



ORIGINAL RESEARCH ARTICLE

Effects of Selected Properties of Semi-Arid Soil of Dutse, Jigawa State on Adsorption of Pb and Cd Ions.

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ABSTRACT

This study determined the effects of some selected physical and chemical properties of semi-arid soil on heavy metal sorption. Soil samples were collected randomly from Federal University Dutse within Nigeria's Sudan Savannah agroecological zone. Nitrate salts were used to prepare three different concentrations (10, 20, 30 mg/kg) of CdCl₂ and PbCl₂. The equilibrium sorption of the study soil was determined. The equilibrium sorption data were fitted into Langmuir and Freundlich isotherms. Langmuir and Freundlich isotherm model's r^2 values (1) were at par. The boundary energy b (1 mg⁻¹) from the Langmuir isotherm model was determined to be -110.0 and 47 for Pb and Cd, respectively. Freundlich isotherm sorption intensity (n) of 1.92 and 1.67 indicated a favorable sorption, revealing physical adsorption rather than chemical adsorption. Correlation analysis established the relationship between the heavy metal sorption capacity and soil properties. The R values of 0.92 and 0.72 showed a positive relationship between Pb and Cd adsorption with soil silt content. Positive relationships (R) were obtained from the organic matter (0.68), Total Nitrogen (0.99 and 0.60), as well as particle size on adsorption of both metals. Adsorption of heavy metals was positively affected by the physical and chemical properties of the semi-arid soil.

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KEYWORDS

Isotherms, Soil properties, Alfisols, Sudan savannah agroecology, Heavy metals.

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INTRODUCTION

Heavy metals' behavior in soil is largely governed by their sorption and desorption reactions with different soil constituents (Singh *et al.*, 2009). Sorption involves removing ions or molecules from soil solution either by absorption or adsorption, while desorption involves the removal or changing from an adsorbed surface to a gaseous or liquid state (Brady and Weil, 2008). Laboratory investigations have clarified the mechanisms controlling heavy metal sorption onto soil and that their adsorption is determined by a number of physicochemical factors or variables and is, therefore, theoretically calculable (Vidal and Rigol, 2008).

The mechanism of heavy metal ions sorption by soil is a complex process involving different processes controlled by different variables that can interact (Guanshu and Baoshan, 2001). It is a major process responsible for the fate of heavy metals in soils since the mobility of these elements is directly related to their partitioning between the soil solid phase and the soil solution in equilibrium (Vidal *et al.*, 2009). These processes are often described by the sorption isotherms, which describe the equilibrium of the sorption of a material on a surface at a constant

temperature and under varying pH. These isotherms are often used as empirical models (Veliev *et al.*, 2006). The most important factors influencing heavy metals accumulation in soils and isotherm shape are soil pH; Eh (redox potential) (Bradl, 2004); clay minerals; cation-exchange capacity (CEC); oxides of Fe, Al, and Mn; calcium carbonate and humic substance associated with natural organic matter (Sparks 2005).

Adsorption of metals by soil may lead to soil pollution, which can cause a lot of damage to human and animal health, plants, tropical rain forests, and the wider environment (Khan and Ghouri, 2011). Much of this research regarding heavy metals sorption has never been conducted on soils of Dutse, Jigawa State, and no information on the properties of these soils may help us understand their influence on heavy metals sorption.

The justification of this study is the derived need to understand, control, or minimize soil contamination with toxic elements, especially heavy metals, that are released into the environment through untreated household sewage and waste from human activities. This has, over

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time, created health problems resulting from the contamination of soil and water bodies (Balali-Mood *et al.*, 2021). With the medium to long-term health risks associated with environmental hazards, there is a need to understand the soil properties that influence the sorption of heavy metals and how they affect the soil, crop, and human health in order to suggest remediation techniques. Common health problems in humans created by the presence of these heavy metals in soil and water include multiple sclerosis, Parkinson's disease, Alzheimer's disease, osteoporosis, cancer, arthritis, kidney damage, autism, mental retardation, tremors, hair loss, chronic ulcer, epilepsy, etc. (Jarup, 2003; Martin and Griswold, 2009; Jaishankar *et al.*, 2014). Also, the bioavailability of heavy metals in soil has been linked to plant uptake with subsequent bioaccumulation over time (Su *et al.*, 2014; Onokebhagbe *et al.*, 2019). The bioaccumulation of heavy metals from soil includes certain processes but is not limited to phytoextraction and rhizofiltration (Alengebawiy *et al.*, 2021). Their presence in plant tissues above established thresholds interferes with metabolic activities causing oxidative stress and cellular damage with subsequent reduction in growth and development of plants' agronomic parameters (Goval *et al.*, 2020).

