EFFECTS OF PHYSICO-CHEMICAL PROPERTIES OF WETLAND SOIL ON THE ADSORPTION OF CADMIUM IONS

G. OTOBO[1] S.C. ORTUTU[2] AND A.I. OBI[3].
[1]Ph.D, [2]PhD [3]MSc
[1,2,3] Department of Pure and Industrial Chemistry Nnamdi Azikiwe University Awka, Nigeria.

ABSTRACT

This work investigated the effect of soil Surface, Soil morphology and broken edge of fadama clays collected from three different locations in Niger Delta on the adsorption of Cadmium ions. The particle size, the contact time, the total organic matter, the pH, and the adsorbent concentration of the different soils were evaluated.
These Soils were prepared to adsorb Cadmium from aqueous solution of different pH, time and adsorbent concentration.

The adsorption behaviors that were characterized, using Adsorption isotherms, Adsorption kinetic, adsorption edge and Diffusion – Chemisorptions show that Soil from Patani (FAP) yielded maximum adsorption capacity for Cadmium at lower pH 2, followed by soil from Uwherun (FAU)and Soil from kokori the least(FAU). Adsorption capacity decreases with increase in pH values in the three soil samples (except for FAK that increases at pH 4) which is in line with [1] that says that in ion exchange mechanism, Cadmium binds to anions sites by displacing protons from acidic groups or existing alkali earth metal e.g Na or Ca from anionic sites at high pH. *This suggest that there is surface and broken edges OH groups that gives the fadama clay particles their electro negativity and their capacity to adsorbed cadmium ions. Application of Diffusion Chemisorptions rate (K_{DC}) for cadmium ions indicated that Fadama clay from Patani (FAP) had the highest Diffusion Chemisorptions rate (K_{DC}) followed by Kokori (FAK) and Uwheru (FAU) the least. This was as a result of available surface area and reduced distance for the sorbate to travel to reach the active Sorption site.*

Keywords: *Adsorption, Fadama (Wetland Soil), Adsorbate and Adsorbent*

INTRODUCTION

Clays, the active mineral portions of the Soils are dominantly colloidal and crystalline. When water pollutants such as lead and cadmium ions are disposed on soil, instead of it leaching to easily pollute the water, they are almost adsorbed to the Cation exchange site. [2]
Soil in general has the ability to immobilize heavy metals ion due the sorption properties which are determined by physiochemical properties (clay and organic fractions, water contents, pH, temperature) of Soils and the properties of the particular metal ions.[3]
Surface charge, pH and the concentration as well as its accompanying anions can affect electrostatic adsorption of metals while organic matter, Fe, Al hydroxides and clay content are recognized as the most significant soil properties. [4,5].
Clay minerals play important roles in the accumulation, adsorption/ desorption as well as ion exchange processes of metals.[6,7]
It is considered that the adsorption of heavy metals ions and complexes on clay minerals occur as a result of ion exchange , surface complexation, hydrophobic interaction and electrostatic interaction [8,9].
In the ion exchange mechanism, Cadmium binds to anions sites by displacing proton from acidic groups or existing alkali earth metal e.g Na or Ca from anionic sites at high pH.[1].
Factors that influence Cations adsorption on clays are pH, presence of surface and broken edge, OH groups (clay content), organic matter and salt content of the soil.

There are at least two negative charges associated with silicate clay particles; the first involves unsatisfied negative charges associated with O_2 and OH groups exposed at the broken edges and flat external surface of minerals such as kaolinite. The presence of broken edge OH groups gives the kaolinite clay particles their electron negativity and their capacity to adsorbed cations.
It was deduced that heavy metals ion adsorption of kaolinites and Smeatites result from pH dependent inner-sphere surface coordination with the edge hydroxyl group and outer sphere ion exchanging with the permanent negative sites.[10,11]
The fadama clays have good Adsorption potential for the adsorption of heavy metals such as Zn^{2+} Cu^{2+}, Co^{2+} , Cd^{2+} and Cr^{3+} released from industries, Agricultural an waste from automobile exhaust [12].
The effect of surface morphology and broken edge of wetland soil on the adsorption of cadmium is discussed in this work.

