

## Original Research Article

### **PHYSICO-CHEMICAL AND THERMODYNAMIC ADSORPTION STUDIES OF A FEW SOILS FROM DELTA AND OYO STATE, NIGERIA**

#### **Abstract**

Comprehensive study of the physico-chemical properties and interactions of cations with soils is a crucial research need for the development of more sustainable agricultural systems. The analysis of physico-chemical and thermodynamic adsorption studies of various soils from Delta and Oyo State, Nigeria, is the main emphasis of this paper.

Two surface soils from the Cocoa Research Institutes of Nigeria (CRIN) and the Isoko North Local Government of Delta State were compared for their physico-chemical properties and heavy metal speciation. The effects of adsorption duration, pH, initial sorbate concentration, and ionic strength were also studied in relation to the adsorption of  $\text{Cd}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Cu}^{2+}$ , and  $\text{Zn}^{2+}$  ions. On the equilibrium and thermodynamics of the adsorption process, more investigation was conducted.

The physico-chemical studies revealed that soil from CRIN had a pH of 6.1 in water and 5.4 in KCl, whereas soil from Isoko North had a pH of 4.3 in water and 3.0 in KCl. The largest percentages of organic matter are found in the soil from Isoko North (3.07%) and CRIN (3.82%). For both soils, the order of exchangeable bases was  $\text{Ca} > \text{K} > \text{Mg} > \text{Na}$ . The heavy metal concentrations in both soils were in the following order:  $\text{Zn} > \text{Cu} > \text{Ni} > \text{Pb} > \text{Cd} = \text{Al}$ ; CRIN: 3.82meq/100g for CEC; Isoko North: 2.85meq/100g for CEC.

In contrast to CRIN soil, Isoko North soil showed a larger bulk density and a superior hydraulic conductivity. Extractable elements were present in both soils in the following order:  $\text{Mn} > \text{Fe} > \text{Zn} > \text{Cu}$ . The base saturation in the CRIN soil was higher than the base saturation in the Isoko North soil, which was lower at 60.73%. Zn, Pb, and Cd were the outcomes of the heavy metal speciation for both soils. The equilibrium adsorption data, which were closely related to the Langmuir isotherm model, showed that the maximum capacity of lead for soil from Isoko North was 5.8140 mmol/g and for soil from CRIN was 7.6335 mmol/g.

Thermodynamic investigations showed that the adsorption process was spontaneous for simply  $\text{Cu}^{2+}$  (for soil from CRIN) and non-spontaneous for other metal ions from both soils. Metal ions from both soils displayed exothermic and endothermic adsorption, respectively, for  $\text{Cd}^{2+}$  and  $\text{Cu}^{2+}$  (for soil from CRIN).

**Keywords: Physico-Chemical, Thermodynamic Adsorption, Cation Exchange, Langmuir, Organic Matter and Selectivity.**

#### **1.1 INTRODUCTION**

Along with water, soil is one of the world's essential resources. Together, they perform a crucial function for our survival. The primary source of nutrients for all living things, from people to microscopic organisms, soil serves as a platform for their structural development. These factors

have made soil science strongly related to human activity. Knowing something about soil has always been necessary, even since agriculture was first practiced in the Neolithic<sup>1</sup>. The propensity of soil to bind different chemicals makes it a significant repository for pollutants. Different forces hold these compounds to soil particles, where they can be found in a variety of forms. Studying these interactions is crucial because the form in which chemicals are found in the environment may have a significant impact on how dangerous they are. Along with pedagogical advancement, the chemical activities in soil also effect soil fertility. Over time, chemical components that are naturally released from the parent material, the soil's minerals, might be transferred to other places in the soil and undergo different kinds of changes. Ion exchange and adsorption are the two most crucial functions of the soil<sup>2</sup>.

One of the main challenges that the majority of tropical countries face today is the soil's capacity to produce enough food and fiber on a sustainable basis in order to meet the demand of the population's ever-increasing size. In Nigeria, where several kinds of soil additives have been introduced, one of these tactics has been applied. These additives include organic and inorganic fertilizers, composted farmyard manure, liming products, and other fertility boosters of a like kind. Even while this may seem commendable, it is unpleasant to note that these treatments are frequently utilized without appropriate consideration for the reactions, long-term repercussions, and potential harm on the receiving soil's properties. Toxic heavy metals including Ni<sup>2+</sup>, Cd<sup>2+</sup>, Ca<sup>2+</sup>, and Zn<sup>2+</sup> are commonly concentrated in today's waste materials, which are primarily deposited on land or soil to be used as landfills.