Dutse in Jigawa State falls within the Sudan Savanna agroecology, predominantly a semi-arid zone in northern Nigeria. Soils within this zone are characterized by slightly acidic to neutral pH, high temperature, low moisture content, low contents of Total Nitrogen, and other fertility indices (Machido *et al.*, 2010). These soils have also been subjected to detailed sorption evaluation of some plant nutrient elements, especially phosphorous, but little or no attention has been given to these soils regarding their heavy metal sorption characteristics (Agbenin, 1995; Nwoke *et al.*, 2003). Therefore, this study aimed to determine the sorption characteristics of the semi-arid soil of Dutse for heavy metals using the Langmuir and Freundlich adsorption isotherms as well as the effects of the physical and chemical properties of the soil on heavy metal sorption.

MATERIALS AND METHODS

Study area

The soil for the study was collected from the Teaching and Research Farm of Federal University Dutse (latitude 11° 46' 39" N and longitude 9° 20' 30" E) in Jigawa state of Nigeria. The sampled site lies within the Sudan Savannah agroecological zone of Nigeria. The mean annual temperature is 26 °C, but the mean monthly value ranges between 21 °C in the coldest months (December/February) and 31 °C in the hottest months (April/march) (Olofin, 2008).

Samples collection, preparation, and analysis

The soil sample was collected using a random soil sampling technique from Federal University Dutse. Soil was taken from the surface (0-15 cm) of the soil using an auger. The sampled soil was mixed to form a

composite sample. The soil was subjected to preparatory procedures such as air drying and sieving before being subjected to laboratory analysis. Physical and chemical analysis was conducted on the soil sample in the Soil Science Department of the Faculty of Agriculture, Federal University Dutse, Dutse, Jigawa State.

Soil classification

The soil of the location (Dutse) has been classified as (Typic Haplustalf) among the ten orders of soils recognized in Soil Taxonomy (Soil Survey Staff, 2003); Alfisol in the USDA soil Taxonomy system (Harpstead, 1973). Dutse soil type is highly weathered and fragile with low activity clay and slightly acidic, making its fertility decline under continuous arable cropping (Odunze, 2006; FFD, 2012). The soil is sandy, attributed to the parent material, mainly pre-Cambrian basement complex rocks (Malgwi *et al.*, 2000; Voncir *et al.*, 2008; Shehu *et al.*, 2015). The soils have a low level of organic matter high proportion of sand fractions, resulting in low water retention and poor physical stability (Salako, 2002). The soil is also characterized by low levels of available phosphorous, nitrogen, and CEC (Mokwunye and Bationo, 2002).

Sorption Studies

Sorption studies were carried out using the batch technique described by Arias *et al.* (2006) and Mulu (2013). The experiments were carried out by evaluating the adsorption of Cd and Pb ions onto the soil in 250 ml flasks. 20 grams of soil samples were equilibrated with three different concentrations of Cd and Pb: 10, 20, 30 mg kg⁻¹ Cd and 10, 20, 30 mg kg⁻¹ Pb prepared from nitrate salts of Cd and Pb. The flasks were constantly agitated to allow adsorption equilibrium at various time intervals (0.5, 1, 2, 5, 10, and 24 hr). The filtered suspension was analysed with the atomic adsorption spectrophotometer (Buck 211VGP AAS) to determine the equilibrium concentrations of Cd and Pb in the suspension. Quantities (Q_e) of adsorbed Cd and Pb were calculated as the differences between the initial and equilibrium concentrations in the solutions. The metal ions sorbed by the soil were calculated based on the relationship proposed by Mulu (2013), as shown in Equation 1.