SAMPLING AREA:
Three different soils samples were collected from three different Wetland areas in Delta State.
Soil samples for the study were made up of Fadama Soils collected from latitude 5^0 45 ^{1}N and longitude 6^07^1 E from Kokori,(Ethiope East LGA), latitude 5^0 46 ^{1}N and longitude 5 ^{0}26 ^{1} N from Uwherun (Ughelli north LGA) and latitude 5^0 32^1 N and longitude 5^0 50 ^{1}E(Patani LGA) all in Delta State.

PHYSICAL PROPERTIES OF SOIL SAMPLES
The Fadama **Soil**s in Niger Delta are moderately acidic with pH value ranging from 5.0-6.0
Texturally, the Fadama soils comprises of particles such as sand, silt, and clay held together by organic substances, iron oxides, carbonates, clay or silica. the Fadama soil (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 montimorilonite group $[(Na,Ca)(Al,Mg)_6(Si_4O_{10})_3(OH)_6.nH_2O$]with Chemical formula Al_2 $(OH)_2(Si_2O_5)$ which expands and having cation exchange capacity.
The Fadama Soil from Uwherun (FAU) is grey colour and Sandy with85% Sand 5% silt and 10% clay, feels gritty when rub between fingers , not plastic or sticky when moist. It belongs to the illite (clay Mica) Al_2 $(Si_2Al_{,})_4O_{10}$ $(OH)_2$.
The Fadama Soil from Patani (FAP) is yellow grey colour and clayey with55% clay, 32% Silt and 13% clay, feels smooth, sticky and plastic when dry and does not expand when wet. It belongs to the Kaolinite with chemical formula $Al_2\,(Si_2Al_{,})_4\,Si_2O_5$.

MATERIALS AND METHODS
The three soil samples collected at a depth of 15-30 cm were selected to represent the major soil series in Niger Delta. [13,14]
Samples were sieved with a 2mm sieve and divided into two portions. A portion was placed in a polythene bag and kept in the refrigerator at 4^oC and the second was air dried at room temperature for 48 hours and stored in tightly sealed bottle. A sub sample of air dried was ground to pass80 mesh sieve for determination of chemical properties [15].
The particle size distributions of the Fadama clay were carried out using Pipette method. 50grams of the three soil samples were weighed and 5ml of hydrogen peroxide was added to remove organic matter and the samples were dried on a hot plate. 50ml of 5% hexametaphosphate (cologne) added and placed on the mechanical shakers for two hours. Using a 0.053mm sieve ,the samples were washed into 1 litre measuring cylinder until the water coming out is clear to remove silt and clay leaving sand fractions on the sieve. The colloidal solution was shaken vigorously. 20ml of the colloidal obtained were oven dried and weighed. This was done again after two hours. The weight obtained is that of silt plus clay.

The pH determination was carried out by weighing 10g of each soil samples into 200ml beaker. 20ml of distilled water were added to the soil samples and allowed to stand for 30 minutes to allow the fine soil particles to settle. The pH meter that was standardize with buffer pH 4 and pH9 was used to determine the pH of the supernatant liquid [12].

The Total organic carbon (TOC) of the soil samples was determined using Walkley and Black method. 10 ml of 0.5 $K_2Cr_2O_7$ was added to one gram of each soil mixture and swirled gently. To each, 20ml of conc. H_2SO_4 was added immediately and allowed to stand for 20minutes. Each was diluted to 250ml mark. 10 ml Conc. H_3PO_5 and 0.5% of diphenylamine were added and blue colour appears. The chromic acid not used up in oxidation was titrated with Iron (II)ammoniumtetraoxosulphate (vi) hexahydrate from burette. The solution changed from blue to green at the end point. Blank titration was carried out [16].

Adsorption test namely, isotherm, kinetic pH edge were perform as batch experiment.

Adsorption experiment were generated with a fixed mass of sorbent and varying cadmium ion, time and pH at 30^0C ,with cadmium ion concentration from varying from 5mg/l to 20mg/l while maintaining the adsorbent dosage of 1g/l. the initial conc. of Cd was prepared by serial dilution of standard mg/l reference solution. The pH of the solution was adjusted to pH5 .6 $\pm$ 0.01. The sealed bottles were placed in a shaker for four hours at 298k. The effects of adsorbent dosage were studied by varying the adsorbent amount from 0.5g/ to2g/l with Cadmium ion concentration of 20mg/l. After equilibration, the supernatants were filtered through UM pore size MF-Millipore mixed cellulose ester membrane filter and then analyzed for dissolved Cd Concentration by AAS. The uptake capacity of Cd adsorbed were calculated by mass balance between initial concentration and final [17].