Additionally, the use of chemical pesticides and other soil additions has a tendency to introduce dangerous chemical species that can harm plants. As a result, numerous dangerous metal ions are concurrently made accessible to the soil during the process.

Numerous cation-exchange substances, such as organic compounds, clay minerals, freshly precipitated iron hydroxides, amorphous silicic acids, and iron hydroxides, can absorb ions from solutions and release equivalent amounts of other ions back into the solutions<sup>3</sup>. The foundation of the mechanism that results in cation exchange is the sorptive properties of negatively charged anionic sites. The release of equivalent charges associated with other species and the preferential adsorption of specific ions are both explained by a selective mechanism. SiOH<sup>-</sup>, MoH<sup>2-</sup>, and FeOH groups found in clay minerals, FeOH groups found in iron hydroxides, and carboxyl and phenolic OH- groups found in organic substances, all directed toward positively charged lattice atoms<sup>4</sup>.

Furthermore, due to the soil's selective retention and competitive adsorption, the concentration of these elements tends to increase in the soil beyond what is tolerated. This process naturally accelerates the flow of heavy metals into the food chain, which may be detrimental to both human health and ecological equilibrium.

## **1.2 MAIN OBJECTIVE**

Determine the physico-chemical and thermodynamic adsorption investigations of various soils from Delta and Oyo State, Nigeria, is the goal of the research

## **1.3 SPECIFIC OBJECTIVES**

The objectives of this project are;

1. To investigate the physico-chemical characteristics of the soil in the Delta State of Nigeria's Isoko North Local Government Area and the Cocoa Research Institutes of Nigeria. Ibadan, Nigeria's Oyo State
2. To research how well these soils, bind heavy metals like Pb<sup>2+</sup>, Cd<sup>2+</sup>, Cu<sup>2+</sup>, and Zn<sup>2+</sup>.

3. To determine the degree of this adsorption, use thermodynamic models and sorption isotherms (Langmuir and Freundlich).

## **2.0 MATERIALS AND METHODS**

### **2.1 THE STUDY AREAS**

(1) The first study region is situated in the southern senatorial district of Delta State in southern Nigeria. The area is located between the equator's longitude 60 151 and 60 251 and latitudes 50 151 and 50 401 and 60 151, respectively. The "Isoko towns" are located in the Isoko North region, which is bordered to the north by Ndokwa West, to the south by Ughelli South Local Government, and to the east by Isoko Local Government. The area experiences moderate to heavy rainfall, which is characterized by extremely worn and poorly draining soil, which causes multiple leachings of soluble elements.

The region (Isoko North) is renowned for producing food crops such as yams, maize, cassava, and plantains, however with decreasing yields. Because this region is a part of Nigeria's Niger Delta, oil drilling is also prevalent there.

(2) The second research area is the Cocoa Research Institutes of Nigeria (CRIN), Ibadan, which is the current capital of Oyo State and the former capital of the Western region. The soil is an alfisol, according to the FAO/UNESCO World Soil Classification, and it is located between longitude 30 511E and latitude 70 311N. The soil is medium grained, reddish brown (with a pink tinge), well drained, and generally clayey.

### **2.2 SOIL SAMPLING AND SAMPLE PRE-TREATMENT**

The soil samples for the analysis were taken from the cocoa research institutes of Nigeria (CRIN) in Ibadan, Nigeria, and the Isoko North Local Government Area of Delta State. Farmers at Erovie, Uruto, Urude, Etevie, Ellu, Owhelogbo, and Delta State Polytechnic Ozoro provided soil samples from their planted and adjacent farmland. In order to ensure that the soil samples were representative samples of the current soil state, the principal parent components of the soil samples were produced to reflect them as much as feasible. Seven randomly selected soil samples from the surface horizon (0.15 cm) of seven cropland undergoing fallowing, all located in the Isoko North Local Government area, and one virgin field in the Cocoa Research Institutes of Nigeria (CRIN), were combined to create one composite bulk soil sample.

### **2.3 SAMPLE PRE-TREATMENT**

Ten days were spent letting the samples air dry. The samples were transferred to a clean porcelain mortar and gently crushed with a pestle once they had been air dried, being careful not to grind any stone, wood, or dirt in the process. The previously coarse ground samples were sieved using a 2.00mm mesh. After properly mixing, this fraction was divided into quarters to create a representative sample, which was then labeled, stored, and placed in polyethene bags for subsequent examination.