$$Q_e = \frac{V_i(C_i - C_e)}{M} \quad (1)$$

Q_e = Quantity of adsorbed metal ions

V_i = Volume of solution

C_i = Initial metal concentration

C_e = Equilibrium metal concentration

M = Mass of adsorbent (soil)

The percentage of metal ions removed from solution will be calculated as follows:

$$\% MR = \frac{(C_i - C_e)}{C_i} * 100 \tag{2}$$

Adsorption Isotherms

The data obtained from the batch experiment data were fitted into the adsorption isotherms to determine which isotherm fits best. These isotherms describe the connection between the amounts of adsorbate on the adsorbent and the adsorptive capacity of the adsorbent. The distribution of the ions between the liquid phase and the solid phase in this study was described by the Langmuir and Freundlich isotherm models. These adsorption isotherms are outlined by Mulu (2013) as presented in equations 3 (Langmuir) and 4 (Freundlich), respectively:

$$C_e/Q_e = 1/bq_{max} + C_e/q_{max} \tag{3}$$

Where Q_e = the amount of metal x sorbed per unit weight of soil ($mg\ g^{-1}$), C_e = equilibrium metal concentration ($mg\ l^{-1}$), q_{max} = metal adsorption maxima ($mg\ g^{-1}$), b = coefficient relating to bonding energy ($l\ mg^{-1}$) and bq_{max} = distribution coefficient ($l\ g^{-1}$).

$$Q_e = K_f C_e^{1/n} \tag{4}$$

Where K_f and n are the Freundlich constants characteristic of the system involved; K_f and n are indicators of the adsorption capacity of soil and adsorption intensity, respectively. The n value indicates the degree of nonlinearity between the solution concentration and adsorption as follows: if $1 < n < 1$, if $n = 1$, adsorption is linear; if $n < 1$, then adsorption is a chemical process; if $n > 1$, then adsorption is a physical process (Mulu, 2013). The equation was linearized, and the constants K_f and n were found by linear regression as given by (Mulu, 2013):

$$\ln Q_e = \ln K_f - 1/n \ln C_e \tag{5}$$

Statistical Analysis

Regression analysis was used to determine the sorption relationship between the soil and the heavy metals. Pearson correlation analysis was used to establish the relationships between Pb and Cd sorption and some measured soil physical and chemical properties. All statistical analysis was carried out using STATA version 13 software packages.

RESULTS AND DISCUSSION

Soil physical and chemical parameters

Table 1 shows the properties of the soils used for the study. The particle size analysis results indicate that the soil's textural class is sandy clay loam. This is characteristic of the soils of the savannah region of northern Nigeria (Ogunwole and Ogunleye, 2005). As obtained from Table 1 for the soils, the soil reaction was 7.2 (pH in KCl_2) and 8.2 (pH in H_2O), indicating slight neutrality to alkaline. An electrical conductivity (EC) value of 0.51, as shown in the

table, indicates the soil's low salinity status according to the limits set by (Schoeneberger *et al.*, 2002).

Organic matter contents of the soils ($13.87\ g\ kg^{-1}$) were below the critical level of $20\ g\ kg^{-1}$ reported by (Aduayi *et al.*, 2002). And hence low. The low level of organic matter with a high proportion of sand particles will normally result in low aggregation, low water retention, and poor physical stability of the soil, therefore, low productivity of crops (Salako, 2002). Also, continuous farming and burning of the residues that farmers could have incorporated into the soil led to the depletion of soil organic matter content (Yakubu, 2001).

