



ISSN: 2141 – 3290  
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## ADSORPTION CHARACTERISTICS OF Zn (II), Pb (II) AND Cd (II) IONS FROM AQUEOUS SOLUTION ONTO NATURAL CLAY MINERALS

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### ABSTRACT

Heavy metal contamination represents a significant environmental issue with adverse implications on ecosystems and human health. Natural clay minerals have unique properties providing good binding sites that make them effective in the removal of metal ions from water and other solutions. Information on the type of clay and sorption of heavy metal ions onto local natural clay minerals from Itu is scarce. Since the adsorption capacities vary depending on the metal and the type of clay, this study focuses on the nature of clay and the sorption mechanisms of Zn, Pb and Cd ions onto clay minerals. Analytical techniques, including X-ray diffraction, X-ray fluorescence (XRF) spectroscopy, and atomic absorption spectroscopy were employed to determine some quality parameters, mineral composition and concentration of clay mineral under investigation. The preliminary analysis, the XRD data revealed the dominance of kaolinite and quartz in the clay samples. Results of elemental analysis - CHNS showed significant levels ranging from 41.06 to 49.85% for Carbon, 3.60 to 4.97% for Hydrogen, 0.51 to 1.74% for Nitrogen and 0.23 to 0.89 % for Sulphur, and varies between 45% and 20%. Results showed that the Freundlich equation characterized  $Zn^{2+}$ ,  $Pb^{2+}$  and  $Cd^{2+}$  sorption data with the regression coefficient,  $R^2$  values ranging between 0.1960 - 0.8655, 0.0106 - 0.8878 and 0.5852 - 0.9368 respectively for all four clay samples. Since the choice among model equations is often made based on the goodness of fit data, therefore, the Freundlich isotherm model provided the best choice for Zn, Pb and Cd sorption calculation against that of Langmuir model. Therefore, this study lays a solid foundation for investigating the efficacy of these minerals in adsorbing heavy metals such as Zn, Pb and Cd ions, vital for developing effective strategies in environmental remediation and water purification.

**KEYWORDS:** Heavy metals, Sorption, Clay minerals, Isotherm

### BACKGROUND INTRODUCTION

Soil contamination by heavy metals has become a significant environmental concern due to their persistence, toxicity, and potential to accumulate in the food chain. Heavy metals, such as Pb, Zn, Cd, As, Hg, Cr, and Ni are released into the environment through various anthropogenic activities, including industrial processes, mining, agriculture, and improper waste disposal (Khan, 2014; Kalisinska and Fijałek, 2016; Khan *et al.*, 2018; Huang and Zhou, 2019). These metal contaminants can have detrimental effects on human health, ecosystem integrity, and agricultural productivity. They are characterized by their toxicological properties and can pose significant risks to human health and the environment. Health effects associated with heavy metal exposure can range from acute toxicity to chronic diseases. Some heavy metals, such as Pb and Hg are known to cause neurological damage, developmental disorders, kidney damage, and various cancers (Kiran and Mukherjee, 2008). Others, such as Cd and As are associated with respiratory problems, cardiovascular diseases, and increased cancer risks (Alloway, 2013).

Clay minerals are a type of soil mineral that are composed of layered sheets of tetrahedral and octahedral units (Khan *et al.*, 2018). These layered sheets provide a large surface area and a high CEC, making clay minerals an important sorbent for heavy metals in soil (Li *et al.*, 2019). The sorption of heavy metals on clay minerals can occur through a range of mechanisms, including ion exchange, complexation, and surface adsorption (Khan *et al.*, 2018; Feng, 2020).

One of the key processes that govern the fate and transport of heavy metals in soil is sorption, which refers to the attachment of metal ions onto the surface of soil particles.

Sorption is influenced by numerous factors, including the properties of the soil and the specific characteristics of the metal ions (Zheng, 2021). Clay minerals, in particular, play a crucial role in heavy metal sorption due to their high specific surface area, cation exchange capacity, and ability to retain metal ions through various mechanisms (Islam, 2015; Toumbakari, 2019). Natural clays, known for their cost-effectiveness and availability, are efficient adsorbents for heavy metals such as As, Cd, Cr, Co, Cu, Fe, Pb, Mn, Ni, and Zn (Gupta, 2008; Huang *et al.*, 2016). The immobilization of heavy metals in soil is a significant step in preventing contamination of other components such as groundwater. The sorption capacity of different types of soils to toxic heavy metals has been studied and the basic mechanisms of metal ion sorption and desorption have been explored (Wang, 2019, Wang 2020, Wu, 2020, Williams *et al.*, 2020). Theories have been developed to explain the processes of sorption of heavy and transition metals by soil minerals.

