorption equally participates in the overall process of Zinc (II) ion adsorption in which one major mechanism is the intraparticle diffusion.



**Figure 7:** Intraparticle diffusion model on the uptake of zinc (II) unto the bentonite (pH,5.0, conc, 20mg/l, Temp, 300K).

### Adsorption Isotherm Models

Adsorption isotherms are important in the design of adsorption systems. The relationship between the amount of an adsorbate adsorbed at constant temperature and its equilibrium concentration in solution is called an adsorption isotherm. In general, the adsorption isotherm explains adsorbate-adsorbent interactions and is important in optimizing the use of adsorbents. Adsorption equilibrium is achieved when the rate at which molecules adsorb onto a surface is equal to the rate at which they desorb. The physical chemistry involved may be complex and no single theory of adsorption has been put forward which satisfactorily explains all systems. However the Langmuir and Freundlich isotherm models have been widely applied in the description of adsorption systems. These two isotherms including the Dubinin-Radushkevich, Temkin and Redlich-Petersons models were applied in this study to the equilibrium data.

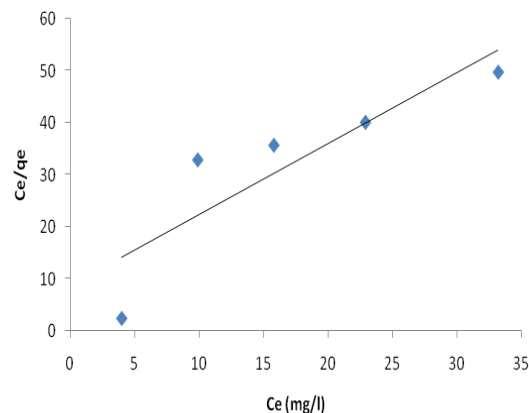
The Langmuir isotherm is based on the assumption that adsorption takes place at specific homogenous sites within the adsorbent which involves a monolayer adsorption process (Langmuir, 1918). The linear form of the Langmuir isotherm equation is given in (8).

$$C_e/q_e = C_e/q_m + 1/q_m K_L \quad (8)$$

Where  $q_m$  (mg/g) is the maximum adsorption capacity for a complete monolayer coverage,  $K_L$  (L/mg) is the equilibrium constant related to the energy of adsorption which quantitatively reflects

the affinity between the adsorbent and adsorbate. The constants  $q_m$  and  $K_L$  were determined from the slope and intercept of the plot of  $C_e/q_e$  against  $C_e$  (Figure 8). The Langmuir isotherm constant parameters are recorded in Table 3. The Langmuir isotherm can be described in terms of a dimensionless constant separation factor  $R_L$ . The  $R_L$  values can be determined using (9).

$$R_L = 1/[1+K_L C_0] \quad (9)$$



**Figure 8:** Langmuir isotherm model on the sorption of zinc (II) ions by the bentonite (pH, 5.0, time, 2hrs, Temp, 300K).

**Table 3:** Equilibrium Isotherm Model Parameters.

Langmuir Model					
$q_m$	$K_L$	$R^2$			
0.156	0.733	0.763			
Langmuir $R_L$ Values					
Co(mg/l)	20	40	60	80	100
$R_L$	0.064	0.033	0.022	0.017	0.013
Freundlich Model					
$1/n$	$n$	$K_f$	$R^2$		
0.679	1.47	0.061	0.994		
Temkin Model					
A	B	$R^2$			
0.418	0.245	0.972			
Dubinin-Radushkevich Model					
$q_D$	$B_D(\text{mol}^2/\text{KJ}^2)$	E(KJ/mol)	$R^2$		
0.533	0.004	11.18	0.845		
Redlich-Peterson Model					
$K_R$	$\alpha_R$	$\beta$	$R^2$		
20.5	73.8	0.834	0.907		

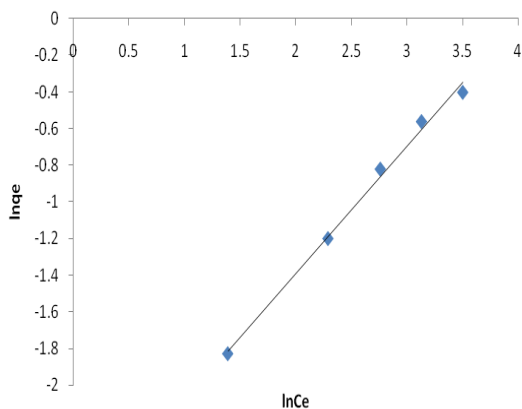
The values of  $R_L$  provide very important information on the nature of adsorption. The  $R_L$  values also indicate the shape of the Langmuir isotherm. When  $R_L=0$ , the process is irreversible,

$R_L=1$  signifies a linear process,  $R_L$  between 0 and 1 indicates a favorable adsorption and the value of  $R_L$  greater than 1 indicates an unfavorable adsorption process. Also, a  $K_L$  value less than 0 indicates a favorable adsorption. The value of  $K_L$  and the  $R_L$  values obtained at different initial concentrations indicated a favorable adsorption process which implies that the bentonite has a high affinity for zinc (II) ion in solution.