Table 1: Physical and chemical properties of the study soil

Soil property	
Clay	26
Silt	14
Sand	60
Textural Class	Sandy clay loam
pH(H_2O)	8.2
pH(KCl_2)	7.2
Electrical Conductivity ($dS\ m^{-1}$)	0.51
Organic Carbon ($g\ kg^{-1}$)	9.74
Organic Matter ($g\ kg^{-1}$)	13.87
Total Nitrogen ($g\ kg^{-1}$)	0.75
Available P ($mg\ kg^{-1}$)	3.82
Exchangeable Bases ($cmol\ kg^{-1}$)	
Ca	1.88
Mg	0.78
K	0.17
Na	0.57
SEB ($cmol\ kg^{-1}$)	3.40

Total N contents of $0.75\ g\ kg^{-1}$ were obtained from soil below the critical level of $1.5\ g\ kg^{-1}$ (Aduayi *et al.*, 2002). Hence, fertilizer responses by crops are likely. Available P values of $3.82\ mg\ kg^{-1}$ for the soils fell below the critical limit of $8\ mg\ kg^{-1}$ of the Bray P⁻¹ rating for soil fertility classes (Aduayi *et al.*, 2002).

The cation exchange capacity of the soil was low ($3.40\ cmol\ kg^{-1}$), which falls below the range of the critical values of < 6 (low), $6 - 12$ (medium), and > 12 (high) reported by Esu, (1991). Exchangeable bases (Ca^{2+} ($1.88\ cmol\ kg^{-1}$), Mg^{2+} ($0.78\ cmol\ kg^{-1}$), K^+ ($0.17\ cmol\ kg^{-1}$), and Na^+ ($0.57\ cmol\ kg^{-1}$) for the soils were low, reflecting poor fertility status of the soils. Kowal and Knabe, (1972) made similar observations in the past for Nigerian soils in

general. The dominant cations on the exchange sites were Ca^{2+} and Mg^{2+} . The findings for the soil are in line with that of Noma *et al.*, (2004) and Yakubu, (2006), who stated that Ca^{2+} and Mg^{2+} are the predominant cations in Nigerian northern guinea savannah soils because of their strong adsorption and rapid release into the soil through mineral weathering.

Adsorption studies

The sorption of Pb and Cd ions from the solutions by the study soil was evaluated as a function of their initial concentration, as shown in Table 2. Lead removal from

the solution by the soil was 100%, while the average cadmium removal from the solutions was 99.90%. The heavy metals adsorption characteristics by soil are shown in Figures 1, 2, 3 and 4. Langmuir and Freundlich isotherms showing the adsorption of Pb and Cd ions by the soil were characterized by the linear plot as shown in Figures 1, 2, 3, and 4. The likeness of these plots shows that the Pb and Cd ions were adsorbed under similar circumstances. It also suggests that the affinity of the soil for the adsorbate is less than that of the aqueous solution when the solution concentration of the adsorbate is low (Essington, 2005; Abdu and Ugbaje, 2013).

Table 2: Metal removal capacity of the study soil

Metals	C_i (mg kg ⁻¹)	C_e (mg kg ⁻¹)	Q_e (mg kg ⁻¹)	% MR
Lead	10	-0.0003	20	100
	20	-0.0013	50	100
	30	-0.0017	72	100
Cadmium	10	0.0075	24.98	99.92
	20	0.026	49.93	99.87
	30	0.034	74.91	99.88