Natural clay minerals have unique properties - high cation exchange capacities (CEC) and large surface areas, providing ample binding sites for heavy metal ions (Anderson, 2018), that make them effective in the removal of metal ions from water and other solutions (Brigante *et al.*, 2018; Benassi *et al.*, 2021). The adsorption capacities vary depending on the metal and the type of clay (Gupta, 2008). The primary characteristics that contribute to their ion exchange capabilities include large surface area due to their small particle size and layered structure, providing numerous sites for metal ions to adsorb onto the clay surface (Chen *et al.*, 1998; Saxena *et al.*, 2013), layered structure such as montmorillonite and kaolinite, allows for the intercalation of

metal ions within the spaces between the layers, a process known as ion exchange (Stucki, 1993); negative charge arising from isomorphous substitutions and broken bonds on the crystal structure which attracts and binds positively charged metal ions (cations) through electrostatic forces (Chen *et al.*, 1998); and variable charge which makes their charge to change depending on the pH of the environment. This distinctive factor enhances their ability to trap metal ions at different pH levels (Ok *et al.*, 2011).

Natural clay, a versatile and abundant natural resource, has been utilized by humans for millennia due to its unique properties and a wide array of applications (Bhattacharyya and Sen Gupta, 2006; Cheng, 2019; Benassi *et al.*, 2021). This note explores the key properties and uses of natural clay, referencing credible sources for a comprehensive understanding. This study aims at assessing the adsorption behavior of zinc, lead and cadmium metals onto natural clay minerals. This will be achieved by using batch experimental procedure, determining the effect of varying initial concentrations of Pb<sup>2+</sup>, Zn<sup>2+</sup> and Cd<sup>2+</sup> ions on the sorption process, assessing the rate of adsorption of these metal ions on to clay minerals.

## MATERIALS AND METHODS

The natural clay deposit located in Ikot Ebom Itam, Itu Local Government Area of Akwa-Ibom State, is situated within Nigeria's South-South geo-political zone (Niger-Delta Region). Its coordinates lie between latitude 5°4'2.1" and longitude 7°53'43.87", and it has an estimated elevation of 78 meters above sea level. Three different types of clay minerals like quartz, kaolinite, and goethite were identified and sampled in different parts of the study site. Four soil profile pits ranging from 30 to 90 cm deep, were opened using a stainless-steel metal tool for sampling of clay soil (Table 1). Samples were collected from each site into a pre-labelled polyethylene bags and taken to the laboratory. In the laboratory, some operations such as removal of stones and other large objects, breaking or splitting of lumps, were carried out. The clay minerals were air-dried for 5 days, and homogenized with an agate mortar and pestle, sieved through a 2 mm mesh size and then dried at 120 °C for 4 hours before analysis.

The clay mineral samples were identified using different characterization techniques. The chemical composition was determined with XRF using the 'Epsilon 5' ED-XRF device, X-ray Diffraction (XRD) analyses were carried out using a high-resolution powder X-ray diffractometer (HRPXRD), using Cu-K $\alpha$  radiation (1.54060 Å) at a goniometer rate of 2 $\theta$  = 4°/min. Atomic Absorption Spectrophotometer (AAS) was used for metal analysis of all samples. The elemental analysis for the determination of the total carbon, hydrogen, nitrogen and sulphur was done using the Perkin Elmer 2400 Series II CHNS/O Elemental Analyzer.

## RESULTS AND DISCUSSION

### Adsorbent Characterization

Silica (SiO<sub>2</sub>) and alumina (Al<sub>2</sub>O<sub>3</sub>) are the predominant constituents as major elemental composition of the natural clay samples using the Energy Dispersive X-ray Fluorescence (ED-XRF) (Table 2). They are found in a SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ratio equal to 1.68, 1.61, 1.76 and 2.25 in samples CA, CB, CC and CD respectively. High ratio obtained is an indication of the presence of free quartz in the clay fraction in large proportion (Ouaddari *et al.*, 2018). Although Fe<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub>, La<sub>2</sub>O<sub>3</sub>, MgO and NiO were also detected in small quantities, other oxides such as CuO, MnO, and Cr<sub>2</sub>O<sub>3</sub> were present as impurities in the samples.

The mineralogical composition of all samples as determined from the X-ray diffractogram showed that the clay minerals comprised predominantly of crystalline phases of kaolinite (Al<sub>2</sub>Si<sub>2</sub>O<sub>5</sub>(OH)<sub>4</sub>), and quartz (Si<sub>6</sub>O<sub>6</sub>) except for CA with predominant peaks attributed to goethite ( $\alpha$ -FeO(OH)). The quartz and kaolinite phases in all the samples had hexagonal and anorthic crystal system respectively.