### **2.4 LABORATORY ANALYSIS**

The Buck Scientific 205 Atomic Absorption spectroscopy on Emission and Absorption mode for metal analysis was used to conduct all of the investigations reported here between May 2023 and September 2023 in the Soil Research laboratory, Department of Agronomy, University of Ibadan.

### **2.5 DETERMINATION OF PHYSICO-CHEMICAL PARAMETERS OF THE SOIL**

The International Institute of Tropical Agriculture's (IITA) manual series No. 1's protocols for performing physico-chemical analysis were followed. The pH of the soil was measured using a

glass electrode pH meter that had previously been calibrated with buffers 4 and 7. The soil pH was determined by shaking 20g of properly air dried soil with 20ml of deionized water (1:1 soil to water suspension) for 30 minutes and letting the solution stand overnight. In the same ratio of 1:1 with the soil samples, 1.0M KCl was used to determine the pH. According to ASTM 15211 hydrometer days from 1965, a particle size distribution was determined. Using the Walkey-Black wet digestion method, organic carbon was measured<sup>5</sup>.

## **2.6 DETERMINATION OF CATION EXCHANGE CAPACITY (CEC)-BATCH METHOD**

The sum of the extractable bases (Ca, mg, K, and Na) in 1.0M ammonium acetate (pH 7.0) was used to calculate the cation exchange capacity.<sup>6</sup> 5g of each type of soil were precisely weighed into 100ml polythene bottles, together with 30ml of ammonium acetate (1.0M pH7) solution in each case. After giving each of these bottles a good shake, we let them stand for two hours. Following centrifugation, each supernatant was collected into a 100 ml standard flask. With 30ml of NH<sub>4</sub>OAc each time, this extraction was performed twice more. The solution was then combined in each case and diluted with NH<sub>4</sub>OAc solution to the appropriate mark. Using the Bulk Scientific 205 AAS on the Absorbance and Emission modes, respectively, it was possible to estimate the (Ca<sup>2+</sup>, Mg<sup>2+</sup>) and (K<sup>+</sup>, Na<sup>+</sup>).

## **2.7 HEAVY METAL SPECIATION STUDIES**

Tessier's (1979) sequential extraction technique was used<sup>7</sup>.

**Tradeable metals Fraction 1:** The soil sample was extracted for 10 minutes at pH 7.0 with 8 ml of 1.0 m MgCl<sub>2</sub> and continuous agitation.

**Carbonates that contain metals: Fraction 2.** The residue from (1) was extracted for 5 hours with 8ml of 1.0m sodium acetate (NaOAc), which was then pH-adjusted with acetic acid to 5.0. Continuous agitation was kept going during the extraction.

**Fe-Mn Oxides-bound metals Fraction 3:** The residue from (ii) was extracted with 20ml of 0.04M NH<sub>2</sub>OH HCl in 25% (v/v) acetic acid for 6 hours at 97<sup>0</sup>C with periodic stirring.

**Metal affixed to oxidizable substance Fraction 4.** After adding 3ml of 0.02M HNO<sub>3</sub> to the residual from (iii), the mixture was heated to 86<sup>0</sup>C for two hours while being occasionally stirred. After cooling, the sample was heated to 86<sup>0</sup>C for 3 hours with occasional agitation using a second 3ml aliquot of 30% H<sub>2</sub>O<sub>2</sub> (pH 2.0 with HNO<sub>3</sub>). After adding 5ml of 3.2M NH<sub>4</sub>OAc in 20% (v/v), HNO<sub>3</sub>, the sample was diluted to 20ml, stirred for 30 minutes, and then tested.

**Metal residue: Fraction 5:** A concentrated 2:1 solution of hydrofluoric and perchloric acids was used to digest the residue from (iv) for 12 milliliters. The sample was then put to 2ml HC10<sub>4</sub> and 10ml HF, and it evaporated almost completely. The sample was then evaporated until white vapors appeared after the addition of 2ml of HC10<sub>4</sub> alone. 30ml of 3M HCl was then used to dissolve the remainder.

## **2.8 ADSORPTION AND THERMODYNAMIC STUDIES**

Investigations were conducted on the two soil samples to determine the impacts of ionic strength, time, pH, and sorbate content of the heavy metals under examination. The metal concentration was calculated using an AAS analysis of the data.

