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Original Research Article

PHYSICO-CHEMICAL AND THERMODYNAMIC ADSORPTION STUDIES OF SOME SOILS FROM DELTA AND OYO STATE, NIGERIA

Abstract

For the development of a better understanding of sustainable agricultural methods, comprehensive knowledge of the physico-chemical characteristics and interactions of cations with soils is a vital research need. As a result, the focus of this work is on the investigation of physico-chemical and thermodynamic adsorption studies of some soils from Delta and Oyo State, Nigeria.

The physico-chemical characteristics and heavy metal speciation of two surface soils, one from the Isoko North Local Government of Delta State and the other from the Cocoa Research Institutes of Nigeria (CRIN), were examined. On the adsorption of Cd^{2+}, Pb^{2+}, Cu^{2+}, and Zn^{2+} ions, the effects of adsorption period, pH, initial sorbate concentration, and ionic strength were also investigated. Further research was done on the adsorption process' equilibrium and thermodynamics.

According to the physico-chemical analyses, soil from Isoko North had a pH of 4.3 in water and 3.0 in KCl, while soil from CRIN had a pH of 6.1 in water and 5.4 in KCl. 3.07% for soil from Isoko North and 3.82% for soil from CRIN have the highest levels of organic matter. Ca > K > Mg > Na was the sequence of exchangeable bases for both soils. For both soils, the concentration of heavy metals was in the following order: Zn > Cu > Ni > Pb > Cd = Al. CRIN, 3.82meq/100g for CEC; Isoko North, 2.85meq/100g.

Isoko North soil had a higher bulk density, while CRIN soil had a better hydraulic conductivity. Both soils had extractable micronutrients in the following order: Mn > Fe > Zn > Cu. Base saturation was higher in the CRIN soil at 78.95% and lower in the Isoko North soil at 60.73%.

For both soils, the results of the heavy metal speciation were Zn > Pb > Cd. Lead had a maximum adsorption capacity of 5.8140 mmol/g for soil from Isoko North and 7.6335 mmol/g for soil from CRIN, according to the equilibrium adsorption results, which were closely associated with the Langmuir isotherm model.

Thermodynamic analyses revealed that the adsorption process was non-spontaneous for other metal ions from both soils and spontaneous for just Cu2+ (for soil from CRIN). Cd2+ and Cu2 (for soil from CRIN) and metal ions from both soils underwent exothermic and endothermic adsorption, respectively.

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

1.1 INTRODUCTION

Soil is one of the main primary resources on earth, together with water. Both act together, playing an essential role in our survival. Soil is the main source of nutrients for living systems,

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and acts as a platform supporting structures for those living systems, at macro- and micro-scale, from humans to microorganisms. Soil science has been closely attached to human activity for those reasons. From the introduction of agriculture in the Neolithic to our days, the requirement for knowledge about soil has been constant[1].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[2].

The ability of the soil to produce enough food and fiber on a sustainable basis in order to meet the demand of the ever-increasing population is thus one of the key difficulties facing the majority of tropical countries today. One of these strategies has been used in Nigeria, where several types of soil additives have been introduced. These additives include inorganic fertilizers, compost farmyard manure, liming materials, and other similar fertility additions.As admirable as this may appear, it is regrettable to note that these procedures are typically used without giving enough thought to the reactions, long-term effects, and potential damage on the receiving soil's qualities. The majority of waste materials nowadays are dumped on land or soil as landfills and are typically concentrated with poisonous heavy metals including Ni^{2+}, Cd^{2+}, Ca^{2+}, and $Zn^{2+.}$

Furthermore, the use of agricultural pesticides and other chemical amendments tends to introduce harmful chemical species that can harm plants into the soil. As a result, during the process, the soil becomes simultaneously accessible to many hazardous metal ions.

Many cation-exchange materials, such as clay minerals, recently precipitated iron hydroxides, amorphous silicic acids, and organic compounds, can sorb ions from solutions and release corresponding amounts of other ions back into the solutions[3]. The sorptive characteristics of negatively charged anionic sites form the basis of the mechanism that leads to cation exchange. A selective process accounts for the preferential adsorption of particular ions and the release of equivalent charges associated with other species. $S1OH^-$, MoH_2^-, and $FeOH^-$ groups in clay minerals, $FeOH^-$ groups in iron hydroxides carboxyl and phenolic OH^- groups in organic substances-towards positively charged of the lattice[4].

