



## Adsorption Potentials of Fadama Clays towards Heavy Metals (Zinc and Cobalt)

**\*OTOBO, G. & \*\*OKPAKO, A. C.**

\*Department of Pure And Industrial Chemistry, University Of Port Harcourt Rivers State Nigeria.

\*\*Department of Integrated Science, College Of Physical Education Mosogar Delta State Nigeria.

E-mail: [otobog@yahoo.com](mailto:otobog@yahoo.com)

### Abstract

*This study investigated the potentials of Fadama Clays (Wetland soil) in the adsorption of heavy metals such zinc and cobalt ions. Fadama Clays collected from three different locations in Delta State were analyzed for Physico-chemical parameters. The effect of pH, contact time and adsorbent dosage were evaluated. The adsorption behavior was characterized using adsorption isotherms, adsorption kinetics (pseudo second order rate equation), diffusion-chemisorptions kinetics and adsorption edge experiments. Application of Langmuir isotherm and adsorption kinetics showed that Fadama soils adsorbed the metal ions at lower pH values of 1 to 4. Adsorption kinetics (pseudo second order rate equation) showed that FAP (Patani Fadama clays) had the highest equilibrium rate constant  $K$  (0.277mg/l/mins and 0.147mg/l/mins) for Zn and Co respectively and next is FAU (Uwherun Fadama clays) (0.214mg/l/mins and 0.000mg/l/mins). FAK (Kokori Fadama clays) has the lowest equilibrium rate constant ( $K$ ) (0.079mg/l/mins and 0.100 mg/l/minis). Application of Diffusion-chemisorptions kinetics indicated FAK yielded maximum adsorption capacities for the two metal ions with  $K_{DC}$  (Zn:0.89mg/g/l Co:0.24mg/g/l) followed by FAP with  $K_{DC}$  (Zn: 0.32mg/g/l Co:0.22mg/g/l) and FAU the least with  $K_{DC}$  (Zn:0.15 mg/g/l Co:0.23 mg/g/l) at lower pH values of 1 to 4. This was as a result of available surface area and reduced distance for the sorbate to travel to reach an active sorption site.*

**Keywords:** Fadama, Adsorption Isotherm, Adsorbent, Diffusion-chemisorptions ( $K_{DC}$ ).

### 1. Introduction

Soil has the ability to immobilize heavy metal ions. The immobilization is due to sorption properties such which are determine by physiochemical properties of soil such as amount of clay and organic fraction, pH, water content, temperature of the soil and properties of the particular metal (Ashok. K. et al.1998). Surface charge, pH and the concentration of cation as well as its accompanying anions can affect electrostatic adsorption of metal while organic matter, Fe and Al hydroxides clay content are recognized as the most significant soil properties influencing sorption reaction (Barry et al., 1995 and Bokin 2003).

In acidic soil, some iron, aluminum oxides are positively charged. They tend to counteract the electronegativity of the larger silicate clays thereby reducing the capacity to adsorbed cations. Adsorption is the accumulation of dissolved particles from a solution on to the surface of an adsorbent. (Ademoroti, 1996) Adsorption in general is found to occur following one or more mechanisms. Analysis of different adsorption systems indicate that adsorption mechanism can be classified into three, namely layer formation, micro Pore filling and capillary condensation (Adamson,1990) Fadama soil (non irrigable land and flood plains and low lying areas underlined by shallow aquifer. (Adeyeye.2005) very rich in organic matter and nutrients than adjacent upland soil (Turner, 1977; Kparmwang and Esu, 1990), are used for growing crops such as maize, guinea corn, tobacco and cattle grazing with little or no addition of organic waste.

Of a particular threat to Fadama land areas are effluents from factories and manufacturing facilities which contaminate the irrigable channels. Consequently, interest is growing in the use of sorbents

made from low-cost materials such as Fadama soils which contain some amount of clay. Clay minerals play an important role in accumulation, adsorption/desorption, as well as in exchange process of metal ions (Apak, R. Guolu and M. H Turgut 1998). It is considered that the adsorption of heavy metal ions and complexes on clay mineral occurs as a result of ion exchange, surface complexation, hydrophobic interaction and electrostatic interaction (Nowack and Sigg, 1996, Jung Cho and Hahn 1998). The **Adsorption** of heavy metal such as Zinc and Cobalt which have tremendous hazard effect in the environment on Fadama Soils are discussed in this research work.

## 2. Materials and Methods

Soil samples of Fadama soils were collected from latitude 5° 45' N and longitude 6° 71' E (Kokori, Ethiope East L.G.A), latitude 5°46' and longitude 5°26' N and longitude 5°46' E (Ughelli, Ughelli North L.G.A,) latitude 5°32'N and longitude 5° 50'E (Patani, Patani L.G.A) all in Delta State., Nigeria.

The Fadama soils in the Niger Delta area are moderately acidic with pH value ranging from 5.0-6.20.

Texturally, the Fadama soils comprise of particles such as sand, silt and clay held together by organic substances, iron oxides, carbonates, clay and or silica. The clay minerals are hydroxides aluminum, magnesium or iron Silicate.