### **2.8.1 DETERMINATION OF EFFECT OF SORBATE CONCENTRATION ON ADSORPTION**

1.00g of the sieved soil sample A and B were placed into each of the five plastic bottles, which were numbered 1 to 5. 1000 ppm is the stock solution's concentration. The bottle was filled with 0, 1, 1.5, 2, 2.5, 3, and 4 milliliters of each of the metal solutions under investigation. The

solution to 20ml was made by adding, in that order, 20ml, 19ml, 18.5ml, 18ml, 17ml, and 16ml of 0.01M KNO<sub>3</sub>, which is utilized as an indifferent electrolyte. This translates to 0, 50, 75, 100, 150, and 200 ppm of Zn, Cd, and Cu in the polythene bottles, respectively. The bottles were shaken for 30 minutes before being allowed to stand at room temperature (280°C), during which time the lead concentration increased to 500 ppm, 400 ppm, 200 ppm, 100 ppm, and 0 ppm with occasional manual shaking. The solution was decanted and put through a filter made of paper. For various metal estimations using AAS, the filtrate was kept.

**2.8.2 EFFECTS OF pH ON ADSORPTION**

1.00g of soil samples A and B, respectively, were then weighed into 8 plastic bottles that were numbered 1 to 8. The stock solution has a concentration of 1000 ppm. The bottles were then filled with 4ml of the metal solutions under investigation. The bottles' 20ml capacity was made up of 16ml of 0.01M KN<sub>3</sub>, which served as an impartial electrolyte. The solutions had 200 ppm of the metal, according to this. (Cd<sup>2+</sup>, Zn<sup>2+</sup>, and Cu<sup>2+</sup>, in that order). Lead was present at a 500 ppm concentration. With 0.1M HNO<sub>3</sub> and 0.1M NaOH, the pH for the bottles (1–8) was changed for each metal to be 3, 4, 5, 6, 7, 8, 9, in that order, and 10. The combinations were stirred for 30 minutes before being allowed to stand at room temperature for 16 to 24 hours while being periodically shaken.

**2.8.3 EFFECT OF IONIC STRENGTH ON ADSORPTION.**

One (1) gram of each of the soil samples A and B was weighed into one of five (5) plastic vials that were numbered 1–5. The stock solution has a concentration of 1000 ppm. The bottles were filled with 0ml, 1ml, 2ml, 3ml, and 4ml of the metal solution under investigation, respectively. As an impartial electrolyte, 0.01M KNO<sub>3</sub> was supplied to the bottle in increments of 20ml, 19ml, 18ml, 17ml, and 16ml. These are equivalent to cations (cadmium, lead, zinc, and copper) at concentrations of 0 ppm, 50 ppm, 100 ppm, 150 ppm, and 200 ppm. This process was replicated using 0.1M and 1M KN<sub>3</sub> as the electrolyte, respectively. Oppm, 100ppm, 200ppm, 400ppm, and 500ppm were the lead solution concentrations. The mixes were stirred for 30 minutes before being allowed to stand at room temperature for 16 to 24 hours with sporadic manual stirring. After that, the material was decanted, filtered, and kept for AAS metal estimate.

**2.8.4 EFFECT OF TIME OF ADSORPTION**

1.00g of soil samples A and B were weighed into 5 polyethylene bottles, which were numbered 1 through 5, and 6ml of stock solutions of the metals under investigation (Pb<sup>2+</sup>, Cd<sup>2+</sup>, Cu<sup>2+</sup>, and Zn<sup>2+</sup>, respectively) in their nitrates were measured into the bottles. The stock solution has a 1000ppm concentration. Then, 14ml of 0.01M KNO<sub>3</sub> was added to them as an unimportant electrolyte. This is equivalent to 300ppm. Lead was present at a higher concentration of 500 ppm. The mixture was stirred for 30 minutes before being allowed to stand for 30 minutes, 1 hour, 3 hours, 6 hours, 12 hours, and 24 hours at room temperature.