The Freundlich isotherm describes adsorption on heterogeneous systems involving multilayer adsorption (Freundlich, 1906). The linear form of the Freundlich isotherm equation is given in (10).

$$\ln q_e = [1/n] \ln C_e + \ln K_f \quad (10)$$

Where  $K_f$  (L/g) is the Freundlich constant corresponding to the adsorption capacity,  $n$  (dimensionless) is a constant describing the adsorption intensity of the adsorbent. The plot of  $\ln q_e$  against  $\ln C_e$  is shown in Figure 9 and the constants  $n$  and  $K_f$  were obtained from the slope and intercept. These isotherm parameters are presented in Table 3. The value of  $R^2$  obtained confirms the applicability of the Freundlich isotherm to the sorption process. If  $n < 1$  it implies that the sorption process is a chemisorptions,  $n > 1$  indicates a favorable physical adsorption process. The value obtained in this study suggests a favorable physical adsorption in which weak van der Waals forces are dominant rather than chemisorptions.



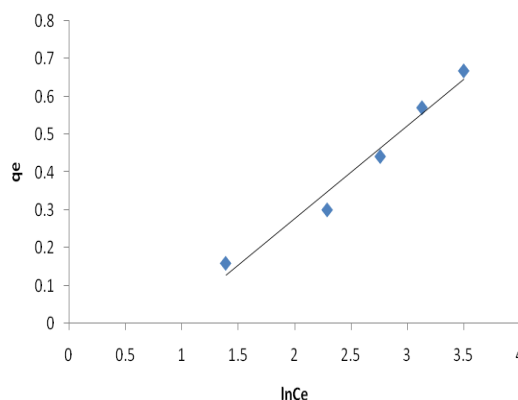
**Figure 9:** Freundlich isotherm model on the sorption of zinc (II) ions unto the bentonite (pH, 5.0, time, 2hrs, Temp, 300K)

The Temkin isotherm is based on the assumption that the free energy of sorption is a function of the

surface coverage (Temkin and pyzhev, 1940). This isotherm unlike the Langmuir and Freundlich takes into account the interactions between metal ions and adsorbents based on the free energy. The linear form of the Temkin isotherm is given in (11).

$$q_e = B \ln A + B \ln C_e \quad (11)$$

Where  $B=RT/B_T$  (J/mol) is a constant related to the heat of adsorption and  $A$  (L/g) is the equilibrium binding constant corresponding to the maximum binding energy,  $R$  is the ideal gas constant (8.314 J/mol/K) and  $T$ (K) is the absolute temperature. The plot of  $q_e$  against  $\ln C_e$  confirms the applicability of the model ( $R^2 > 0.96$ ) and is shown in Figure 10. The Temkin isotherm parameters are given in Table 3.



**Figure 10:** Temkin isotherm model on the sorption of zinc (II) ions unto the bentonite (pH, 5.0, time, 2hrs, Temp, 300K)

The Dubinin-Radushkevich (D-R) isotherm was used to determine the heterogeneity of the surface energies and the apparent porosity of the adsorbent (Dubinin, E.D. Zaverina, 1947). The linear form of the D-R isotherm equation is given in (12).

$$\ln q_e = \ln q_D - B_D \mathcal{E}^2 \quad (12)$$

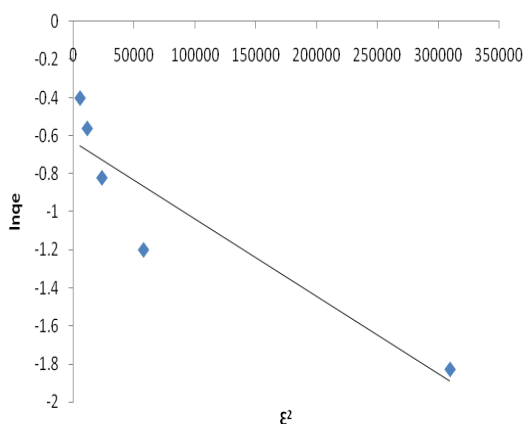
$$\mathcal{E} = RT \ln [1 + 1/C_e] \quad (13)$$