The calculated density of the quartz and kaolinite minerals were 3.85 and 2.61 g/cm<sup>3</sup>, 2.65 and 2.61 g/cm<sup>3</sup>, 3.85 and 2.56 g/cm<sup>3</sup>, and 2.57 and 2.65 g/cm<sup>3</sup> for samples CA, CB, CC and CD, respectively (Table 3). The broad and low-intensity peaks around 2 $\theta$  value of 50° and 60° in all samples and except for CSA which was between 30° and 40° revealing the amorphosity of the kaolinite, quartz (around 60-70°) and goethite phases attributed to the presence of organic matter (Fazlzadeh *et al.*, 2017).

Table 1. Site location, description and location co-ordinates

S/N	Site	Location	Latitude	Longitude
1	BA	Ikot Ebom Itam 1 (Grey clay)	5.0721681 N 5°4'19.80516"	7.9011961 E 7°54'4.30596"
2	BB	Ikot Ebom Itam 2 (Fire clay)	5.0723712 N 5°4'20.53632"	7.901314 E 7°54'4.7304"
3	BC	Ikot Ebom Itam 3 (Yellow clay)	5.0724316 N 5°4'20.75376"	7.9013815 E 7°54'4.9734
4	BD	Ikot Ebom Itam 4 (White clay - Ndom)	5.0704904 N 5°4'13.76544"	7.9006088 E 7°54'2.19168"

Table 2. Chemical composition of the clay samples

Elemental composition	Weight (%)			
	CA	CB	CC	CD
SiO <sub>2</sub>	37.470	41.990	45.520	52.150
Al <sub>2</sub> O <sub>3</sub>	22.280	25.950	25.890	23.180
Fe <sub>2</sub> O <sub>3</sub>	12.353	2.389	2.087	1.320
TiO <sub>2</sub>	10.385	1.078	1.099	1.208
La <sub>2</sub> O <sub>3</sub>	4.311	3.455	3.599	3.774
MgO	4.098	5.099	4.009	5.099
CdO	2.009	0.500	0.500	0.610
NiO	1.605	1.617	1.626	1.616
K <sub>2</sub> O	0.470	0.230	0.260	0.300
CaO	0.043	0.031	0.014	0.010
Cr <sub>2</sub> O <sub>3</sub>	0.024	0.016	0.014	0.011
<b>CHNS</b>				
Carbon (%)	41.06	44.38	46.68	49.85
Hydrogen (%)	4.77	3.67	4.97	4.94
Nitrogen (%)	1.09	1.74	0.77	0.51
Sulphur (%)	0.23	0.63	0.89	0.78

Table 3. Crystallographic parameters for quartz and kaolinite clay samples

Crystallographic parameters	Quartz (Si <sub>6</sub> O <sub>6</sub> )				Kaolinite (Al <sub>2</sub> Si <sub>2</sub> O <sub>9</sub> H <sub>4</sub> )			
	CA	CB	CC	CD	CA	CB	CC	CD
Crystal system	An	An	An	An	Hex	Hex	Hex	Hex
a (Å)	4.930	4.912	4.930	4.913	5.152	5.152	5.155	5.153
b (Å)	4.930	4.912	4.930	4.913	5.154	5.154	5.155	5.153
c (Å)	5.415	5.404	5.415	5.405	7.391	7.391	7.405	7.406
Alpha (°)	90.00	90.00	90.00	90.00	74.954	74.954	84.116	84.118
Beta (°)	90.00	90.00	90.00	90.00	84.223	84.223	75.138	75.136
Gamma (°)	120.00	120.00	120.00	120.00	60.196	60.196	60.176	60.186
Calculated density (g/cm <sup>3</sup> )	3.85	2.65	3.85	2.65	2.61	2.61	2.56	2.57
Volume of cell (10 <sup>6</sup> pm <sup>3</sup> )	113.98	112.92	113.98	112.98	164.37	164.37	164.93	164.83
RIR	1.96	3.16	1.96	3.14	1.07	1.07	1.18	1.17

An = Anorthic, Hex = Hexagonal

### Effects of initial concentration on adsorption of Zinc

The results of the batch experiment for adsorption characteristics of Zn<sup>2+</sup>, Pb<sup>2+</sup> and Cd<sup>2+</sup> for the four studied clay mineral samples with initial concentrations ranging from 10 – 40 mg L<sup>-1</sup> (for Zn), 5 – 20 mg L<sup>-1</sup> (for Pb) and 5 – 20 mg L<sup>-1</sup> (for Pb) are presented in Figure 1 (a), (b) and (c) respectively. Results obtained showed increased concentration for sorbed Zn<sup>2+</sup> with increasing levels of added Zn. The highest mean sorbed Zn concentration, 18.5±15.1mg L<sup>-1</sup> (72.1±41.00 %) was recorded at CB, with sample CD recording the least Zn sorption with mean value, 17.7±14.7mg L<sup>-1</sup> (69.1±38.92 %).