Fadama soil from Kokori (FAK) is a brown sandy loam soil with 65% sand, 20% silt and 15% clay and it feels a bit smooth and powdery but sticky when moist. This soil belongs to the montmorillonite group with chemical formula  $Al_2(OH)_2(Si_2O_5)$  which expands and is having higher cation exchange capacity.

Fadama soil from Uwheru (FAU) is grey in colour and sandy with 85% sand 5% silt and 10% clay. It feels gritty when rubbed between fingers, not plastic or sticky when moist. This soil clay mineral belongs to the illite (clay mica) group.

Fadama soil from Patani (FAP) is a yellow grey colour with 55% clay 32% silt and 13% sand. It feels smooth, sticky and plastic when dry and does not expand when wet. This soil belongs to the kaolinite group with chemical formula  $Al_2(OH)_4Si_2O_5$ .

The physiochemical properties of soil which affect the sorption properties of soil are concentrated in the lower (15-30cm) than the upper depth [Alloway 1995;Tsadilas 2000] Therefore, the various soil samples which were collected at a depth of 15-30cm Samples were sieved with a 2mm sieve and divided into two portions. One portion was placed in polyethylene bag and stored in a refrigerator at 4°C and the second was air dried at room temperature for 48 hours and stored in a tightly sealed bottle. A sub-sample of air dried was ground to pass 80 mesh sieves (180µm) for determination of chemical properties (Chae and Tabatabai 1986).

1g each of soil samples were first treated with 10ml of 0.1M NaOH to precipitate some of the dissolved ions as their hydroxide which was then separated from the clay. For example,  $Al(OH)_2^+$  at low pH block the active site of the adsorbent making exchange site unavailable. Raising the pH, ions from NaOH form  $Al(OH)_3$  thereby releasing negative charged site. These base-treated clays were then boiled with 20ml of 0.04M  $HNO_3$  for 1 hour to activate them. They were then washed several times with distilled water, dried and served. The soil samples were activated with  $HNO_3$  to open up micro-pores of the adsorbent thereby making the soil ready for adsorption

10g of each soil sample was weighed into 200ml beaker. 20ml of distilled water were added to the soil mixtures and was allowed to stand for further 30 minutes and stir occasionally with glass rod and allow the fine soil particles to settle. The pH meter (model Kent Ek7020) which was standardized with buffer pH 4 and pH 9 was inserted into the partly settled suspension to determine the pH (Ademoroti, 1996)

### 3. Batch Experiments

2.2032g analytical grade anhydrous Cobalt (II) Chloride ( $\text{CoCl}_2$ ) was dissolved in distilled water and made up to 1 litre mark [1ml = 1mg Co]. Standard Co was prepared by withdrawing 10 ml of Co stock solution into 1 litre volumetric flask and made up to the mark [1ml = 10  $\mu\text{g}$  Co].

100mg 30-mesh analytical grade Zinc metal was dissolved in slight excess of HCl (about 1ml is required) which was distilled water and made up to 1 litre [1ml = 1mg Zn]. To prepare standard Zn, 10ml of the stock solution was withdrawn and made up to 100ml mark : 1ml = 100 $\mu\text{g}$  Zn. (Ademoroti, 1996)

All absorption tests, namely, isotherm, kinetics and pH-edge, were performed as batch experiments. Adsorption isotherm was generated with a fixed sorbent mass and varying initial metal ions concentration (Co) from 5mg/l to 30mg/l while maintaining the adsorbent dosage of 1 g/l.

The effect of adsorbent dosage was studied by varying the adsorbent amount from 5mg/l to 20mg/l with metal ions concentration of 20mg/l.

The effect of time and pH were studied at 30°C with metal ion concentration of 20mg/l and adsorbent dosage of 1g. The initial concentration of Co and Zn were prepared by serial dilution of standard mg/l reference solution. The pH of the solution was adjusted to pH  $5.6 \pm 0.1$ . The sealed bottles were placed in a shaker (model TT 12F Technical and Technical USA) for 4hour at 298k. After equilibration, the supernatants were filtered through UM pore size MF- Millipore mixed cellulose ester membrane filter and then analyzed for dissolved Co and Zn concentration by BUCK Scientific Atomic Absorption Spectrometer (model 200). The uptake capacity amount of Co and Zn ( $q_e$ ) adsorbed were calculated by mass balance between Co (initial conc. of metals) and (final conc.)  $C_e$ . (Wahba and Zaghloul 2007).

Adsorption kinetic experiments were performed in a solution with 1.0g of sample, pH  $\pm 5$ . Initial Co and Zn concentration of the solution were 20mg/l and the solution pH was maintained by using 0.1M  $\text{HNO}_3$  And 0.1M KOH. The suspension was stirred by a magnetic bar and was placed on digitally operated high speed centrifuge (model TGL-16G) for centrifugation. The supernatant was collected at various time intervals during the one and half hours experiment using decantation method. The sampling time for the experiment were 20, 40, 60, 80 to 100 minutes and the concentration of heavy metals using atomic absorption spectroscopy were taken (Cottenie 1982).