Additionally, there is a tendency for the concentration of these elements in the soil to rise above and above tolerable limits as a result of the selective retention and competitive adsorption by the soil. The flow of heavy metals into the food chain is naturally accelerated by this process, which could have negative impacts on both human health and the ecological balance.

1.2 MAIN OBJECTIVE

The aim of the research is to determine the physico-chemical and thermodynamic adsorption studies of some soils from Delta and Oyo State, Nigeria

1.3 SPECIFIC OBJECTIVES

The objectives of this project are;

1. To study physico-chemical properties of the soil from Isoko North Local Government area of Delta State of Nigeria and Cocoa Research Institutes of Nigeria. Ibadan, Oyo State, Nigeria
2. To study the adsorption of heavy metals (Pb^{2+}, Cd^{2+}, Cu^{2+} and Zn^{2+}) of these soils.

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3. Using sorption isotherms (Langmuir and Freundlich) and thermodynamic models to know the extent of this adsorption.

2.0 MATERIALS AND METHODS

2.1 THE STUDY AREAS

(1) The first study area is located in the southern senatorial district of Delta State in south southern, Nigeria. The region lies between latitude 50 151 N and 50 401 N and longitude 60 151 E and 60 251 E of the equator. The “Isoko towns” is in the Isoko North region bounded to the North by Ndokwa West, to the south by Ughelli South Local Government, to east by Isoko Local Government area. The region is witnessed by moderate to high rainfall and this is characterized by highly weathered and poorly drained soil resulting in several leaching of soluble constituents. The area (Isoko North) is typical known for the production of food crops such as Yam, Maize, Cassava and Plantain, but with dwindle yields. Oil exploration is also prominent in this area because it forms parts of the Niger- Delta region of Nigeria.

(2) The second study area is Cocoa Research Institutes of Nigeria (CRIN), Ibadan which is located in old Western region capital but now capital of Oyo State. From the FAO/UNESCO World Soil Classification, the soil is Alfisol, which lays between longitude 30 511E and latitude 70 311N. The soil is well drained, medium textured, reddish brown (with pink tinge), and fairly clayey soils

2.2 SOIL SAMPLING AND SAMPLE PRE-TREATMENT

The soil samples used for the analysis were obtained from Isoko North Local Government Area of Delta State and Cocoa Research Institutes of Nigeria (CRIN) Ibadan Nigeria. Soil from cultivated and following farmland were collected from Erovie, Uruto, Urude, Etevie, Ellu, Owhelogbo and Delta State Polytechnic Ozoro. The soil samples collected were made to reflect as much as possible the major parent materials in order to ensure that the soil were representative samples of the prevailing soil condition. One composite bulk soil sample was prepared made from seven randomly collected soil samples from the surface horizon (0.15cm) from seven farmland undergoing fallowing, all located in Isoko North Local Government area and a virgin land in Cocoa Research Institutes of Nigeria (CRIN).

2.3 SAMPLE PRE-TREATMENT

The samples were air dried over a period of ten days. The air dried samples were then treated by transferring then onto a clean porcelain mortar and crushed gently with a pestle making sure that no stone, wood or dirt are ground alongside. The ground samples which were now fine particles were sieved through a 2.00mm mesh. This fraction was then thoroughly mixed to obtain a composite sample reduced by quartering to obtain representative sample which was stored and label in polyethene bags for further analysis.