The pattern for Pb adsorption showed increased concentration for sorbed Pb<sup>2+</sup> with increasing levels of added Pb at low concentrations, but with higher concentrations, adsorption of Pb decreased (Figure 1 (b)). The highest mean sorbed Pb concentration, 7.38±8.61 mg L<sup>-1</sup> (47.25%) was recorded at sample CA. Among the four studied soil samples, CD showed the least Pb ion sorption with mean

value, 4.35±5.01mg L<sup>-1</sup> (28.89%). Cadmium, as a very toxic metal ion also showed increasing sorption concentration with increased level of added Cd. Results obtained showed the highest mean sorbed Cd concentration, 8.2±7.5 mg L<sup>-1</sup> (59.1%) recorded at CA, with the least Cd<sup>2+</sup> sorption, 7.8±6.9 mg L<sup>-1</sup> (59.2%) recorded at sample CC.

### Effect of pH – contact time on Zn adsorption

The percentage sorption and extent of adsorption at equilibrium, Q<sub>s</sub>, as a function of variable soil-pH ranging between 4.2, 6.8 and 9.0 after 24 and 72 hours are shown in Figure 2 (i) and (ii) respectively. Results showed that sorption within 24 hours gave a steady increase across the pH levels except for sample CB which was observed to have given an abrupt decrease in pH level 9.0. After careful observation for 72 hours, the Zn ions adsorption was observed to have both increasing and decreasing sorption characteristics, only sample CB was observed to have a steady decrease across the pH levels (Table 3).

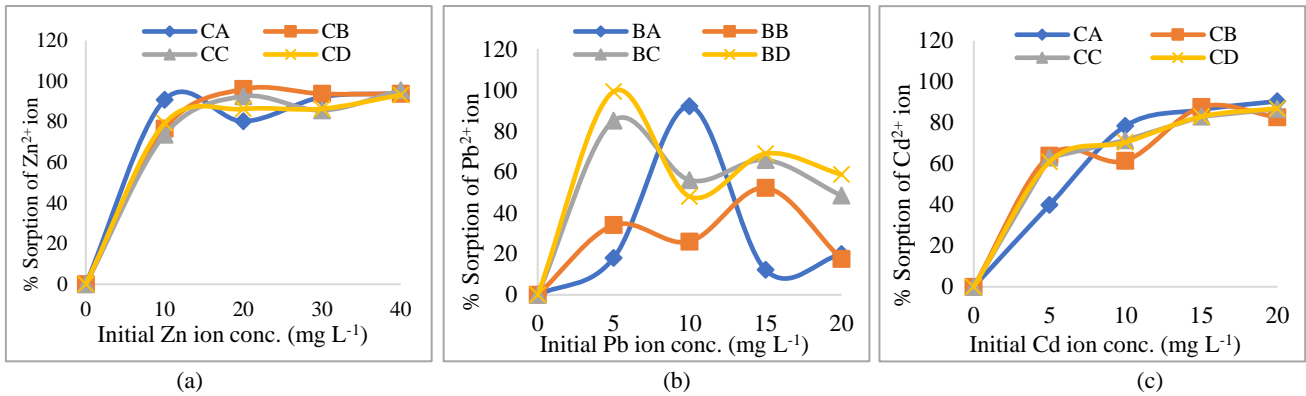


Figure 1. Percentage metal ion sorption (a) Zn<sup>2+</sup>, (b) Pb<sup>2+</sup> and (c) Cd<sup>2+</sup> ions with initial concentration

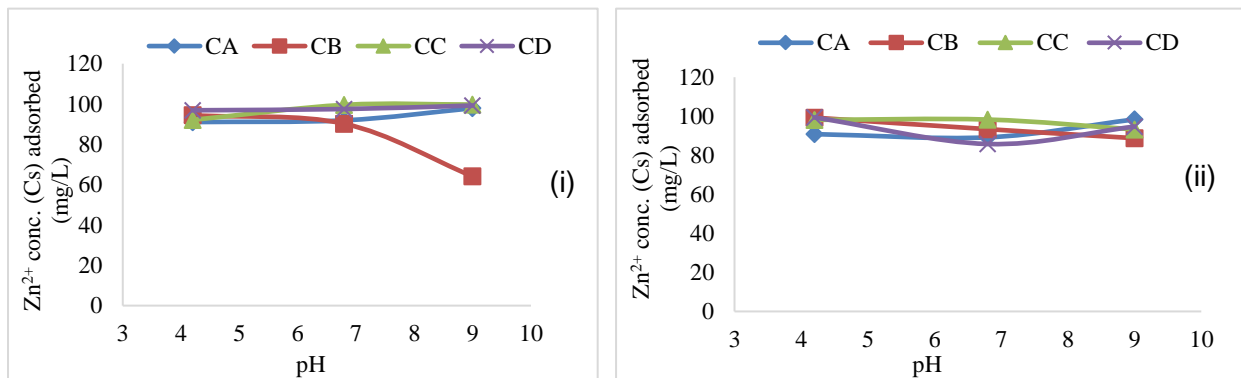


Figure 2. Effect of soil-solution pH on Zn<sup>2+</sup> sorption after (i) 24 hours and (ii) 72 hours