Adsorption edge (pH effect) experiments were conducted in 40ml samples tubes containing 1g of the samples and 30ml of 20mg/l Co and Zn solution at different pH values of 2, 4, 6, 8. The sample tubes were placed in a shaker for 4hrs. pH of final Co and Zn concentration in the filtrate were determined after equilibration using pH meter (model: EL17050)

### 4. Results and Discussion

The study of the three Fadama soil samples (FAK, FAP and FAU) before adsorption of metals indicated that the three Fadama soils samples were acidic with the pH values of 4.47, 4.36 and 4.35 respectively which correspond to the pH of the Niger Delta region (Isirimah, 1987; Odu et al., 1985). It could be suggested here that the acidic nature of the soils could be as a result of the aluminum (iii) ion which was in the soil no longer existing as aluminum (iii) ion but has been converted to aluminum hydroxyl. This in line with (Brady, 1974) who said that exchangeable  $\text{H}^+$  ions that are released by base forming cations move into the solution where they react with OH to form water.

At pH 2 and 4, FAK had the highest adsorption capacity for the two metal ions (Zn and Co). This is followed by FAP and FAU had the least adsorption capacity.

At pH 8 the three soil samples adsorption capacity decreased in this order FAK < FAU < FAP as shown in figure 1 and 2.

Increase adsorption between the pH 2 and pH 4 indicated that hydroxyl groups are the major functional group responsible for the removal of these metals ions at that low pH values. It showed that the hydroxyls present in the silicate particles dissociate slightly and the colloidal surface is left with a negative charge carried by the oxygen which attracts the metal ions to itself. That is to say that the mechanism of adsorption of these ions is the ion exchange mechanism which involves the release of light metal ion during heavy metal uptake (Crist et al, 1999) and electrostatic interaction (Do, (1998).

Adsorbent dosage as shown in figure 3 and 4 had greater effect on the adsorption of the metal ions in the three soil samples. It was observed that the three soil samples had good adsorption capacity for the two metal ions with increase in the adsorbent dosage. This could be attributed to the fact that minute silicate clay colloidal particles referred to as micelles ordinarily carry negative charges and hundreds of thousands of positively charged ions or cations are attracted to each colloids (Buseck1993).

Adsorption of these metals was higher with FAK followed by FAU and then FAP. There was a maximum adsorption for these metal ions at maximum dosage of adsorbent. This suggested that a good solid adsorbent must have a combination of two pore ranges: the microspore range and the macropore range (Do1998)

Contact time appeared to have noticeable effect on the adsorption of the metal ions. There is similarity in adsorption of zinc and cobalt on the three Fadama soils. In a nutshell, some levels of adsorption of zinc, and cobalt were maintained with time.

FAK had the maximum adsorption for the two metal ions at 20 and 60 minutes as shown in Fig 5 and 6.

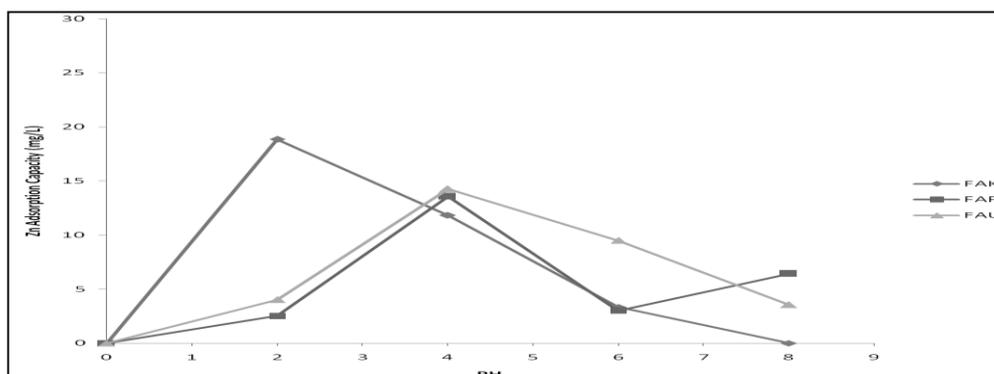


Figure 1: Effect of pH on the Adsorption of Zinc on Fadama Soils

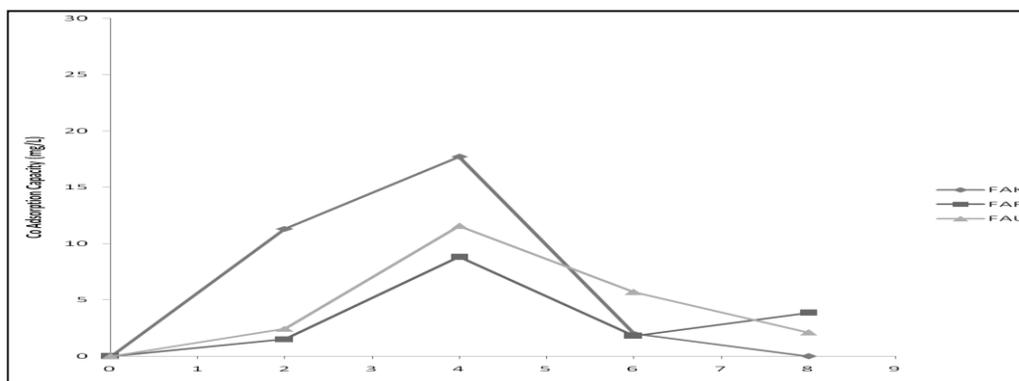


Figure 2: Effect of pH on the Adsorption of Cobalt on Fadama Soils.