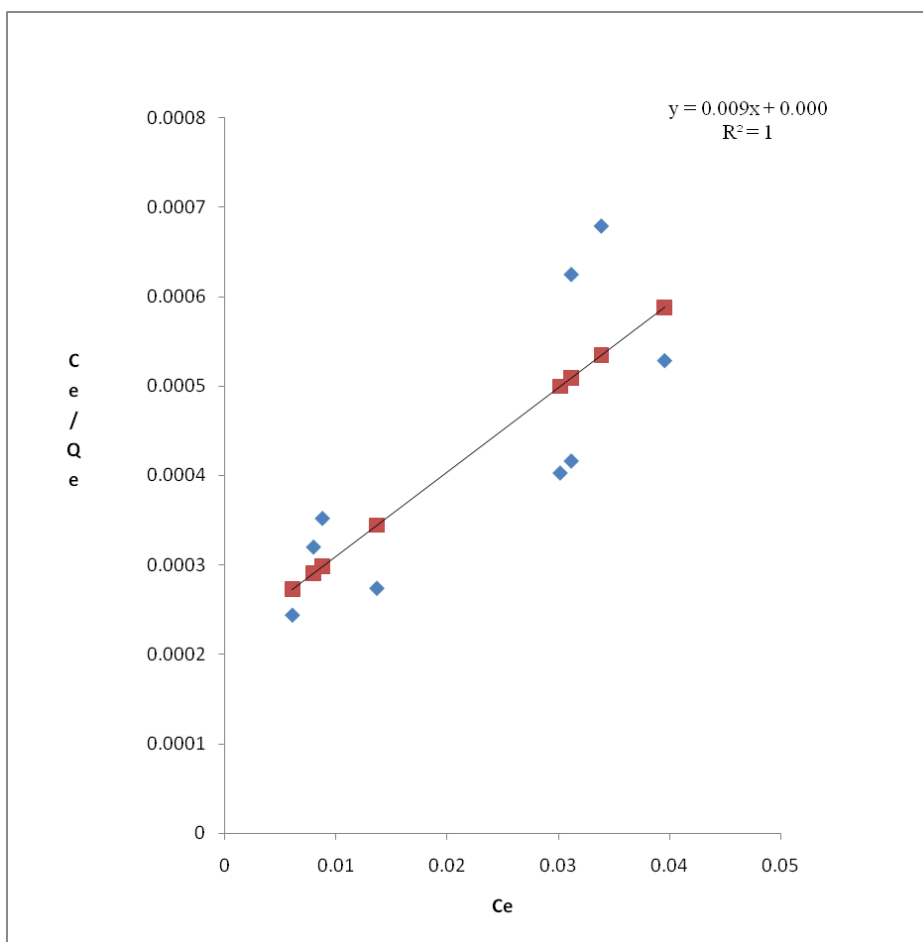


Figure 1: Langmuir isotherm showing Cd adsorption on study soil.