#### Effect of pH – contact time on Pb Adsorption

The percentage sorption and extent of adsorption at equilibrium,  $Q_s$ , as a function of variable solution pH ranging between 4.2, 6.8 and 9.0 for 24 hours and 72 hours are presented in Table 4. respectively. The sorption showed both increasing and decreasing sorption characteristics across the pH levels for both 24 and 72 hours.

#### Effect of pH-contact time on Cadmium adsorption

The percentage sorption and extent of adsorption at equilibrium,  $Q_s$ , as a function of different clay mineral solution-pH ranging between 4.2, 6.8 and 9.0 for 24 hours and 72 hours are shown in Table 5. Results obtained showed both increasing and decreasing amount of Cd<sup>2+</sup> adsorbed with increasing solution pH, majorly within the first 24 hours after experimentation. After careful observation for 72 hours, the Cd<sup>2+</sup> adsorption was observed to have favoured the basic solution (9.0) except for CD which showed maximum sorption at pH level of 6.8 (Table 5).

#### Equilibrium modelling for Pb, Zn and Cd adsorption

To understand the estimation of Zn<sup>2+</sup>, Pb<sup>2+</sup> and Cd<sup>2+</sup> sorption capacities for the four clay minerals studied at different concentrations 10, 20, 30 and 40 mg Zn<sup>2+</sup> L<sup>-1</sup>; 5, 10, 15 and 20 mg Pb<sup>2+</sup> L<sup>-1</sup>, and 5, 10, 15 and 20 mg Cd<sup>2+</sup> L<sup>-1</sup>, the experimental data obtained were fitted into the Langmuir and Freundlich isotherm equations. The Langmuir equilibrium adsorption model is expressed according to Equation (1):

$$\frac{C_e}{Q_e} = \frac{1}{Q_{\max} K_L} + C_e / Q_{\max} \quad (1)$$

where,  $Q_{\max}$  and  $K_L$  are the Langmuir constant relating the sorption capacity of the adsorbent and the energy of the sorption process respectively. The sorption parameters,  $Q_{\max}$  and the Langmuir constant,  $K_L$ , values for each soil sample calculated from the slope and intercept of each plot. Therefore, from Equation (1), a plot of  $C_e/Q_e$  against  $C_e$  was applied to find the best adsorption isotherm that could best describe the experimental data. Results obtained showed that the Langmuir equation characterized Zn<sup>2+</sup>, Pb<sup>2+</sup> and Cd<sup>2+</sup> sorption data for all four-clay minerals with regression coefficient ( $R^2$ ) values ranging between 0.2712 - 0.7061, 0.0207 - 0.4266 and 0.2106 - 0.4865 respectively for the clay minerals under study. Similarly, the experimental data were fitted into the Freundlich isotherm according to Equation (2):

$$\ln Q_s = \ln K_F + 1/n_F (\ln C_e) \quad (2)$$

where,  $K_F$  and  $n_F$  are empirical constants indicating the adsorption capacity and adsorption intensity respectively. A plot of  $\ln Q_s$  against  $\ln C_e$  (Figure 6) helps in determining the constant,  $K_F$  and  $n_F$ , from the slope and intercept of the graph respectively (Table 6). Results obtained showed that the Freundlich equation characterized Zn<sup>2+</sup>, Pb<sup>2+</sup> and Cd<sup>2+</sup> sorption data gave the regression coefficient,  $R^2$  values ranging between 0.1960 - 0.8655, 0.0106 - 0.8878 and 0.5852 - 0.9368 respectively for all four clay samples (Table 6).

Table 4: Effect of soil-pH on Pb<sup>2+</sup> adsorption with 20 mg L<sup>-1</sup> after 24 hours and 72 hours

Site	Reaction type	Sorbed Pb <sup>2+</sup> Q <sub>s</sub> (mg g <sup>-1</sup> ) with variable pH					
		24 hours			72 hours		
		4.2	6.8	9.0	4.2	6.8	9.0
CA	Amt. adsorbed (Q <sub>s</sub> )	173	163	176	44.5	46.5	118.5
	Percentage (% S)	(86.3)	(81.5)	(88.0)	(88.9)	(79.5)	(76.8)
CB	Amt. adsorbed (Q <sub>s</sub> )	131	156.5	122	60	99.5	97
	Percentage (% S)	(65.5)	(78.3)	(60.8)	(78.4)	(97.2)	(99.4)
CC	Amt. adsorbed (Q <sub>s</sub> )	8.5	92.0	95.5	170.5	134.5	135
	Percentage (% S)	(4.25)	(46.0)	(47.8)	(92.3)	(54.1)	(88.9)
CD	Amt. adsorbed (Q <sub>s</sub> )	90	99.5	138	152	169.5	172.5
	Percentage (% S)	(45.0)	(49.8)	(68.8)	(24.3)	(99.4)	(77.9)