Adsorption kinetic experiments were performed in a solution with 1.0g of samples pH$\pm$5. With initial concentration of cadmium of 20mg/l, pH was maintained by using 0.1M HNO3 and 0.1MkOH. The suspensions were stirred by a magnetic bar and supernatant was collected at various time intervals during the one and half hour experiment. The sampling times for the experiment were: 20,40,60,80 and 100 minutes. The concentration of Cd was taken using AAS [18]

The adsorption edge(pH)effects experiment were conducted in 40 ml samples tube containing 1g of the samples and 30 ml of 20mg/l cadmium at different pH values of 2,4,6,8. pH and final cadmium concentration in the filtrate were determine after equilibrate.

RESULTS AND DISCUSSIONS.

The particle size, and total organic compound concentration results in Table 1show that, the Fadama Soils comprises of particles such as sand, silt, and clay held together by organic substances. The Fadama Soil (FAK) is made up of 65% sand, 20% silt and 15% clay which made it feels a bit smooth and powdery but sticky when moist.

The Fadama Soil from Uwherun (FAU) is with 85% sand 5% silt and 10% clay, feels gritty when rub between fingers , not plastic or sticky when moist.

The Fadama Soil from Patani (FAP) has 55% clay 32% Silt and 13% sand, feels smooth, sticky and plastic when dry and does not expand when wet.
The base line study of the of the soil samples (FAK, FAP and FAU) pH shows that the three soil samples were acidic with pH values o f 4.47, 4.36, and 4.35 respectively. This is in line with the pH of the Niger delta soil.[19,20] .

This is as a result of Al ions in the soil no longer existing Al^{3+} but Aluminum Hydroxyl as shown below.

$Al3+ + H2O \rightarrow Al(OH)^2 + H^+$

$M(OH)^{3+} + H2O \rightarrow M(OH)^{3+} + H^+$

This is as result of exchangeable H^+ ions that are released by base forming cations moving into the solution where they react with OH to form water.

At pH2 (table 2), adsorption is highest in FAP. The increase in adsorption is an indication that the hydroxyl groups are the major functional group responsible for the adsorption of Cd ions to the negative site of the OH in the process. That is, the mechanism of Cadmium adsorption on FAP is ion exchange mechanism which involves the release of light metal ion during heavy metal uptake with monolayer adsorption [1].

There is greater adsorption in FAP than FAU and FAK with decrease in pH values. This is an indication that the adsorption of Cd on FAP is a physical adsorption with the finest pores (micro pores, radii< 15Å); the adsorption followed the mechanism of volume filling the adsorption phase rather than the mechanism of surface coverage [21].

There is influence of opposite walls frequently overlapped in narrow pores and the intensity of an adsorption force field is substantially increased. There is decrease when the pores are completely filled.

FAK: In microspores radii less than 500Å, there is increase in the adsorption due to increase in pressure (as a result of large size) increase in the multilayer adsorptions when continues, allows the layer on the opposite walls of the adsorbent to join leading to multilayer adsorption [22,23].

Total organic carbon: The total organic matter as seen in Table 1 is lower in this order: FAU < FAP <FAK. This could have contributed to the texture and the surface area of the soils which allows the entrance of oxygen that leads to the decomposition of organic matter as shown in table 1below.

Table 1: Particle Size, Percentage Total Organic Carbon and PH

Concentration of the Soil Samples

PARTICLES	FAK	FAP	FAU
SAND	65%	13%	85%
SILT	20%	32%	5%
CLAY	15%	55%	10%
TOC	0.19	0.18	0.17
PH	4.47	4.36	4.35

Table 2: Adsorption Edge pH on The Adsorption of Cadmium ion Fadama Soils

pH Edge	FAK	FAP	FAU
pH2	3.360	19.365	16.880
pH4	46.310	17.560	9.717
pH6	19.391	14.562	2.421
pH8	0.000	0.091	5.700