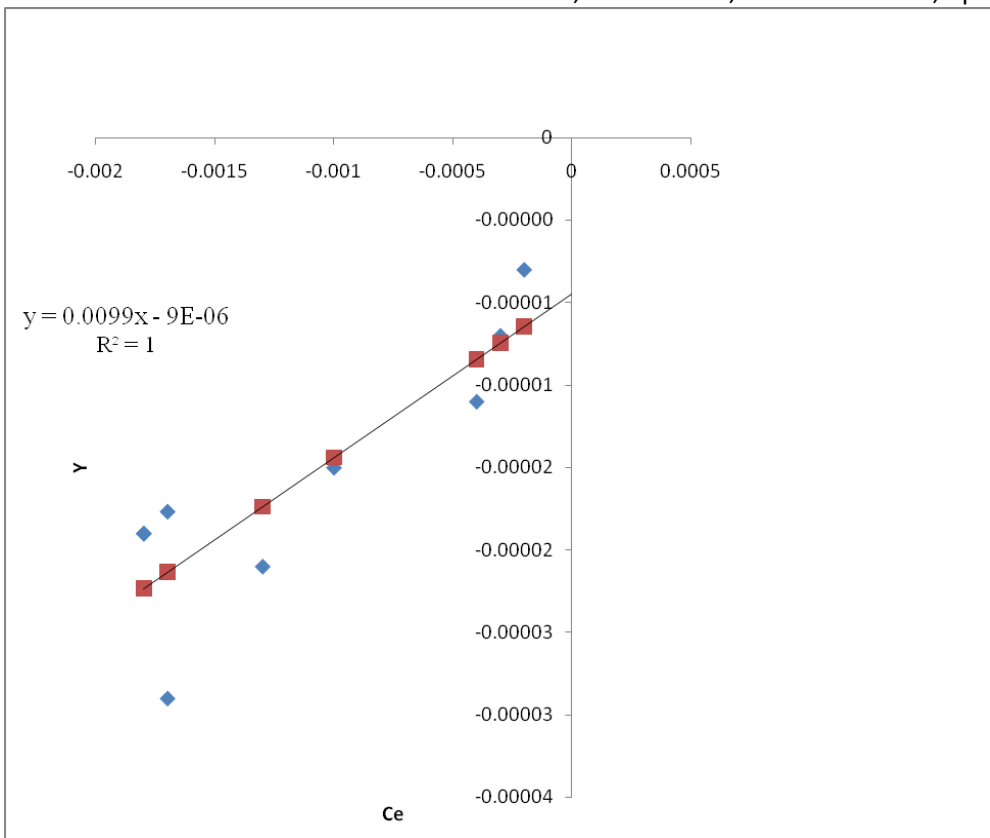


Figure 2: Langmuir isotherm showing Pb adsorption on study soil

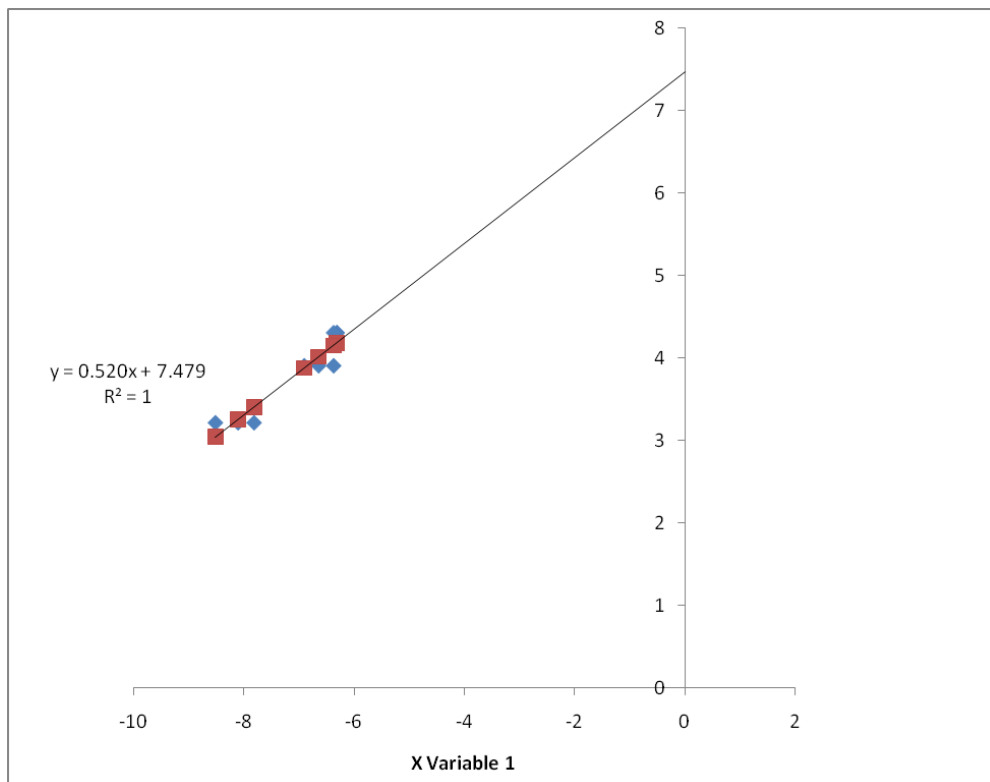


Figure 3: Freundlich isotherm showing Pb adsorption on study soil

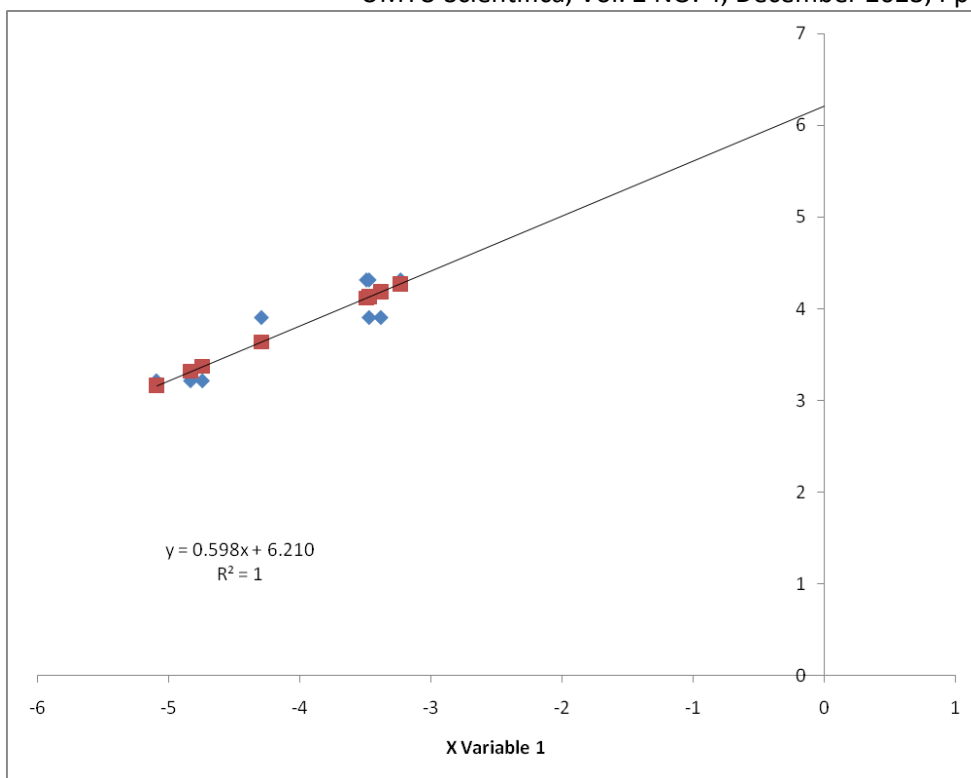


Figure 4: Freundlich isotherm showing Cd adsorption on study soil

The adsorption constants of the adopted isotherms and regression coefficients (R^2) calculated are presented in Table 3. The data were adapted to Langmuir and Freundlich isotherm models to determine the appropriate metal ion adsorption model. The results revealed that both adsorption isotherms were the best-fit models for Pb and Cd ions onto soil with $R^2 = 1$.

Langmuir parameters which include the boundary energy at the surface of the soil particles ($b \text{ l mg}^{-1}$), which is a measure of the affinity of lead and cadmium ions for the soil; the maximum adsorption capacity ($q_{\text{max}} \text{ mg g}^{-1}$) calculated from the data plotted on Figures 1 and 2 are presented in Table 3. The Langmuir equation gave maximum adsorption values of 101.01 mg g^{-1} for Pb ions onto soil and 106.38 mg g^{-1} for Cd ions onto soil. The boundary energy obtained was -110.0 Pb ions , 47 mg^{-1} for Cd ions onto the soil, as shown in Table 2. The linear plot of specific adsorption (C_e/q_e) against the equilibrium

concentration (C_e) (Figures 1 and 2) shows that the adsorption obeys the Langmuir model.