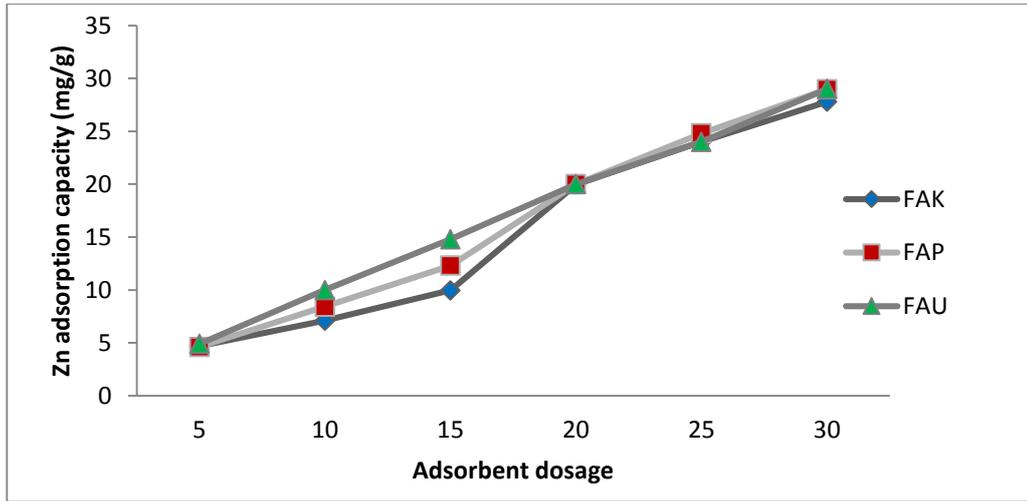


Figure 3: Effect of Adsorbent Dosage on the Adsorption of Zinc ions on Fadama Soils

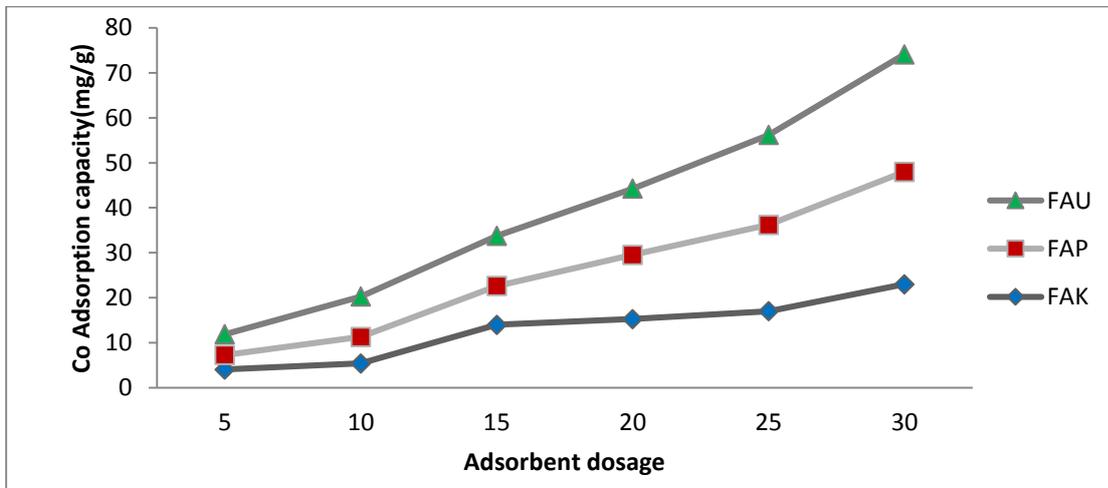


Figure 4: Effect of Adsorbent Dosage on the Adsorption of cobalt ions on Fadama Soils