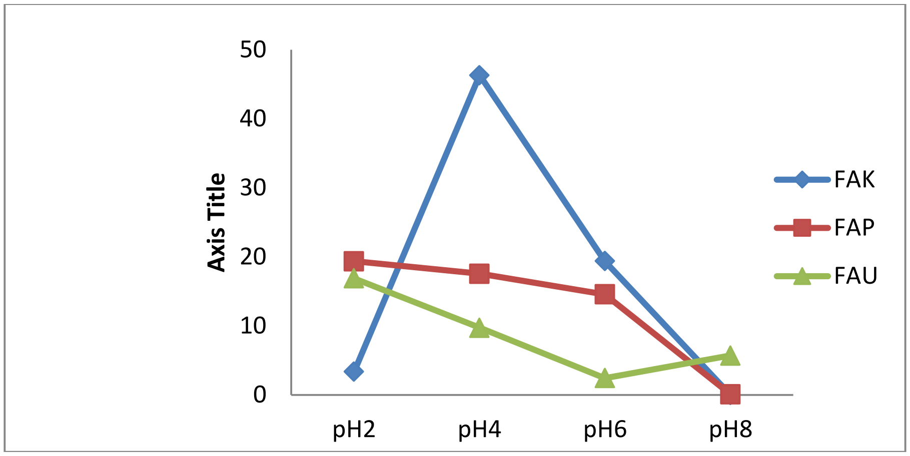

Figure 1: Adsorption Edge pH of Cadmium ion Adsorption on Fadama Soils

Adsorption for cadmium increases with pH increase for FAK and FAP and FAU decreases with pH values. This could be attributed to lesser H^+ released into the solution and not much available site space is ready for adsorption at higher pH values of FAP and FAU at higher pH values

TABLE 3: Effects of Adsorbent dosage on the adsorption of cadmium ion

Adsorbent dosage in mg/l	FAK Amount adsorbed	FAP Amount adsorbed	FAU Amount adsorbed
5mg/l	4.561	7.420	0.315
10mg/l	11.471	12.620	5.902
15mg/l	17.512	17.343	8.293
20mg/l	18.123	6.553	10.071

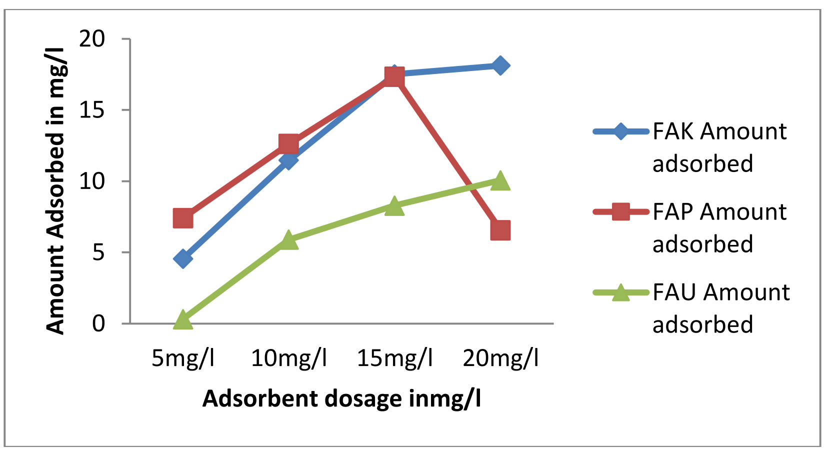

Figure 2: Effects of Adsorbent dosage on the Adsorption of Cadmium ion

Increase adsorbent dosage favors the adsorption of Cd in the three soil samples. 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 particles. The positively charged particles or cations are attracted to each colloid. [24]

Table 4: Effects of contact time on the adsorption of Cadmium ion

Time	FAK Amount adsorbed	FAP Amount adsorbed	FAU Amount adsorbed
20mins	6.562	14.52	9.125
40mins	4.332	13.491	8.405
60mins	7.931	2.777	3.829
80mins	69.10	0.552	3.332