The values of the components of the linear regression equations for the Freundlich adsorption isotherm are shown in Table 2. Values of K_f and n were calculated from the intercepts and slopes of the Freundlich plots, respectively, and are shown in this table. The calculated n values in the equations were 1.92 for Pb and 1.67 for Cd, respectively (Table 3). In this study, the situation $n > 1$ indicates its physical adsorption of Pb and Cd ions onto the soil rather than the chemical adsorption of the ions onto the soil. As the K_F value increased, the adsorption intensity increased, too. Therefore, the higher K_F for Pb ions, as shown in Table 3, was confirmed by this model, that the adsorption capacity by the study soil for Pb ions is of greater intensity than that of Cd ions. Summarily, the soil exhibited preferences for Pb ions adsorption more than Cd ions adsorption.

Table 3: Metal removing capacity of the soil

Isotherm model	Metal ion	$b \text{ (l mg}^{-1}\text{)}$	$q_{\text{max}} \text{ (mg}^{-1}\text{)}$	R^2
Langmuir	Pb	-110.0	101.01	1
	Cd	47	106.38	1
Freundlich		K_F	n	R^2
	Pb	2.01	1.92	1
	Cd	1.83	1.67	1

Assessment of some selected properties of soil on Pb and Cd sorption

Relationships between some selected soil properties and heavy metal (Pb and Cd) sorption were established using Pearson correlation analysis. The results of the correlation analysis conducted to identify some key properties of the soil affecting Pb and Cd sorption are presented in Table 4. The results showed that silt strongly correlated with the sorption of the two heavy metals under the tried experimental settings. As shown in Table 4, the silt was strongly correlated with both Pb and Cd sorption with Pearson's R values of 0.92 and 0.72, respectively.