2.4 LABORATORY ANALYSIS

All the studies described here were carried out in the Soil Research laboratory, Department of Agronomy, University of Ibadan between May, 2023 to September, 2023 using Buck Scientific 205 Atomic Absorption spectroscopic on Emission and Absorption mode for metal analysis

2.5 DETERMINATION OF PHYSICO-CHEMICAL PARAMETERS OF THE SOIL

Physico-chemical analysis was carried out using the procedures as described in the International Institute of Tropical Agriculture (IITA) manual series No 1. The soil pH was determined by shaking 20g of properly air dried soil with 20ml of de-ionized water (1:1 soil to water suspension) for 30 min. and letting the solution stand overnight and then measuring the pH of the

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solution with a glass electrode pH meter which had earlier been calibrated with buffer 4 and 7. The pH was also determined using 1.0M KCl in the same ratio. 1:1 with the soil samples. A particle size distribution was by the hydrometer method using ASTM 15211 hydrometer days (1965). Organic carbon was determined by the Walkey –Black wet digestion method. (Jackson,1958).

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

The Cation exchange capacity was determined by the summation of 1.0M ammonium acetate (pH 7.0) extractable bases (Ca, mg, K and Na)[6]. 5g each of the various soils were weighed accurately into 100ml polythene bottles and 30ml of ammonium acetate (1.0M pH7) solution was added in each case. Each of these bottles was shaken thoroughly and left to stand for 2 hours. Thereafter, they were centrifuged and each supernatant collected into 100ml standard flask. This extraction was repeated two more times each with 30ml NH_4OAC. The solution was then pooled together in each case and made up to mark with NH40Ac solution. The (Ca^{2+}, Mg^{2+}) and (K^{+}. Na^{+}) was determined using the Bulk scientific 205 AAS on Absorbance and Emission mode respectively.

2.7 HEAVY METAL SPECIATION STUDIES

The sequential extraction method by Tessier (1979) was adopted[7].

Exchangeable metals: - Fraction 1: The soil sample were extracted for 10 min with 8ml of 1.0m $MgCl_2$ at pH 7.0 with continues agitation.

Metals bound to carbonates: - Fraction 2. The residue from (1) was extracted with 8ml of 1.0m sodium acetate (Na0Ac) for 5 hours adjusted to pH 5.0 with acetic acid continuous agitation was maintained during the extraction.

Metals bound to Fe-Mn Oxides:Fraction 3: The residue from (ii) was extracted for 6 hours at 970C with 20ml of 0.0.4M NH_20H HCl in 25% (v/v) acetic acid with occasional agitation.

Metal bound to oxidizable matterFraction 4. 3ml of 0.02M $HN0_3$ was added to the residue from (iii) and the mixture was heated to 86oC for 2 hours with occasional agitation. A second 3ml aliquot of 30% H_20_2 (pH 2.0 with $HN0_3$) was then added and the sample heated again to 86oC for 3 hours with intermittent agitation after cooling. 5ml of 3.2M NH_4OAC in 20% (v/v), HN03 was added and the sample diluted to 20ml and agitated for 30 minutes.

Residual metal: Fraction 5: The residual from (iv) was digested with 12ml of a 2:1 mixture of concentrated hydrofluoric and perchloric acids. Subsequently 2ml $HC10_4$ and 10ml HF was added and the sample evaporated to near dryness. Finally, 2ml HC104 alone was added and the sample evaporated until the appearance of white fumes. The residue was then dissolved in 30ml of 3M HCl.

2.8 ADSORPTION AND THERMODYNAMIC STUDIES

The effects of ionic strength, time, pH and sorbate concentration of the heavy metals under study were investigated on the two soil samples. The results were analyzed by AAS to determine the metal concentration.

2.8.1 DETERMINATION OF EFFECT OF SORBATE CONCENTRATION ON ADSORPTION

5 polyethylene bottles were set and numbered 1-5. 1.00g each of the sieved soil sample A & B were added into the bottle. Concentration of the stock solution is 1000ppm. 0ml, 1ml, 1.5ml, 2ml, 3ml and 4ml of each metal solution being investigated was added to the bottle respectively.

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20ml, 19ml, 18.5ml, 18ml, 17ml and 16ml of 0.01M KNO_3 which is used as an indifferent electrolyte was added in that order respectively to make up the solution to 20ml. This corresponds to 0ppm, 50ppm, 75ppm, 100ppm, 150ppm and 200ppm for Zn, Cd and Cu in the polythene bottles. The bottles were agitated for 30mins and left to stand at room temperature (280C) during which the concentration of Lead was increases to 500ppm, 400ppm, 200ppm, 100ppm and 0ppm with manual shaken intermittently. The solution was decanted, filtered using filter paper. The filtrate was retained for different metal estimation using AAS.