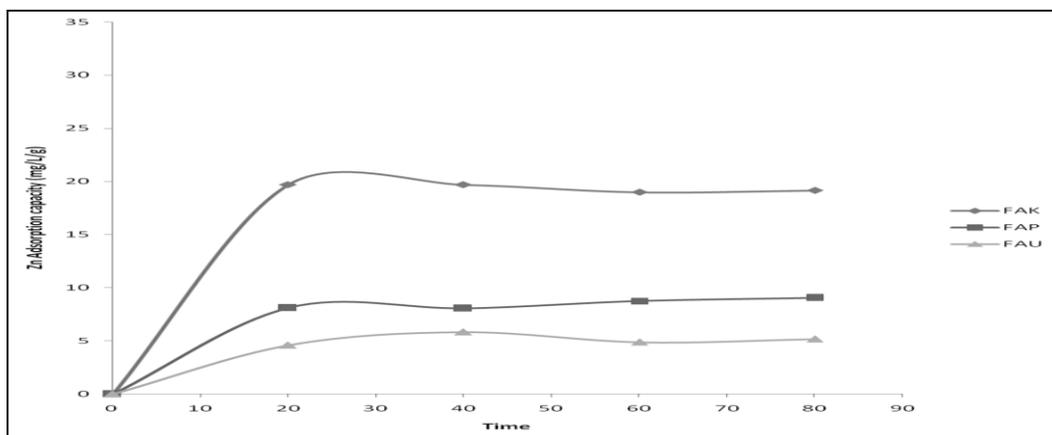


Figure 5: Effect of Contact Time on the Adsorption of Zinc ions on Fadama Soils

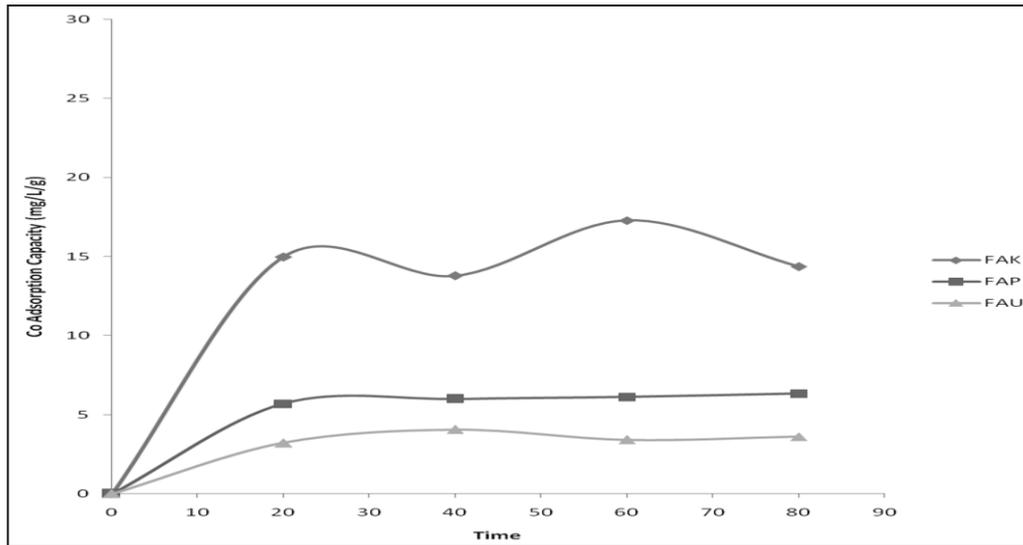


Figure 6:

Effect of Contact Time on the Adsorption of Cobalt ions on Fadama Soils.

### 5. Adsorption Isotherm

Langmuir equation yielded a satisfactory fit. The linearized Langmuir equation has the following form.

$$1/q_e = 1/q_{max} + b C_e / q_{max} \quad (1.2)$$

Where  $C_e$  is the equilibrium metal ion concentration in mg/l,  $q_e$  is the amount of metal sorbed in mg/l,  $q_{max}$  is the maximum metal sorption capacity in mg/l,  $b$  is a constant, related to the strength of adsorption l/mg. The sorption capacities are of close range with those determined from pseudo- second order kinetics model.