**2.9 THERMODYNAMIC STUDIES**

The thermodynamics of the adsorption of Pb<sup>2+</sup>, Zn<sup>2+</sup>, Cd<sup>2+</sup>, and Cu<sup>2+</sup> ions onto the two soil samples adsorbent were investigated by adding 0.1g of the adsorbent to 20ml volume samples of the individual metal ions solutions at various concentrations (0-500mg/l) at a room temperature, stirring the systems, and collecting the samples after 5 hours for metal ion analysis at 303K and 323K,

$$\ln b = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \dots\dots\dots (3.0)$$

Where  $b$  is the energy-related Langmuir constant. The slope and intercept of the linear plot of  $\ln b$  vs  $1/T$  are equal to  $\Delta H_0$  and  $\Delta S_0$ , respectively. The Gibbs relationship can then be used to these variables to compute  $\Delta G_0$ .

$$\Delta G_0 = \Delta H_0 - \Delta S_0 \dots \dots \dots (3.1)$$

It is assumed that the enthalpy does not change with temperature when the temperature is constant while determining the values of the thermodynamic parameters. The relationship was used to compute the amount of  $Pb^{2+}$ ,  $Zn^{2+}$ ,  $Cd^{2+}$ , and  $Cu^{2+}$  adsorbed.

$$q_e \text{ (mg/g)} = \frac{(C_0 - C_e) V}{W} \dots \dots \dots (3.2)$$

Where  $V$  is the volume of metal ion solution used (in ml),  $C_0$  is the initial concentration of metal ions (in mg/l),  $C_e$  is the equilibrium concentration of metal ions (in mg/l), and  $q_e$  is the amount of metal ions adsorbed (in mg/g).

### 3.0 RESULTS AND DISCUSSION

#### 3.0.1 The Physico-Chemical Studies.

The results of the physico-chemical experiments conducted on the soil samples from Isoko North and CRIN that were less than 2.0 mm in thickness are shown in table 1 below.

##### 3.0.1.1 Soil pH

The soil from Isoko North and the soil from CRIN had pH values that ranged from 4.3 to 6.1 and 3.0 to 5.4, respectively, were measured in a 1:1 soil to deionized water and 1.0M KCl solution. This denotes soils ranging from mostly neutral to very slightly acidic. Isoko North soils have a pH of 3.0 in 1.0M KCl and 4.3 in deionized water. While the soil from CRIN had a pH of 5.4 in KCl and 6.1 in deionized water. Because potassium ion ( $K^+$ ) in solution displaces hydrogen ion ( $H^+$ ) from the soil's cation exchange sites, the pH value in 1.0M KCl was slightly lower than pH in de-ionized water. The findings indicate that CRIN soil is less acidic than soil from Isoko North.

##### 3.0.1.2 Soil Organic Matter

The soil samples from the two soils had usually low levels of organic matter, ranging from 3.07% to 3.82%. In terms of organic matter, soil from Isoko North had a lower value than soil from CRIN, which had a greater value of 3.82%. In soil with a larger organic matter level, adsorption is probably more likely.

##### 3.0.1.3 Soil Texture

The range of 73.2% to 85.2% for the particle size determination indicated a significant amount of sand. The range for the silt contents was 5.4% to 15.4%. In the range of 9.4% to 11.4%, the clay content was significantly lower than the silt content. Isoko soil has a maximum sand content of 85.2% and a minimum silt and clay content of 9.4% and 5.4%, respectively. On the other hand, CRIN soil had a larger percentage of clay and silt (11.4% and 15.4%, respectively) and a lower percentage of sand (73.2%). It is important to remember that soil adsorption increases with soil clay mineral particle content and decreases with soil sand particle content.

##### 3.0.1.4 Base Saturation

Base saturation for soil from Isoko North was 60.73%, whereas base saturation for soil from CRIN was 78.95%. CRIN soil has a greater potential for adsorption than Isoko North soil.

##### 3.0.1.5 Heavy Metal Concentration

In terms of heavy metal concentration in the soils, CRIN soil had the highest levels of zinc, whereas Isoko North soil had the highest levels of aluminum. In general, the heavy metal

concentration trend in the soil from CRIN was in the following order: Zn > Cu > Ni > Pb > Cd = Al, whereas the trend in the soil from Isoko North was Al > Zn > Cu > Pb > Cd.