Table 5: Effect of soil-pH on Cd<sup>2+</sup> adsorption with 20 mg Cd L<sup>-1</sup> after 24 hours and 72 hours

Site	Reaction type	Sorbed Cd <sup>2+</sup> Q <sub>s</sub> (mg g <sup>-1</sup> ) with variable pH					
		24 hours			72 hours		
		4.2	6.8	9.0	4.2	6.8	9.0
CA	Amt. adsorbed (Q <sub>s</sub> )	178	159	154	171	198	199
	Percentage (% S)	(88.9)	(79.5)	(76.8)	(85.6)	(98.9)	(99.4)
CB	Amt. adsorbed (Q <sub>s</sub> )	157	194	199	191	147	196
	Percentage (% S)	(78.4)	(97.2)	(99.4)	(95.6)	(73.5)	(97.8)
CC	Amt. adsorbed (Q <sub>s</sub> )	185	108	178	177	169	196
	Percentage (% S)	(92.3)	(54.1)	(88.9)	(88.4)	(84.5)	(97.8)
CD	Amt. adsorbed (Q <sub>s</sub> )	49	199	156	194	197	189
	Percentage (% S)	(24.3)	(99.4)	(77.9)	(97.2)	(98.3)	(94.5)

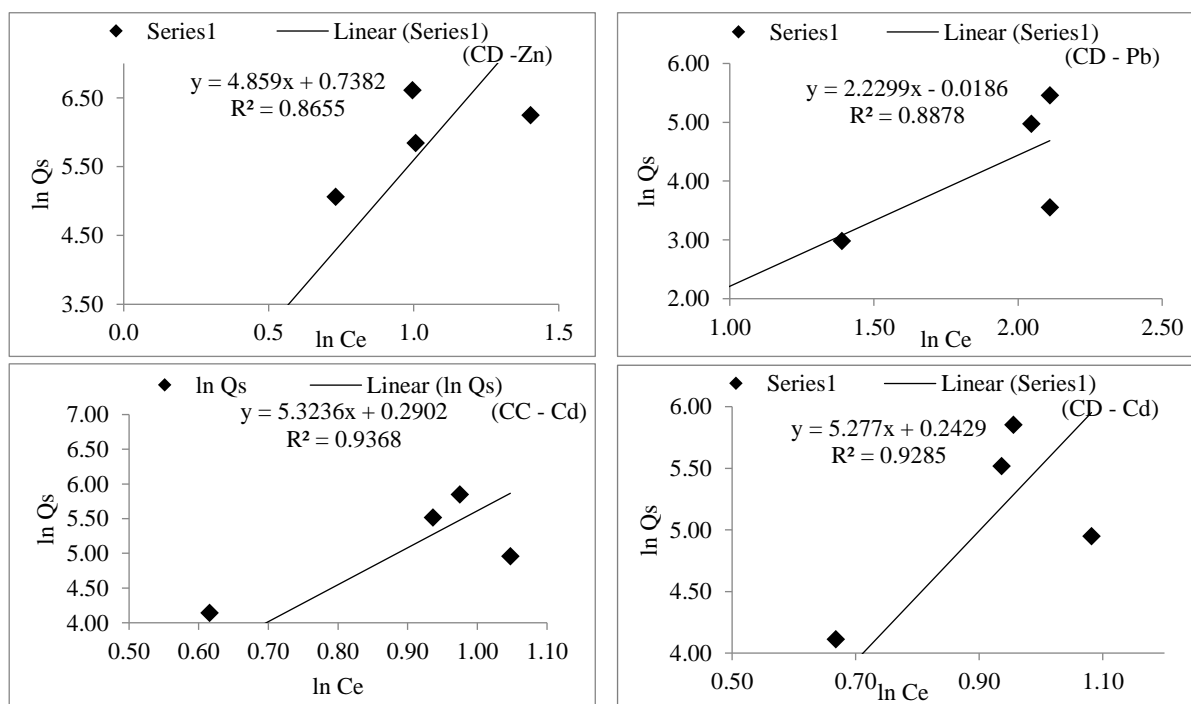


Figure 6. Linear fit for Freundlich isotherms of Zn<sup>2+</sup>, Pb<sup>2+</sup> and Cd<sup>2+</sup> sorption for



Table 6: Langmuir and Freundlich adsorption constants for Zn<sup>2+</sup>, Pb<sup>2+</sup> and Cd<sup>2+</sup> sorption