2.8.2 EFFECT OF pH ON ADSORPTION

8 polyethylene bottles were set and numbered 1-8. 1.00g of the soil samples A and B respectively were then weighed into the bottles. Concentration of the stock solution is 1000ppm. 4ml of the metal solutions being investigated were then added to the bottles. The content of the bottles was made up to 20ml with 16ml of 0.01M $KN0_3$ as an indifferent electrolyte. This corresponded to 200ppm of the metal in the solutions. (Cd^{2+}, Zn^{2+}, Cu^{2+} respectively). The concentration for lead was 500ppm. The pH for the bottles (1-8) was adjusted for each metal respectively to 3, 4, 5, 6, 7, 8, 9, 10 in that order with 0.1M $HN0_3$ and 0.1M Na0H. The mixtures were agitated for 30 minutes and left to stand at room temperature for 16-24 hours with intermittent shaking.

2.8.3 EFFECT OF IONIC STRENGTH ON ADSORPTION.

Five (5) polyethylene bottles were set and numbered 1-5. 1.00g each of the soil samples A and B respectively was then weighed into the bottles. Concentration of the stock solution is 1000ppm. Oml, 1ml, 2ml, 3ml, and 4ml of the metal solution being investigated were added to the bottles respectively. 20ml, 19ml, 18ml, 17ml and 16ml of 0.01M $KN0_3$ as an indifferent electrolyte was added respectively to the bottle to make up to 20ml mark. These correspond to 0ppm, 50ppm, 100pm, 150ppm and 200ppm of the cations (Cadmium, Lead, Zinc and Copper). This procedure was repeated with 0.1M $KN0_3$, and 1M $KN0_3$ respectively as a different electrolyte. The concentrations for lead solution were Oppm, 100ppm, 200ppm, 400ppm and 500ppm. The mixtures were agitated for 30 minutes and left to stand at room temperature with intermittent manual agitation for 16-24hr. At the end the contents were decanted, filtered and stored for metal estimation using AAS.

2.8.4 EFFECT OF TIME OF ADSORPTION

5 polyethylene bottles were set and numbered 1-5. 1.00g of the soil samples A and B respectively were then weighed into the bottles and 6ml of the stock solutions of the metal being investigated (Pb^{2+}, Cd^{2+}, Cu^{2+} and Zn^{2+} respectively) in their nitrates were then measured into the polyethylene bottles. Concentration of the stock solution is 1000ppm. They were then made up with 14ml of 0.01M KNO_3 as an indifferent electrolyte. This corresponds to 300ppm. The concentration for lead was increased to 500ppm. The mixture was agitated for 30 minutes and left to stand for the contact time of 30 minutes, 1hr, 3hr, 6hr, 12hr and 24hr at room temperature.

2.9 THERMODYNAMIC STUDIES

The thermodynamics of the adsorption of Pb^{2+}, Zn^{2+}, Cd^{2+} and Cu^{2+} ions onto the two soil samples adsorbent were studied by adding 0.1g of the adsorbent to 20ml volume sample of the individual metal ions solutions at various concentrations (0-500mg/l) at a room temperature. These systems were then agitated, with samples being collected after 5hrs for metal ion analysis. This was done at 303K and 323K respectively. The thermodynamic parameters; ΔHO ΔSO and ΔGO for the adsorption process were calculated using the relationship.

In b = $\underline{\Delta S}$ - $\underline{\Delta H}$

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R RT ……………………………………………….. (3.0)

Where b is the Langmuir constant related to energy. The linear plot of ln b versus 1/T yields a slope and intercept whose value correspond to ∆HO and ∆SO respectively. These values can then be used to compute ∆GO applying the Gibbs relationship.