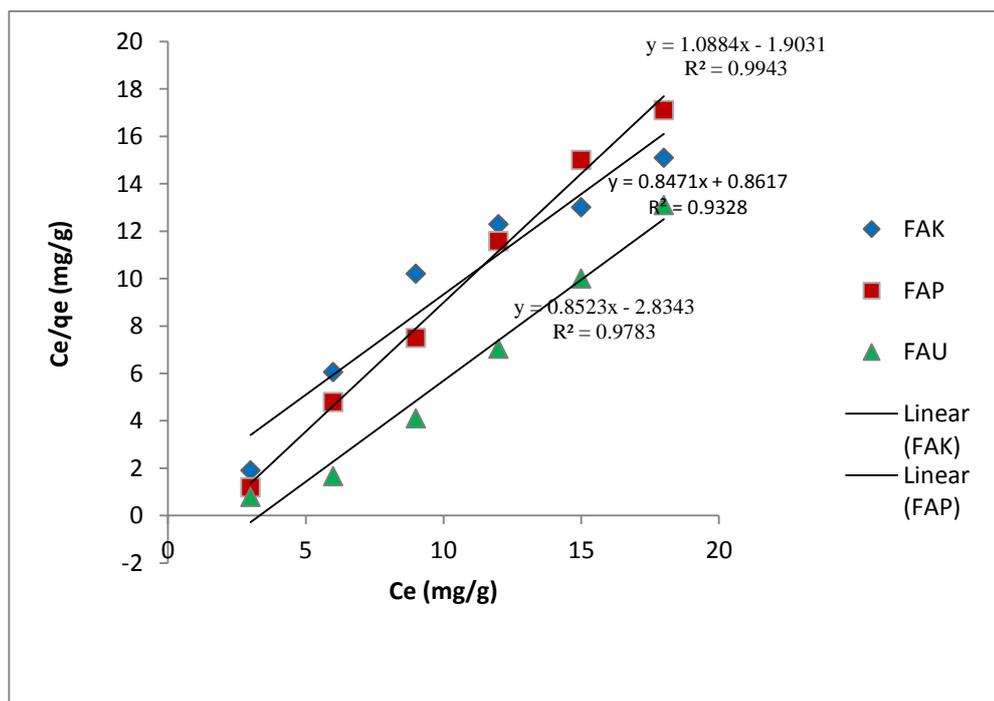


Figure 7: Langmuir Isotherm for Zinc Ions Adsorption on Fadama Clay

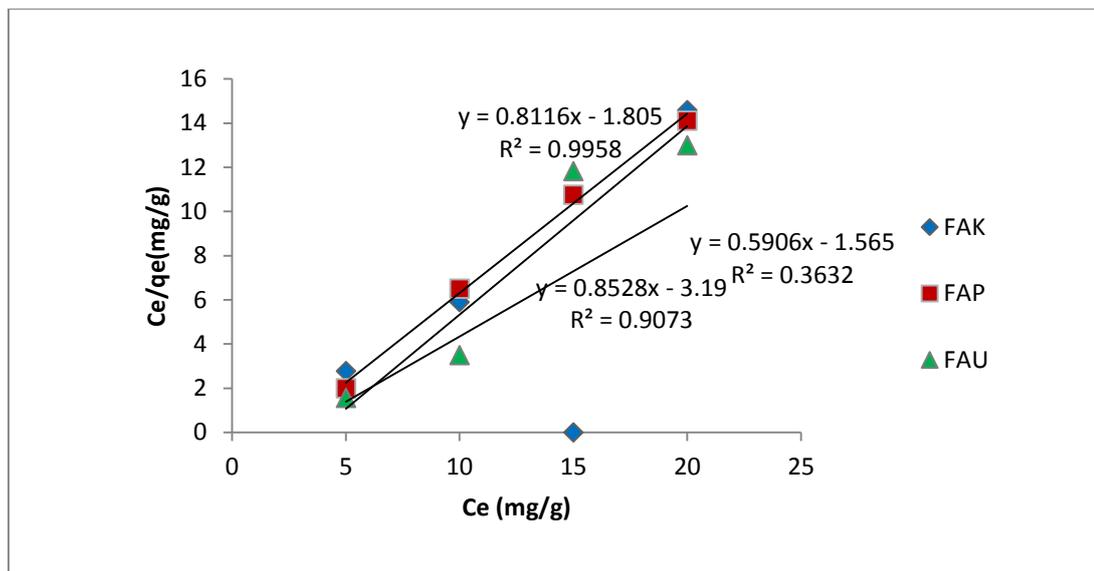


Figure 8: Langmuir Isotherm for Cobalt Ions Adsorption on Fadama Clays

Table 1: Isotherm Constants for Adsorption of Zn (II) Ions on Fadama Soils

Soil sample	Langmuir Isotherm		Pseudo-Second Order Rate Kinetics	
	qm(mg/g)	b(mg/g)	k (mg/l/min)	qe(mg/g)
FAK	4.41	0.227	.079	11
FAP	9.01	0.111	.277	6
FAU	15.87	0.063	.214	4

Table 2: Isotherm Constants and Adsorption Kinetics of Co (II) Ions on Fadama Soils

Soil sample	Langmuir Isotherm		Pseudo-Second Order Rate Kinetics	
	qm(mg/g)	b(mg/g)	k (mg/l/min)	qe(mg/g)
FAK	8.00	0.125	.100	14
FAP	8.47	0.118	.147	15
FAU	8.77	0.114	.222	3

FAK = Kokori Fadama Clay

FAP = Patani Fadama Clay.

FAU = Uwheru Fadama Clay

qm = Minimum adsorption capacity (mg/g)

b = Langmuir constant

k = rate constant

qe = sorption capacities

### 6. Adsorption Kinetics

Data from the kinetics experiment were fitted to the pseudo second order rate equation [1.3] to determine Zn and Co, sorption capacities ( $q_e$ ) and rate constant  $k$ . This model conformed that the adsorption followed the Langmuir equation. The kinetic rate equation can be written as shown below.

$$dq_t / t = k (q_e - q_t)^2 \tag{1.3}$$

Where  $q_t$  and  $q_e$  are the amount of metals adsorbed at time  $t$  and at equilibrium (mg/l/g), respectively, and  $k$  is the equilibrium rate constant for second order sorption (mg/g/min). By integrating equation for the boundary condition  $t=0$  to  $t=t$ ,  $q_t=0$  to  $q_t=q_t$  the following linearized form is obtained.

$$t/q_t = 1/kq_e^2 + 1/q_e t \tag{1.4}$$

A plot of  $t$  versus ( $t_0/q_t$ ) was used to determine value of  $k$  as shown in Figures 9 and 10. This model described the data adequately when fitted into equation (1.4)