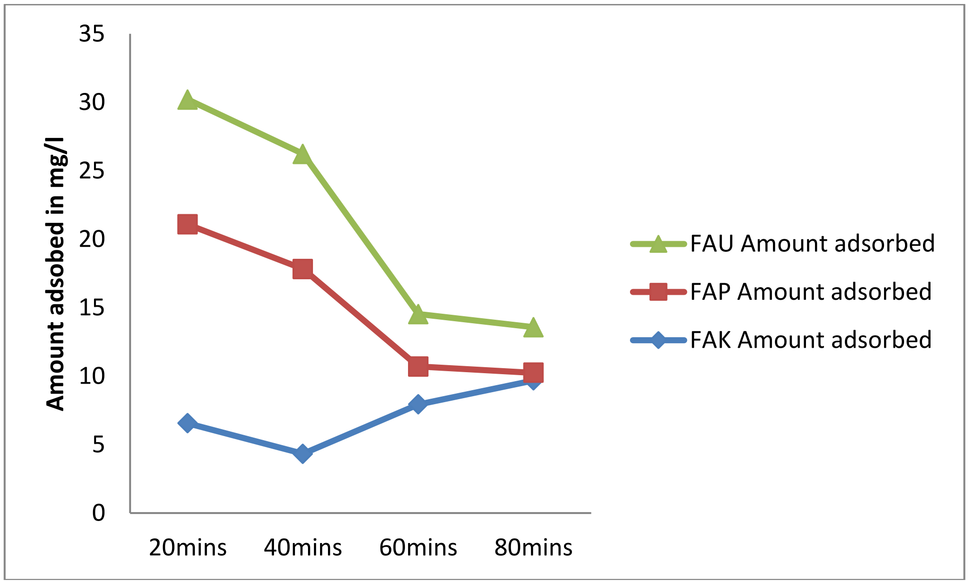

Figure 3: Effects of contact time on the adsorption of Cadmium ion

Increase in adsorption of Cd ion with time for FAP and FAU is attributed to the availability of surface area at the beginning of adsorption. The decrease with time could be attributed to the multi layer filling which does not have micro and macro pores ready for adsorption.

Adsorption Isotherms.

On application of Langmuir equations, Langmuir equation ($\frac{1}{qe} = \frac{1}{qmax^{b}} + \frac{1}{qmax}$ where Ce is the equilibrium metal ion concentration in mg/l, qe is the amount of metal adsorbed and qmax is the maximum metal sorption capacity ,b is conc constant) gives the satisfactory fit. The sorption capacity is of close range with those from pseudo – second order kinetic model.

Table 5 : Adsorption Isotherms for Cd^{2+} Ions on Fadama Clays

	FAK		FAP		FAU	
Initial conc. in mg/l	Equilibrium conc. .(mg/l)qe	Amount adsorbed on mol/g adsorbate	Equilibrium conc. .(mg/l)qe	Amount adsorbed on mol/g adsorbate	Equilibrium conc. .(mg/l) qe	Amount adsorbed on mol/g adsorbate
5mg/l	0.027	0.017	0.029	0.015	0.028	0.0168
10mg/l	0.067	0.022	0.074	0.015	0.360	0.053
15mg/l	0.050	0.053	0.102	0.031	0.040	0.092
20mg/l	0.102	0.075	0.112	0.066	0.052	0.125

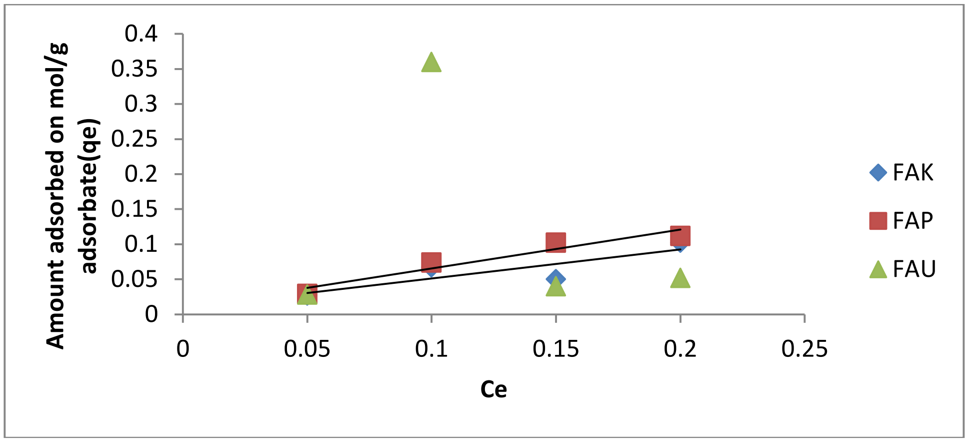

Figure 4: ADSORPTION ISOTHERMS FOR Cd^{2+} IONS ON FADAMA CLAYS

Table 6: KINETIC DATA FOR PSEUDO SECOND ORDER

TIME IN MINS	FAK $log\ ^{qt}/_{qe}$	FAP $log\ ^{qt}/_{qe}$	FAU $log\ ^{qt}/_{qe}$
20	3.048	0.726	42.192
40	9.234	2.965	4.759
60	9.565	21.600	15.669
80	11.577	15.326	24.009