$\Delta GO = \Delta HO - \Delta S0$……………………………………………………… (3.1)

at constant temperature, in deriving the values of the thermodynamic parameters, it is assumed that the enthalpy does not change with temperature. The amount of Pb^{2+}, Zn^{2+}, Cd^{2+} and Cu^{2+} adsorbed were calculated from the relationship,

$$qe\ (mg/g) = \frac{(Co-Ce)\ V/1000}{W\ (g)} \ldots\ldots\ldots (3.2)$$

Where Co is the initial concentration of metal ion (mg/l), Ce the equilibrium concentration of metal ion (mg/l), V is the volume of metal ion solution employed (ml) while qe is the amount of metal ion adsorbed (mg/g)

3.0 RESULTS AND DISCUSSION

3.0.1 The Physico-Chemical Studies.

The physico-chemical studies result of the less than 2.0mm fraction of the soils from Isoko North and CRIN are presented in the table 1 below.

3.0.1.1 Soil pH

The pH values of the soil from Isoko North and soil from CRIN measured in 1:1 of soil to de-ionized water and 1.0M KCl varied between 4.3 to 6.1 and 3.0 to 5.4 respectively. This indicates very slightly acidic to mainly neutral soils. Soils from Isoko North have a pH value of 3.0 in 1.OM KCl and 4.3 in deionised water. While a pH value 5.4 in KCl and 6.1 in deionised water was recorded for soil from CRIN. The pH value in 1.0M KCl was slightly lower than pH in de-ionized water because potassium ion (K^+) in solution displaces hydrogen ion (H+) from the soils cation exchange sites. The results show that soil from Isoko North is more acidic than soil from CRIN.

3.0.1.2 Soil Organic Matter

The organic matter content of the soil samples observed in two soils was generally low varying from 3.07% to 3.82%. The higher value of 3.82% was for soil from CRIN and the lower value of organic matter was for soil from Isoko North. Adsorption is likely to be more in soil with higher organic matter content.

3.0.1.3 Soil Texture

The particle size determination showed a high amount of sand at the range of 73.2% to 85.2%. The silt contents came next with a range of 5.4% to 15.4%. The clay contents were considerably lower than the silt in the range of 9.4% to 11.4%. Isoko soil had a maximum of 85.2% of sand and subsequently had a minimum silt particles and clay particle of 9.4% and 5.4% respectively. CRIN soil on the other hand had a lower value of sand (73.2%) and hence higher in clay and silt value (11.4% and 15.4% respectively). It is pertinent to note that, the higher the clay mineral particles of the soil, the lower the sand particles and the more the adsorption.

3.0.1.4 Base Saturation

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The value of base saturation for soil from Isoko North was 60.73% compared to that of soil from CRIN which has a value of 78.95%. The soil from CRIN has the higher capacity for adsorption than soil from Isoko North.

3.0.1.5 Heavy Metal Concentration

Heavy metal concentration in the soils showed that Zinc has the highest concentration with that in soil from CRIN while Aluminum had the highest values in soil from Isoko North. Generally, the observable trend of the heavy metal concentration soil from CRIN was in order of Zn > Cu > Ni > Pb > Cd = Al while that of soil from Isoko North was in order of Al > Zn > Cu >Pb > Cd.

Table 1: Physico-Chemical Parameters of the soil from Isoko North and CRIN.

Parameters	**Isoko North**	**CRIN**
pH in H_2O	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^{2+} (meq/100g)	1.34	1.40
Mg^{2+} (meq/100g)	0.68	0.68
Na^{+} (meq/100g)	0.90	0.10
K^{+} (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^{3+} (ppm)	55.6	0.5
$Cd^{2+(}$ppm)	0.6	0.5
Cu^{2+}(ppm)	43.6	30.1
Pb^{2+}(ppm)	1.1	0.9
$Zn^{2+(}$ppm)	51.83	66.51

3.0.1.6 Exchangeable Bases

The two soil samples showed appreciable amount of the exchangeable bases such as Mg, Ca, K and Na. Although, moderately low, exchangeable Ca has the highest value compared to the other exchangeable cations varying from 1.34 to 1.40meq/100g. Soil from CRIN has the higher value (1.40meq/100g) while soil from Isoko North has the lower value (1.34meq/100g). Exchangeable Mg and K have the same values of 0.68meq/100g and 0.14meq/100g for both soil samples. Exchangeable Na was comparably lower than other exchangeable cations and has the range of 0.09meq/100g to 0.10meq/100g. Exchangeable Na was observed to be higher in soil sample from CRIN and lower in soil sample from Isoko North. Soil from CRIN seems to have the higher

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value of exchangeable bases compared to the soil from Isoko North. The general order of metal ions concentrations in soil is Ca > Mg > K > Na. This implies that soil from CRIN has low potential for ions such aluminium which are toxic.