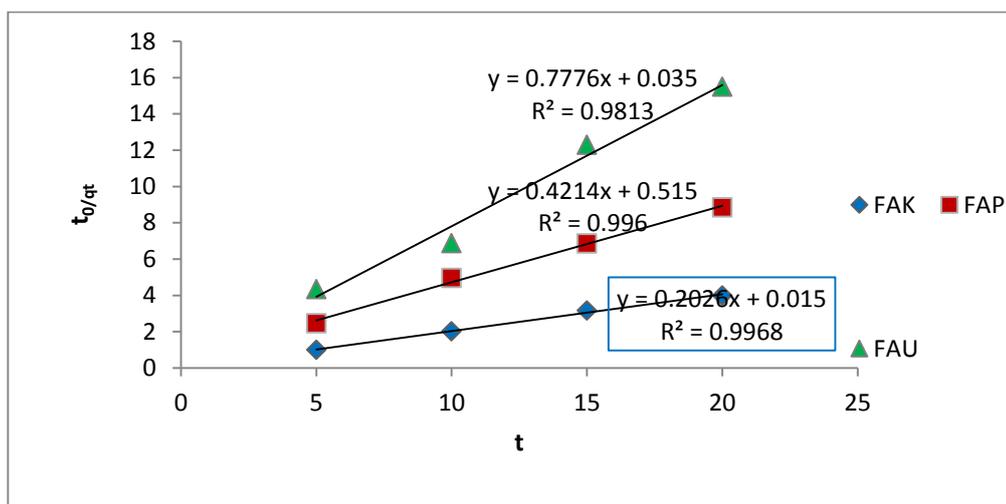


Figure 9: Pseudo-Second Order Rate Kinetics For Adsorption of Zinc (II) Ions on Fadama Clays.

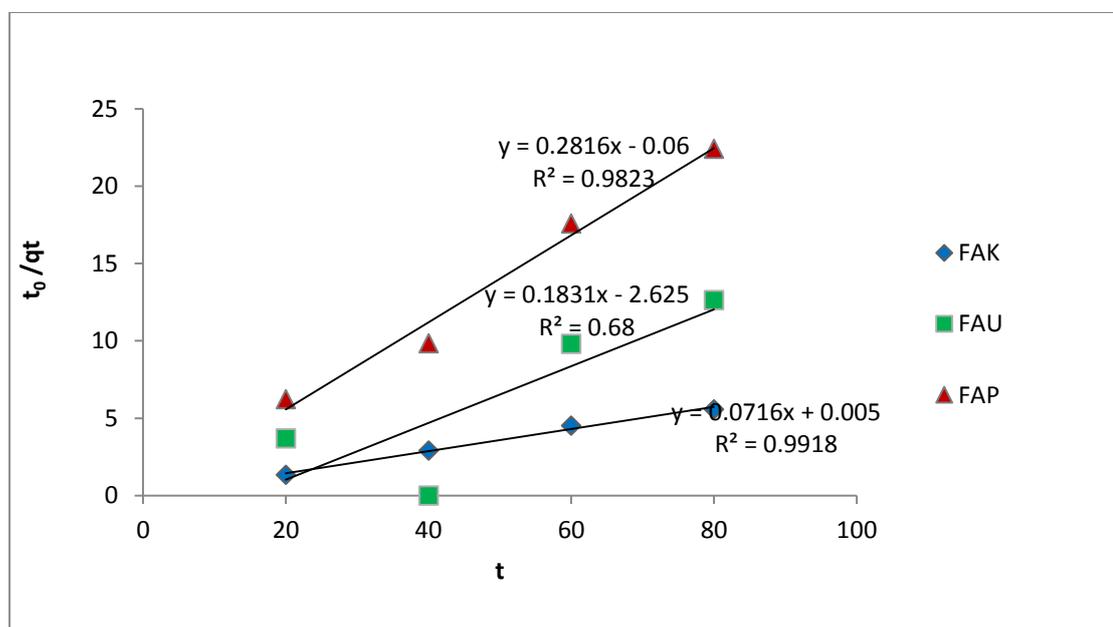


Figure 10: Pseudo-Second Order Rate Kinetics For Adsorption of Cobalt (II) Ions on Fadama Clays.

### 7. Diffusion-Chemisorptions Kinetics

Initial metal concentration of different sorbent sizes greatly affects the amount of the heavy metal adsorbed by each soil sample. Adsorption of the metal ions (Zn, Co) increase with increase concentration of the adsorbate

A plot Diffusion-Chemisorptions' rate constant ( $K_{DC}$ ) versus initial metal concentration for various sorbent sizes as shown in figures 13 and 14 indicated that  $K_{DC}$  increased with increased sorbent size .This was as a result of available surface area and reduced distance for the sorbate to travel to reach an active sorption site.