Isotherm Parameters	Zn <sup>2+</sup> sorption values					Pb <sup>2+</sup> sorption values					Cd <sup>2+</sup> sorption values				
	CA	CB	CC	CD	Mean	CA	CB	CC	CD	Mean	CA	CB	CC	CD	Mean
<i>Langmuir isotherm</i>															
R <sup>2</sup>	0.7061	0.3857	0.3565	0.2712	0.4299	0.4253	0.4266	0.0207	0.0985	0.2428	0.4865	0.381	0.2106	0.2209	0.3248
r	0.8402	0.6210	0.5971	0.5208	0.6448	0.6522	0.6531	0.1439	0.3138	0.4408	0.6975	0.6173	0.4589	0.4700	0.5609
Q <sub>max</sub>	10000	-2500.0	909.1	400.0	2202.3	-65.8	303.0	217.4	243.9	174.63	-65.8	303.0	217.4	243.9	174.63
K <sub>L</sub>	0.04	-0.11	0.41	1.47	0.45	-0.66	0.40	0.51	0.45	0.17	-0.78	0.60	1.02	0.82	0.42
Q <sub>max</sub> *K <sub>L</sub>	400.0	285.7	370.4	588.2	411.1	43.3	122.0	109.9	108.7	96.0	51.3	181.8	222.2	200.0	163.8
R <sub>L</sub>	0.172	-0.079	0.020	0.006	0.030	-0.013	0.020	0.016	0.018	0.011	-0.011	0.014	0.008	0.010	0.005
<i>Freundlich isotherm</i>															
R <sup>2</sup>	0.3621	0.1960	0.4254	0.8655	0.4623	0.0106	0.2019	0.8434	0.8878	0.4859	0.5852	0.6325	0.9368	0.9285	0.7708
r	0.6017	0.4427	0.6522	0.9303	0.6568	0.1030	0.4493	0.9184	0.9422	0.6032	0.7650	0.7953	0.9679	0.9636	0.8729
n <sub>F</sub>	0.278	0.344	0.313	0.206	0.2850	-4.322	1.111	0.342	0.448	-0.6050	0.154	0.225	0.188	0.190	0.1892
1/n <sub>F</sub>	3.602	2.907	3.198	4.859	3.642	-0.231	0.900	2.928	2.230	1.456	6.481	4.444	5.324	5.277	5.381
K <sub>F</sub>	8.575	25.439	13.148	2.092	12.314	29.044	12.090	0.820	0.982	10.734	0.549	1.461	1.337	1.275	1.155

Q<sub>max</sub> = maximum adsorption capacity (mg g<sup>-1</sup>); K<sub>L</sub> = Langmuir adsorption constant (L mg<sup>-1</sup>); Q<sub>max</sub>\*K<sub>L</sub> = maximum buffering capacity (L g<sup>-1</sup>); n<sub>F</sub> = heterogeneity factor of adsorption sites (dimensionless); K<sub>F</sub> = Freundlich constant (L g<sup>-1</sup>).

Since the choice among model equations is often made based on the goodness of fit data, therefore, the Freundlich isotherm model provided the best choice for Zn, Pb and Cd sorption calculation against that of Langmuir model. The regression coefficient (R<sup>2</sup>) values calculated from the

Freundlich adsorption isotherm showed sample CD having the highest regression coefficient (R<sup>2</sup>) value of 0.8655 for Zn and 0.8878 for Pb, and sample CC recorded the highest regression coefficient (R<sup>2</sup>) value of 0.9368 for Cd (Figure 6).

## CONCLUSION

In this study, we delved into the intricate world of heavy metal sorption onto natural clay minerals, with a particular focus on Zn<sup>2+</sup>, Pb<sup>2+</sup> and Cd<sup>2+</sup> ions. It is apparent that natural clay minerals from the study area are endowed with a remarkable capacity to adsorb these metals. The findings highlight the potential for utilizing these minerals as effective adsorbents in various applications, from soil remediation to water treatment. Moreover, we discovered that the initial concentration of Zn, Pb and Cd ions in solution significantly influences the sorption capacity. The relationship between initial concentration and sorption capacity follows a pattern of increasing sorption with increasing concentration, although with diminishing returns. This observation has practical implications for optimizing sorption processes in applications where heavy metal removal is paramount. The role of solution pH in the sorption process for the studied clay minerals in influencing the efficiency of heavy metal sorption onto clay minerals was also estimated. The sorption process is most effective under acidic conditions, suggesting the need for meticulous pH control in practical applications.

Kinetic studies revealed that the sorption Zn, Pb and Cd ions is time-dependent. This time-dependent behavior stresses the importance of understanding the kinetics of heavy metal sorption when designing efficient remediation and water treatment processes. Therefore, the sorption capacities of natural clay minerals for these metal ions as determined, provided essential background for assessing the potential of clay minerals in environmental remediation and water treatment.