3.0.1.7 Cation Exchange Capacity (CEC)

The cation exchange capacity (CEC) of the soil was calculated by the summation of exchangeable cations (effective cation exchange capacity). The CEC varied from 2.85 to 3.82meq/100g. Soil from CRIN has the higher value of 3.82meq/100g, while that from Isoko North had the lower value of 2.85meq/100g. This implies that exchange in soil from CRIN has a higher capacity to exchange for cations than soil from Isoko North.

3.0.1.8 Heavy Metal Speciation

The results of the heavy metal speciation studies which are in microgram per gram (µg/g) and percentage (%) are as presented in table 2 below. The result showed that Zinc generally has the highest total concentration in the two soils compared to the other metals. The total heavy metal concentration for both soils are in the order of Zn > Cd > Ni > Pb. Zinc has a value of 5.21 µg/g for soil from Isoko North and 5.14 µg/g for soil from CRIN. In terms of exchangeable fraction, Zinc has a value of 1.04 µg/g for soil from Isoko North and 1.10 µg/g for soil from CRIN. Both Cadmium and Lead a value of 0.01 µg/g for both soils. However, from the results, the value of the exchangeable fraction of the metal ions in both soils was very low and so do not pose any immediate potential risk.

Table 2: Results of Heavy Metal Speciation of both soils in microgram and percentage.

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
	SUM	**0.330**	**100**	**0.55**	**100**	**5.205**	**100**
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
	SUM	**0.029**	**100**	**0.049**	**100**	**5.139**	**100**

A = Soil from Isoko North
B = Soil from CRIN
F1 = Exchangeable Fraction
F2 = Metals bound to Carbonate
F3 = Metals bound to Fe-Mn-Oxide
F4 = Metals to Oxidizable Matter
F5 = Metals bound to Residue Matter.

3.1 EFFECT OF CONTACT TIME ON SORPTION

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The effect of time on sorption was investigated so as to verify how long it will take the two soils to adsorb the metal ions at their maximum pH. The data for the effect of time on the adsorbed of the four metals adsorption by the two soils samples are presented in Table 3 to 6 The data show that as the contact time increases from 30 to 180 minutes, the amount of metal removed by both soil samples increased. This represents between 37 to 49% of metal ions adsorbed by soil from Isoko North and 39 to 81% for the soil from CRIN. The adsorption equilibrium is reached between 720 to 1440 mins for all the metals. This was collaborated with the work of Haiyan Yu et althat highlighted that with an increase in contact time, the adsorption rate decreased and the adsorption process gradually approached equilibrium within 48 hrs.[6]

Table 3: Effect of Time on the Adsorption of Pb onto the Soils

Time (Min)	**Isoko North (mg/g)**	**CRIN (mg/g**
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: Effect of Time on the Adsorption of Cu onto the Soils

Time (Min)	**Isoko North (mg/g)**	**CRIN (mg/g**
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: Effect of Time on the Adsorption of Cd onto the Soils

Time (Min)	**Isoko North (mg/g)**	**CRIN (mg/g**
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: Effect of Time on the Adsorption of Zn onto the Soils

Time	**Isoko North**	**CRIN**

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(Min)	**(mg/g)**	**(mg/g**
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 values for the investigation of the sorption capability of the two soils for metal ions (Cd^{2+}, Cu^{2+}, Pb^{2+} and Zn^{2+}) at different pH values (3-10) are shown in Table 7 to 10

Table 7: Effect of pH on the Adsorption of Pb onto the Soils

P^H	**Isoko North (mg/g)**	**CRIN (mg/g**
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: Effect of pH on the Adsorption of Cd onto the Soils