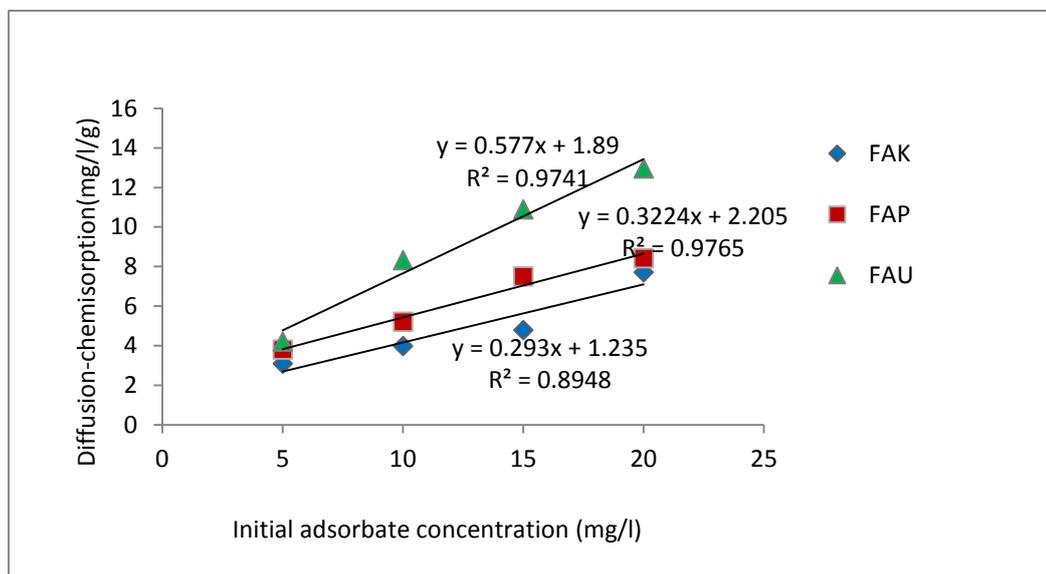


Figure 11: Diffusion chemisorptions Rate of Adsorption of Zinc ions on Fadama Soil

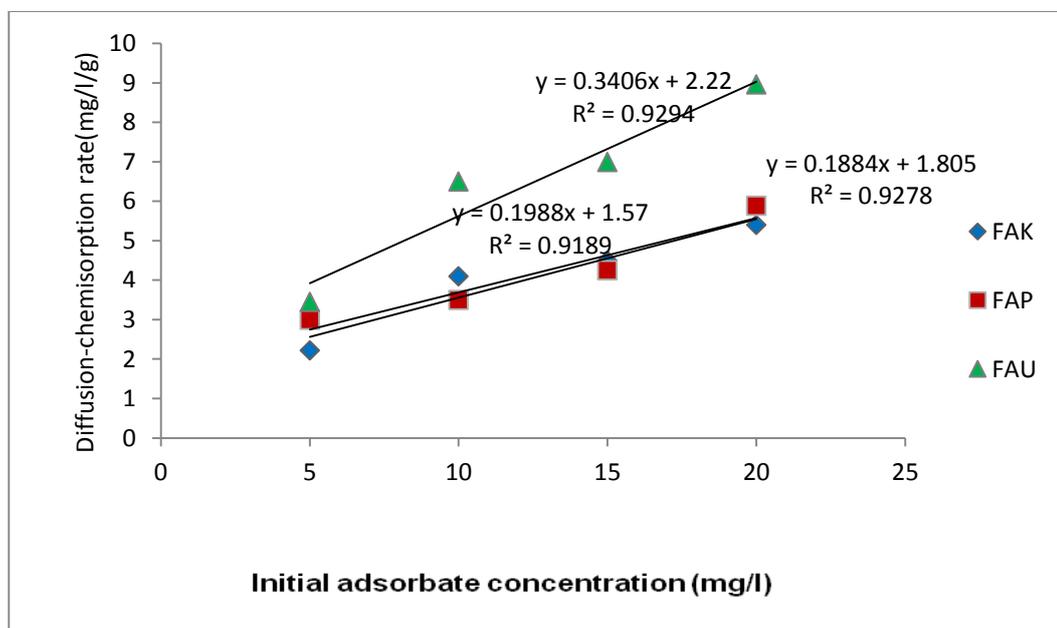


Figure 12: Diffusion chemisorptions Rate of Adsorption of cobalt ions on Fadama Soil

## 8. Conclusion

The adsorption of  $Zn^{2+}$  and  $Co^{2+}$  ions depend on the chemistry and the surface morphology of the Fadama clays and on the concentration of these clays as shown in Figure 9 and 10. This was in line with fact that surface sites responsible for the adsorption are assumed to be the permanent charges,  $SiO_4$  (silanol) group, Carboxyl group, aluminol group and phenol group (Julide and Resat, 2006),).

The isotherm model of Langmuir and the kinetic model of pseudo-second order rate equation as well as Diffusion-Chemisorptions adsorption rate equation were found to be quite suitable to characterize the adsorption of heavy metal ions on Fadama clays. In a nutshell, the adsorption of  $Zn^{2+}$  and  $Co^{2+}$  ions on the soil samples decreased with increased pH and increased with increased adsorbent dosage, contact time and the adsorbate concentration. This confirmed that the Fadama clays have good adsorption potential. From the Langmuir Isotherm, the Chemisorption-Difussion kinetics and the kinetic model of pseudo-second order results of the soil samples, it was seen that the soils could work as adsorbent for heavy metals in neutral and acidic solutions.

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