**Table 1: Isoko North and CRIN soil's physico-chemical characteristics.**

Parameters	Isoko North	CRIN
pH in H <sub>2</sub> O	4.3	6.1
pH in KCl	3.0	5.4
% Organic Matter	3.07	3.82
% Organic Carbon	1.84	2.29
CEC (meq/100g)	2.85	3.82
Base Saturation (%)	60.73	78.95
Exchangeable Acidity (meq/100g)	0.6	1.5
Ca <sup>2+</sup> (meq/100g)	1.34	1.40
Mg <sup>2+</sup> (meq/100g)	0.68	0.68
Na <sup>+</sup> (meq/100g)	0.90	0.10
K <sup>+</sup> (meq/100g)	0.14	0.14
Clay (%) (PSA)	9.4	11.4
Sand (%) (PSA)	85.2	73.8
Silt (%) (PSA)	5.4	15.4
Al <sup>3+</sup> (ppm)	55.6	0.5
Cd <sup>2+</sup> (ppm)	0.6	0.5
Cu <sup>2+</sup> (ppm)	43.6	30.1
Pb <sup>2+</sup> (ppm)	1.1	0.9
Zn <sup>2+</sup> (ppm)	51.83	66.51

### 3.0.1.6 Exchangeable Bases

There were noticeable amounts of exchangeable bases such Mg, Ca, K, and Na in the two soil samples. When compared to the other exchangeable cations, which range from 1.34 to 1.40meq/100g, exchangeable Ca has the highest value despite being somewhat low. The greater value is for soil from CRIN (1.40meq/100g), whereas the lower value is for soil from Isoko North (1.34meq/100g). For both soil samples, exchangeable Mg and K have the same values of 0.68meq/100g and 0.14meq/100g. Exchangeable Na has a range of 0.09meq/100g to 0.10meq/100g, which is comparable to other exchangeable cations. Exchangeable Na was found to be higher in the CRIN soil sample and lower in the Isoko North soil sample. In comparison to soil from Isoko North, soil from CRIN appears to have a larger value of exchangeable bases. Ca > Mg > K > Na is the normal order of metal ion concentrations in soil. This suggests that soil from CRIN has less potential for harmful ions like aluminum.

### 3.0.1.7 Cation Exchange Capacity (CEC)

In order to determine the soil's effective cation exchange capacity, exchangeable cations were added together. A range of 2.85 to 3.82meq/100g was the CEC. The larger value was found in soil from CRIN, 3.82meq/100g, whereas the lower value was found in soil from Isoko North,

2.85meq/100g. As a result, it may be concluded that soil from CRIN has a greater capacity for cation exchange than soil from Isoko North.

### 3.0.1.8 Heavy Metal Speciation

The results of the investigations on the speciation of heavy metals are shown in table 2 below in terms of micrograms per gram (g/g) and percentages (%). The findings demonstrated that, when compared to the other metals, zinc typically had the highest overall content in the two soils. Zn is the most abundant heavy metal overall in both soils, followed by Cd, Ni, and Pb. Isoko North soil contains 5.21 g/g of zinc, while CRIN soil contains 5.14 g/g of zinc. Zinc has a value of 1.04 g/g for soil from Isoko North and 1.10 g/g for soil from CRIN in terms of exchangeable percentage. For both soils, cadmium and lead have a value of 0.01 g/g. The value of the exchangeable percentage of the metal ions in both soils, according to the results, was very low and does not, therefore, offer any immediate potential harm.

**Table 2: A Heavy Metal's results Specification of both soil types in terms of microgram and %.**

No	ID No	µg/g Cd	% Cd	µg/g Pb	% Pb	µg/g Zn	% Zn
1	AF1	0.007	21.2	0.012	21.80	1.043	20.00
2	AF2	0.07	21.2	0.011	20.00	1.031	19.90
3	AF3	0.006	18.2	0.010	18.20	0.986	18.90
4	AF4	0.007	21.2	0.012	21.80	1.032	19.80
5	AF5	0.006	18.2	0.010	18.20	1.113	21.40
	<b>SUM</b>	<b>0.330</b>	<b>100</b>	<b>0.55</b>	<b>100</b>	<b>5.205</b>	<b>100</b>
6	BF1	0.005	17.2	0.009	18.40	1.098	21.40
7	BF2	0.006	20.70	0.011	22.90	1.311	25.50
8	BF3	0.008	27.70	0.012	24.50	0.741	14.40
9	BF3	0.005	17.20	0.009	18.40	0.923	18.00
10	BF5	0,005	17.20	0.008	16.30	1.066	20.70
	<b>SUM</b>	<b>0.029</b>	<b>100</b>	<b>0.049</b>	<b>100</b>	<b>5.139</b>	<b>100</b>

Isoko North soil equals A.

B is the soil from CRIN.

F1 is an interchangeable fraction.

Metals linked to Carbonate, or F2.

F3: Metals bonded to Fe-Mn-Oxide

Metals to Oxidisable Matter = F4

F5: Metals that are bonded to residue.