P^H	**Isoko North (mg/g)**	**CRIN (mg/g**
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: Effect of pH on the Adsorption of Cu onto the Soils

P^H	**Isoko North (mg/g)**	**CRIN (mg/g**
3	1.63	3.08
4	1,81	3.44

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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: Effect of pH on the Adsorption of Zn onto the Soils

P^H	**Isoko North (mg/g)**	**CRIN (mg/g**
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

The data show lesser metal uptake at low pH for all the metals by the two soil samples investigated which indicate that the excess protons also compete for the same binding sites with the metal ions. Increase in pH which results in increase in metal retention shows pH dependence of the sorption process. This can be attributed to preferential adsorption of hydrolysed metal species to free metal ions, the proportion of which increases with pH[8,9 10]. However, there is a decreasing order of metal retention of metals at pH above 8 for almost all the metal ions by the two soils. At pH above 7 there is solubilisation of organic complexing ligands which effectively compete with the soil surface for the metal ions[11].

3.3 EFFECT OF INITIAL SORBATE CONCENTRATION ON SORPTION.

Increasing the initial metal ions concentration from 50mg/l to 500mg/l leads to the increase in amount of metals adsorbed, but decrease in percentage (%) adsorbed. Thus with increasing metal concentration in solution, a decreasing percentage of adsorption of metal ions is observed. The values for the effect of sorbate concentration of all the four metals by both soils is presented on Tables 11 to 12 are collaborated with research carried out in India titles Kinetic Sorption Studies of Heavy Metal Contamination on Indian Expansive Soil[7].

Table 11: Effect of Initial Sorbate Concentration on the adsorption of Cd onto the two Soils

(mg/L)	**Isoko North (mg/g)**	**CRIN (mg/g)**
50	0.99	0.99
75	1.12	1.49
100	1.48	1.99
150	1.76	2.82

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200	1.90	3.41

Table 12: Effect of Sorbate Concentration on the adsorption of Cu onto the two Soils

(mg/L)	**Isoko North (mg/g)**	**CRIN (mg/g)**
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

Table 13: Effect of Sorbate Concentration on the adsorption of Zn onto the two Soils

(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: Effect of Sorbate Concentration on the adsorption of Pb onto the two Soils.

(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

With subsequently higher initial concentrations this ratio progressively increases due to number of sorption sites becoming fewer compared to the amount of sorbate available, and therefore a decreasing trend in percent sorption from a lower to a higher concentration seen. Obviously, the fractional sorption becomes progressively become initial concentration dependent as the initial concentration is increased. Similar trend has been reported[12].

3.7 SUMMARY AND CONCLUSION

From the physico-chemical study of the soil samples, soil from Isoko North was more acidic and the soil from CRIN less acidic. The organic matter content was low for both soils; Isoko North has lesser clay and silt content of the two soils. Both have low values of exchangeable bases, extractable micronutrients, bulk density and heavy metal concentrations values were higher for soil from Isoko North. The value of cation exchange capacity, hydraulic conductivity and base saturation were higher for soil from CRIN. Heavy metal speciation study results show low

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concentrations of metal for both soils. The equilibrium studies showed a similar trend for both soils in terms of the parameters studied. However, soil from Isoko North has lesser adsorption capacity than the soil from CRIN. Both soils show pH dependence in which adsorption of heavy metals with increase in pH, increasing the initial metal concentrations lead to a decreasing level of the percentage of metal adsorbed by the soils. The percentage of metal adsorbed increased in both soils with increase in contact time, there is a general trend of decreased in the percentage of metal adsorbed with increasing ionic strength of the electrolyte used. Equilibrium modelling shows a better fitting of the adsorption pattern to Langmuir isotherm model than Freundlich isotherm model.