Table 4: Effect of soil properties on heavy metals adsorption

Soil properties	Q_ePb	Q_eCd
	R	
Clay	0.76	0.60
Sand	0.72	0.76
Silt	0.92	0.72
pH(H ₂ O)	-0.50	0.50
pH(KCl ₂)	-0.50	-0.50
Organic matter	0.68	0.68
Total Nitrogen	0.99	0.60

Similar results obtained by Mustapha *et al.* (2017) revealed that a higher quantity of Pb was strongly correlated to silt-clay fraction in soils of Kano as compared to Cd. Since sorption is particle diffusion controlled, the increase in micro pores increases the number of accessible sites, increasing the amount of metal adsorbed. This may also be attributed to the higher external surface available with smaller particles at a constant total mass, as stated by Ho *et al.* (2002) and Saueprasearsit *et al.* (2010).

A weak correlation in pH was obtained with the sorption of the two heavy metals. Negative pH correlation coefficients (-0.50) obtained for Cd and Pb show an inverse relationship between pH (KCl₂) and Cd and Pb concentrations in the soil. In other words, an increase in the soil pH will lead to increased Cd and Pb sorption by the soil particles with a corresponding reduction in heavy metals' ionic activities in the soil solution. Similarly, R values obtained from studies by Campillo-Cora *et al.* (2020) revealed that pH plays an important role in soil cation retention, further stating that soils with neutral to alkaline pH are characterized by high heavy metal retention capacity. Also, reports of studies conducted by Pierangeli *et al.* (2001) and Cruz-Lopes *et al.* (2021) revealed increased heavy metal adsorption with increased soil pH. These reports further corroborate and relate the observed pH of the study soil to its high heavy metal adsorption capacity.

Correlation coefficients (R) of Pb and Cd adsorption as influenced by the organic matter component of the study soil were statistically at par. These positive correlations obtained from the relationships could be due to the formation of complexes (inner and outer) by the heavy metals with organic components in the soil largely due to the chelating effects of its functional groups. The result obtained in this study is consistent with the reports of Elbana *et al.* (2018) and Seidou *et al.* (2022), which found that organic matter in soils showed strong sorption with heavy metals. The R value (0.68) obtained also largely reflected the quantity of organic matter content in the study soil, which was low, as shown in Table 1. Reports by Huang *et al.* (2013) have shown that soil organic matter largely affects the availability of heavy metals in the soil. Solubility of soil organic matter has been shown to increase with an increase in soil pH with a corresponding increase in its complexation and retention of heavy metals in the soil (Yang *et al.*, 2005).

Statistical high R correlation values of 0.92 and 0.72 were also identified for the Total Nitrogen contents of the study soil for Pb and Cd sorption, respectively though they were not significant, as shown in Table 4. This also suggests the possibility of N containing functional groups such as amine from decomposed organic matter being involved in the Pb and Cd sorption process (Yantasee *et al.*, 2004). Reports have also shown that the retention of heavy metals by soil particles is largely not influenced by the nitrogen content itself but rather by the presence and activities of microorganisms utilizing nitrogen (Hamsa *et al.*, 2017).

CONCLUSION

This study evaluated the influence of some selected properties of a semi-arid soil on Pb and Cd ion adsorption. These adsorptions of Pb and Cd by semi-arid soils were well described by Langmuir and Freundlich adsorption isotherms. Lead and Cd ions adsorption onto the soil particles was largely a physical process. The ionic adsorption of Pb was also largely influenced by the organic matter and Total nitrogen contents of the soil, as its adsorption was highly intense when compared to Cd adsorption. Adsorption of Cd in the soil was notably influenced by the sand fraction, pH as well as the organic matter content of the soil. Therefore, proposed remediation techniques should focus on these properties that enhance the fixation and retention of heavy metals in the soil, thereby minimizing their plant availability and uptake.

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