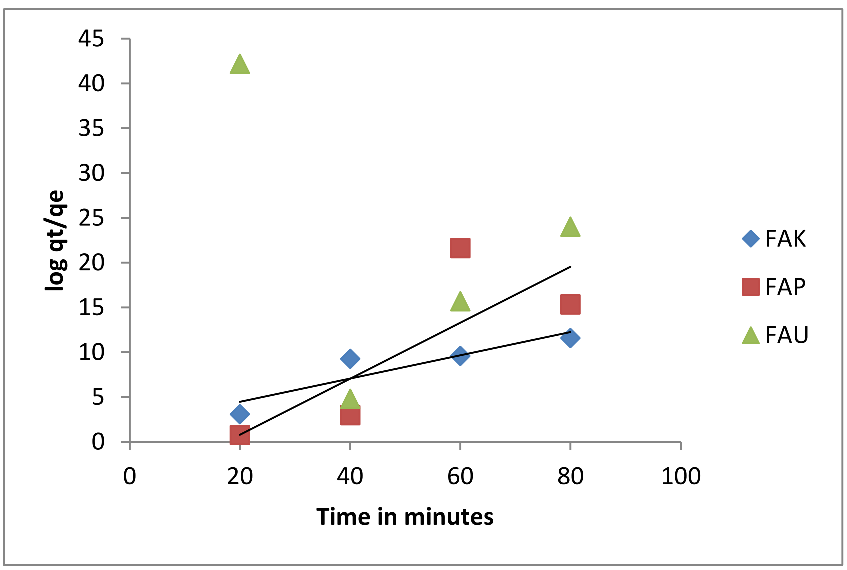

Figure 5: Pseudo second order Rate kinetics for adsorption of Cd^{2+} on Fadama Cays

Table 7 : Amount of Cd^{2+} adsorbed on Fadama clays in mg/l/g of initial metal concentration at different dosage sizes

Initial conc, in mg/l/g	FAK (amount adsorbed in mg/l/g	FAP (amount adsorbed in mg/l/g	FAU (amount adsorbed in mg/l/g
5mg/l/g	3.105	3.322	3.111
10 mg/l/g	7.564	8.321	4.000
15 mg/l/g	9.000	11.600	4.569
20 mg/l/g	11.471	12.620	5.902

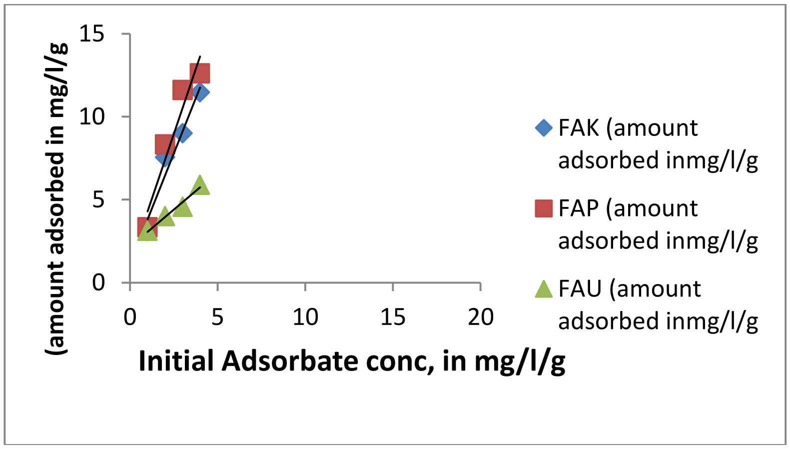

Figure 6: Diffusion-Chemisorptions Rate of adsorption of Ca^{2+}on Fadama clays

CONCLUSIONAND RECOMMENDATIONS

The adsorption of Cd^{2+} depends on the chemistry and surface morphology of the Fadama clays as well as the salt contents of the soil. This is due to site charges, OH groups, Alumina and phenol group.

The three soil samples have good adsorption capacity for cadmium adsorption but FAP has the highest potential. This is in line with the approach of physisorption, where the adsorbate is held on the surfaces by occupying the active site on the random distribution as the solid is regarded as the source of the adsorption site.

In a nutshell the three Fadama soils are good adsorbent if all the factors (pH, dosage size, surface area soil content and soil morphology) are in favorable conditions. In a nutshell The Fadama clay from Patani (FAP) is recommended for the adsorption of cadmium ions. .

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