Where  $q_D$  (mol/g) is the theoretical saturation capacity,  $B_D$  (mol<sup>2</sup>/J<sup>2</sup>) is a constant corresponding to the mean free energy of adsorption per mole of the adsorbent and  $\mathcal{E}$  is the Polanyi potential,  $R$  is the ideal gas constant and  $T$  (K) is the absolute temperature. The plot of  $\ln q_e$  against  $\mathcal{E}^2$  is shown in Figure 11 and the constants  $B_D$  and  $q_D$  are

calculated from the slope and intercept. The mean free energy  $E$  (KJ/mol) of sorption per molecule of the adsorbate when it is transferred to the surface of the solid from infinity in the solution was calculated using (14).

$$E = 1/[2B_D]^{1/2} \quad (14)$$

The D-R isotherm parameters are shown in Table 3. If the value of  $E$  lies between 8 and 16 KJ/mol, it denotes a chemisorptions process while  $E$  values less than 8 KJ/mol indicates a physical adsorption process. The value of  $E$  obtained (11.18KJ/mol) showed a chemical adsorption between the bentonite and zinc (II) ions.



**Figure 11:** Dubinin-Radushkevich isotherm model on the sorption of zinc (II) ions onto the bentonite (pH, 5.0, time, 2hrs, Temp, 300K).

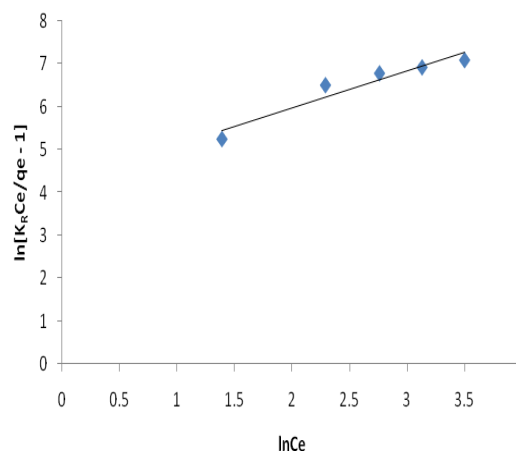
The Redlich-Peterson (R-P) isotherm is composed of three major parameters and can be applied either in homogenous or heterogeneous systems due to its high versatility. The linear form of the R-P isotherm equation is given in (15):

$$\ln[K_R C_e / q_e - 1] = \ln \alpha_R + \beta \ln C_e \quad (15)$$

Where  $K_R$  (L/g) is the R-P isotherm constant,  $\alpha_R$  (L/mg) is also a constant,  $\beta$  is the exponent which lies between 0 and 1. At low concentration the R-P isotherm approximates to Henry's law and at high concentrations its behavior approaches that of the Freundlich isotherm. Although, a linear analysis is not possible for a three-parameter isotherm, a trial method has been applied to the R-P isotherm to obtain values of the isotherm constants [32]. This method involves varying the isotherm parameters  $K_R$  to obtain the maximum value of  $R^2$  for the plot of  $\ln[K_R C_e / q_e - 1]$  against

$\ln C_e$  shown in Figure 12. The R-P isotherm parameters are given in Table 3. This isotherm is expected to produce a good regression  $R^2$  value as obtained in this study, since the method used to derive the isotherm parameters maximizes the  $R^2$  coefficient.

However, comparing the isotherms applied in this study. The best fit was obtained with the Freundlich isotherm,  $R^2$  (0.994) followed by the Temkin,  $R^2$  (0.972), then the Redlich-Peterson isotherm,  $R^2$  (0.907) and the Dubinin-Radushkevich isotherm,  $R^2$  (0.845) and the least the Langmuir isotherm with  $R^2$  (0.763).



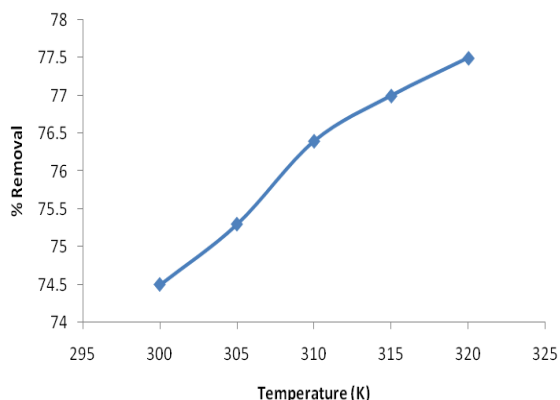
**Figure 12:** Redlich-Peterson isotherm model on the sorption of zinc (II) ions onto the bentonite (pH, 5.0, time, 2hrs, Temp, 300K).