### 3.1 EFFECT OF CONTACT TIME ON SORPTION

To determine how long it will take the two soils to adsorb the metal ions at their maximum pH, the impact of time on sorption was examined. Tables 3 to 6 give the data for the time-dependent adsorption of the four metals by the two soil samples. The statistics demonstrate that both soil samples eliminated more metal as the contact period rose from 30 to 180 minutes. In terms of metal ions adsorbed, the soil from Isoko North absorbed between 37 and 49% of them, while the soil from CRIN adsorbed between 39 and 81%. For all the metals, it takes between 720 and 1440 minutes to reach the adsorption equilibrium. This was done in conjunction with the study of Haiyan Yu et al., which showed that the adsorption process progressively neared equilibrium after 48 hours and that the adsorption rate reduced with increasing contact time<sup>6</sup>.

**Table 3: Influence of Time on Pb Adsorption into Soils**

<b>Time (Min)</b>	<b>Isoko North (mg/g)</b>	<b>CRIN (mg/g)</b>
30	2.28	2.40
60	2.32	2.62
180	2.58	3.28
360	2.59	3.88
720	2.70	4.08
1440	2.72	4.16

**Table 4: Influence of Time on Cu Adsorption into Soils**

<b>Time (Min)</b>	<b>Isoko North (mg/g)</b>	<b>CRIN (mg/g)</b>
30	1.97	2.36
60	2.00	2.81
180	2.23	3.14
360	2.24	3.66
720	2.28	4.01
1440	2.28	4.16

**Table 5: Influence of Time on Cd Adsorption into Soils**

<b>Time (Min)</b>	<b>Isoko North (mg/g)</b>	<b>CRIN (mg/g)</b>
30	2.44	4.57
60	2.33	4.58
180	2.26	4.60
360	1.10	4.61
720	2.52	4.61
1440	2.51	4.85

**Table 6: Influence of Time on Zn Adsorption into Soils**

<b>Time (Min)</b>	<b>Isoko North (mg/g)</b>	<b>CRIN (mg/g)</b>
30	2.02	2.36
60	2.02	2.81
180	2.20	3.14
360	2.46	3.66
720	2.79	4.01
1440	2.93	4.16

### 3.2 EFFECT OF pH ON SORPTION

The results of the examination of the two soils' ability to bind metal ions ( $\text{Cd}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Pb}^{2+}$ , and  $\text{Zn}^{2+}$ ) at various pH levels (3-10) are displayed in Tables 7 to 10.

**Table 7: Influence of pH on Pb Adsorption into Soils**

<b>P<sup>H</sup></b>	<b>Isoko North (mg/g)</b>	<b>CRIN (mg/g)</b>
3	5.78	9.83
4	5.81	9.91
5	6.33	9.90
6	7.30	10.00
7	7.42	9.97
8	7.56	9.99
9	7.89	9.98
10	7.99	9.98

**Table 8: Influence of pH on Cd Adsorption into Soils**

<b>P<sup>H</sup></b>	<b>Isoko North (mg/g)</b>	<b>CRIN (mg/g)</b>
3	2.60	3.41
4	2.75	3.41
5	2.87	3.45
6	3.56	4.01
7	3.75	4.01
8	3.64	4.00
9	3.57	4.00
10	3.34	3.99

**Table 9: Influence of pH on Cu Adsorption into Soils**

<b>P<sup>H</sup></b>	<b>Isoko North (mg/g)</b>	<b>CRIN (mg/g)</b>
3	1.63	3.08
4	1,81	3.44
5	1.90	3.45
6	2.41	3.85
7	2.74	3.85
8	3.83	3.85
9	3.79	3.84
10	3.85	3.80

**Table 10: Influence of pH on Zn Adsorption into Soils**

<b>P<sup>H</sup></b>	<b>Isoko North (mg/g)</b>	<b>CRIN (mg/g)</b>
3	2.34	2.90
4	2.83	3.84
5	2.93	3.88
6	3.13	4.01
7	3.28	2.77
8	4.03	2.34
9	4.06	3.84
10	4.07	3.85

Data from the two soil samples under investigation demonstrate that all of the metals had lower metal absorption at low pH, which suggests that extra protons compete with the metal ions for the same binding sites. The sorption process is pH dependent, as evidenced by a rise in pH that causes an increase in metal retention. This is explained by the preferred adsorption of hydrolyzed metal species to free metal ions, whose fraction rises with pH<sup>8,9, and 10</sup>. For practically all of the metal ions in the two soils, there is a diminishing order of metal retention at pH levels over<sup>8</sup>. Organic complexing ligands become soluble at pH levels over 7, effectively competing with the soil surface for metal ions<sup>11</sup>.