Thermodynamic studies did not show any general trend for the two soils. The standards Gibbs free energy values showed that adsorption was non spontaneous for all the metal ions adsorbed into the soil from both soils at both temperatures (303K and 323K) except for Copper adsorption that are negative for soil from CRIN. Spontaneity is only observed in the adsorption of Copper at the two temperatures for soil from CRIN. The enthalpy change values showed that adsorption was exothermic for Cadmium and Copper by soil from CRIN. All other metal ions adsorption was endothermic for both soils. The results from the standard entropy showed that there was an orderly arrangement of the Cadmium, Copper ions for both soils and Zinc ion (CRIN) at equilibrium; while others showed disorderly arrangement at equilibrium. Therefore, data obtained from thermodynamic and equilibrium adsorption studies can provide useful information needed in soil remediation. Therefore, it is recommended that desorption studies of both soils be carried so as to obtain more information that are necessary for soil remediation.

REFERENCES

1. Nieves Barros (2021): Thermodynamics of Soil Microbial Metabolism: Applications and Functions. Appl. Sci. 2021, 11(11), 4962; https://doi.org/10.3390/app11114962

Received: 27 April 2021 / Revised: 24 May 2021 / Accepted: 26 May 2021 / Published: 28 May 2021.

2. Hansen, L.D.; Popović, M.; Tolley, H.D.; Woodfield, B.F. Laws of evolution parallel the laws of thermodynamics. J. Chem. Thermodyn. 2018, 124, 141–148. [Google Scholar] [CrossRef].
3. Leifeld, J.; Klein, K.; Wüst-Galley, C. Soil organic matter stoichiometry as indicator for peatland degradation. Sci. Rep. 2020, 10, 7634–7642. [Google Scholar] [CrossRef] [PubMed]
4. Song, H.-S.; Stegen, J.C.; Graham, E.B.; Lee, J.-Y.; Garayburu-Caruso, V.A.; Nelson, W.C.; Chen, X.; Moulton, J.D.; Scheibe, T.D. Representing Organic Matter Thermodynamics in Biogeochemical Reactions via Substrate-Explicit Modeling. Front. Microbiol. 2020, 11, 531756. [Google Scholar] [CrossRef] [PubMed]
5. Alloy, B.J 1995. Soil Processes and the Behaviour of Heavy Metals in Soils. Glasgow, Blackie. Environmental Science Technology. 26:703-709
6. Haiyan Yu, Yongfeng Liu, Xingquan Shu, Han Fang, Xiaojing Sun, Yuwei Pan & Limin Ma (2020): Equilibrium, kinetic and thermodynamic studies on the adsorption of atrazine in soils of the water fluctuation zone in the Three-Gorges Reservoir. Environmental Sciences Europe volume 32, Article number: 27 (2020)

.

7. M. K. Gupta, A.K. Singh and R. K. Srivastava (2009): Kinetic Sorption Studies of Heavy MetalContamination on Indian Expansive Soil. ISSN: 0973-4945; CODEN ECJHAOE-Journal of Chemistryhttp://www.e-journals.net 2009, 6(4), 1125-1132
8. N. S. Bolan, J. K. Syers, R. W. Tillman (1986): Ionic strength effects on surface charge and adsorption of phosphate and sulphate by soils. European Journal of Soil Science. First published: September 1986 https://doi.org/10.1111/j.1365-2389.1986.tb00371.
9. Flora Amarh et al (2021): Effects of soil depth and characteristics on phosphorus adsorption isotherms of different land utilization types: Phosphorus adsorption isotherms of soil. Elsevier. Soil and Tillage Research, Volume 213, September 2021, 105139
10. A. H. Fitter, C. D. Sutton (1975): The use of the freundlich isotherm for soil phosphate sorption data. European Journal of Soil Science. First published: September 1975 https://doi.org/10.1111/j.1365-2389.1975.tb01947.
11. Adebowale K.O, Unuabonnah I.A and Olu-Owolabi B.I (2005): Adsorption of some heavy metals ions on sulphate- and phosphate modified Kaolin. Applied Clay Science 20: 145-148

12. K.H Chu and M.A Hashim: (2007): Copper biosorption on immobilized seaweed biomass: Column breakthrough characteristics. Journal of Environmental Sciences

Volume 19, Issue 8, 2007, Pages 928-932. https://doi.org/10.1016/S1001-0742(07)60153-3

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