### Thermodynamics

The result on the influence of temperature on the adsorption capacity of the bentonite for zinc (II) ions is shown in Figure13. The graph indicated a slight increase in adsorption of Cu with increase in solution temperature from 27-45<sup>o</sup>C. This suggests that the adsorption process is endothermic in nature. Temperature increase increased slightly the energy of the solution which helped in the diffusion of Cu (II) ions unto the active sites of the clay. This increase in adsorption capacity with temperature suggests chemical interaction (chemisorptions) between Zinc (II) ions and the bentonite. This however is restricted to just one layer of molecules on the surface and metal ions can also be adsorbed physically on additional layers present on the initial chemically adsorbed layer. However, studies on the effect of temperature on



adsorption have presented different types of results. An increase in adsorption with temperature increase has been reported (Ajmal et al., 2003). A decrease in the adsorption capacity with temperature increase has also been observed (Aksu, 2001). Also, temperature-independent effect on adsorption was also obtained (Ahuja et al., 1999).



**Figure 13:** Effect of temperature on the sorption of zinc (II) ion onto the bentonite. (pH 5.0, conc 20mg/L, time 2hrs).

The thermodynamic parameters were obtained from the data deduced on the effect of temperature on zinc (II) ions adsorption onto the bentonite. Thermodynamic parameters such as change in Gibb's free energy,  $\Delta G^0$ , Enthalpy change,  $\Delta H^0$  and Entropy change  $\Delta S^0$  were determined from Equations (16) - (18).

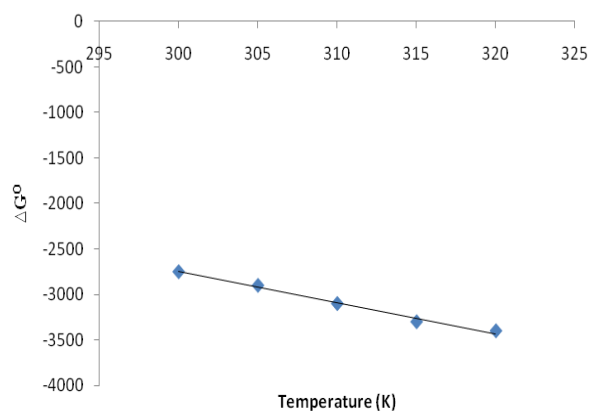
$$K_{ad} = C_{ad}/C_e \quad (16)$$

$$\Delta G^0 = -RT \ln K_{ad} \quad (17)$$

$$\Delta G^0 = -\Delta S^0(T) + \Delta H^0 \quad (18)$$

Where  $K_{ad}$  is the equilibrium constant of adsorption, it can change with temperature and therefore was used to determine the change in free energy,  $\Delta G^0$ .  $C_{ad}$  is the concentration of zinc (II) ions on the adsorbent at equilibrium in mg/L,  $C_e$  is the equilibrium concentration of zinc (II) ion in solution in mg/L.  $T(K)$  is the absolute temperature and  $R$  is the universal gas constant, (8.314J/molK). The plot of the changes in free energy against temperature is shown in Figure 14. The value of the regression coefficient, ( $R^2$ ) obtained, (0.9733) showed a good fit to the experimental data. The Enthalpy change,  $\Delta H^0$ , (6.953kJ/mol) and Entropy change,  $\Delta S^0$ ,

(32.23J/molK) were obtained from the slope and intercept, respectively. The negative values of  $\Delta G^0$  obtained indicate a spontaneous process. The positive values of  $\Delta S^0$  showed a disordered process, this implies that there would be an increase in the number of steps involved in the sorption of zinc (II) ions by the bentonite. The positive value also indicates the affinity of the adsorbent for zinc (II) ions. Similarly, the positive enthalpy change observed showed that the sorption process is an endothermic one. Therefore it is expected that an increase in temperature should increase the adsorption process, this confirms the result obtained in Figure 13 where an increase in adsorption with temperature was recorded.



**Figure 14:** Thermodynamic Plot on the sorption of zinc (II) ion onto the bentonite. (pH 5.0, Metal conc 20mg/L, Contact time 2hrs).

## CONCLUSION

The result of this study showed that Afuze bentonite can be used as a low cost adsorbent for zinc (II) ions from aqueous solution. Kinetic models revealed chemical as well as physical adsorption mechanism between Zinc (II) ions and Afuze bentonite.

The equilibrium sorption isotherms applied such as the Langmuir, Freundlich, Temkin, Dubinin-Radushkevich and Redlich-Peterson models indicated the potential of Ekulu clay as a low-cost material for zinc (II) ion removal from aqueous stream. Thermodynamic studies indicated a spontaneous, disordered and endothermic adsorption between copper ions in solution and Ugwuoba clay.

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