### **3.3 EFFECT OF INITIAL SORBATE CONCENTRATION ON SORPTION.**

The amount of metals adsorbed increases when the starting concentration of metal ions is increased from 50 mg/l to 500 mg/l, while the proportion (%) of metals adsorbed decreases. Thus, a decreasing percentage of metal ion adsorption is seen with increasing metal concentration in solution. The results of research conducted in India titled Kinetic Sorption Studies of Heavy Metal Contamination on Indian Expansive Soil<sup>7</sup> are combined with the values for the influence of sorbate concentration of all four metals by both soils, which are provided on Tables 11 to 12.

**Table 11: The two soils' ability to adsorb Cd is affected by the initial sorbate concentration.**

<b>(mg/L)</b>	<b>Isoko North (mg/g)</b>	<b>CRIN (mg/g)</b>
50	0.99	0.99
75	1.12	1.49
100	1.48	1.99
150	1.76	2.82
200	1.90	3.41

**Table 12: The two soils' ability to adsorb Cu is affected by the initial sorbate concentration.**

<b>(mg/L)</b>	<b>Isoko North (mg/g)</b>	<b>CRIN (mg/g)</b>
50	0.62	0.99
75	0.89	1.48
100	1.16	1.99
150	1.73	2.86

200	2.05	3.35
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**Table 13: The two soils' ability to adsorb Zn is affected by the initial sorbate concentration.**

(mg/L)	Isoko North (mg/g)	CRIN (mg/g)
50	0.10	1.00
75	1.18	1.50
100	1.19	2.00
150	1.64	2.65
200	1.97	3.22

**Table 14: The two soils' ability to adsorb Pb is affected by the initial sorbate concentration.**

(mg/L)	Isoko North (mg/g)	CRIN (mg/g)
100	1.91	2.00
200	2.98	3.77
300	3.53	5.28
500	5.40	7.29

Because there are fewer sorption sites accessible relative to the available sorbate at higher initial concentrations, there is a declining trend in the % sorption from lower to higher concentrations. Evidently, as the initial concentration is raised, the fractional sorption gradually becomes initial concentration dependent. Similar trends have been noted<sup>12</sup>.

### 3.7 SUMMARY AND CONCLUSION

According to the physico-chemical analysis of the soil samples, the soil from CRIN was less acidic and the soil from Isoko North was more acidic. Both soils had low levels of organic matter, with Isoko North having the lowest levels of clay and silt of the two. Exchangeable bases, extractable micronutrients, bulk density, and heavy metal concentrations all have low values, with soil from Isoko North having greater values. For soil from CRIN, the values for cation exchange capacity, hydraulic conductivity, and base saturation were greater. The findings of the heavy metal speciation investigation indicate that both soils have modest metal contents. For the parameters examined, the equilibrium studies for both soils revealed a similar pattern. The soil from Isoko North, however, has a lower capability for adsorption than the soil from CRIN. Both soils exhibit pH dependence, with a rise in pH causing heavy metal adsorption, while an increase in starting metal concentrations causes a decrease in the percentage of metal adsorbed by the soils. While there is a general tendency for the proportion of metal adsorbed to decrease with increasing ionic strength of the electrolyte used, the percentage of metal adsorbed rose with extended contact time in both soils. The adsorption pattern fits the Langmuir isotherm model better than the Freundlich isotherm model, according to equilibrium modelling.

Thermodynamic analyses for the two soils did not reveal any overarching trends. Except for copper adsorption, which is negative for soil from CRIN, the standard Gibbs free energy values indicated that all metal ions absorbed into the soil from both soils at both temperatures (303K and 323K) were not adsorbed spontaneously. Only the Copper adsorption at the two temperatures for soil from CRIN exhibits spontaneity. The enthalpy change results demonstrated that the adsorption of Cadmium and Copper by soil from CRIN was exothermic. For both soils, the adsorption of all other metal ions was endothermic. According to the results of the standard entropy, the Cadmium, Copper, and Zinc ions (CRIN) were arranged in an ordered fashion at

equilibrium, whereas other results indicated a disorganized arrangement. As a result, information from equilibrium and thermodynamic adsorption studies can be used to help in soil remediation. Desorption investigations of both soils are therefore advised in order to gather more data necessary for soil rehabilitation.

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