## REFERENCES

- Alloway, B. J. (2013). Heavy metals in soils: Trace Metals and Metalloids in Soils and their Bioavailability (3rd ed.). Springer Science, New York.
- Anderson, B. (2018). Sorption of Heavy Metals on Montmorillonite. *Journal of Clay Science*, 32(4), 321-337.
- Benassi, L., Stefani, A., and Tosti, G. (2021). Clay mineral characteristics and soil management in the vineyard: an overview. *Biology and Fertility of Soils*, 57(3): 371-380.
- Bhattacharyya, K. G. and Sen Gupta, S. (2006). Removal of heavy metals by natural clays and their modified forms, kaolinite and montmorillonite: A review. *Environmental Science and Technology*, 40(3): 1217-1227.
- Brigante, M., Erlicher, S., García, R. and De Vera, G. (2018). The role of clay minerals in the environment. *Clay Minerals in Nature*, 31-52.
- Chen, B., Green, P. G. and Ingram, J. C. (1998). The influence of clay minerals on metal adsorption onto soils and sediments: A review. *Critical Reviews in Environmental Science and Technology*, 28(2): 75-137.
- Chen, X. (2019). Enhancement of heavy metal sorption by organoclay materials. *Applied Clay Science*, 45(2): 123-136.
- Fazlzadeh, M., Rahmani, K., Zarei, A., Abdoallahzadeh, H., Nasiri, F. and Khosravi, R. (2017). A novel green synthesis of zero valent iron nanoparticles (NZVI) using three plant extracts and their efficient application for removal of Cr(VI) from aqueous solutions. *Advance Powder Technology*, 28: 122-30.
- Feng, X. (2020). Adsorption behavior of Zn (II) on zeolite-modified bentonite in aqueous solutions. *Journal of Environmental Chemical Engineering*, 8(5): 104316.

- Gupta, V. K. (2008). Application of low-cost adsorbents for dye removal: A review. *Journal of Environmental Management*, 90(8): 2313-2342.
- Huang, J. H. and Zhou, S. L. (2019). Remediation of heavy metal contaminated soils: A review. *Ecotoxicology and Environmental Safety*, 174: 567-574.
- Huang, L., He, D., Yang, T., and Liu, L. (2016). Characterization and application of clay minerals in sunscreen. *Applied Clay Science*, 129: 32-39.
- Islam, M. S. (2015). Analysis of major, minor and trace elements in soil of CHT by X-ray fluorescence (XRF) spectrometry. *Journal of Nuclear and Particle Physics*, 5(2): 36-44.
- Kalisinska, E., and Fijałek, Z. (2016). Determination of lead and cadmium in soils and sediments by atomic fluorescence spectrometry. *Analytical Letters*, 49(6): 873-884.
- Kiran, B. R. and Mukherjee, A. B. (2008). Atomic absorption spectrometry in occupational and environmental health practice. *Journal of Occupational and Environmental Hygiene*, 5(11): 748-755.
- Khan, M. M. H. (2014). Determination of heavy metals in water samples using XRF technique. *IOSR Journal of Applied Physics*, 6(6): 49-53.
- Khan, S., Cao, Q., Zheng, Y. M., Huang, Y. Z. and Zhu, Y. G. (2018). Health risks of heavy metals in contaminated soils and food crops irrigated with wastewater in Beijing, China. *Environmental Pollution*, 242(Pt B): 103-112.
- Langmuir, I. (1918). The adsorption of gases on plane surfaces of glass, mica, and platinum. *Journal of the American Chemical Society*, 40(9): 1361-1403.
- Li, Y., Wang, X. and Chen, Y. (2019). Effects of clay minerals on the sorption of heavy metals: A review. *Environmental Pollution*, 244: 307-318.
- Liu, Y. (2019). Adsorption behavior of zinc on agricultural waste-derived biochar. *Water Science and Technology*, 79(6): 1150-1159.
- Mellah, A. and Chegrouche, S. (1997). Adsorption of Zn(II) on natural bentonite. *Industrial & Engineering Chemistry Research*, 36(11): 4142-4148.
- Ok, Y. S., Oh, S. Y. and Choi, J.-W. (2011). Natural clay minerals: Environmental properties and applications. *Journal of the Korean Ceramic Society*, 48(2): 97-106.
- Ouaddari, H., Karim, A., Achiou, B., Saja, S., Aaddame, A., Bennazha, J., El Amrani El Hassani, I., Ouammou, M. and Albizane, A. (2019). New low-cost ultrafiltration membrane made from purified natural clays for direct Red 80 dye removal. *Journal of Environmental Chemical Engineering*, 7(4): 103268.
- Saxena, V. K., Tripathi, B. D. and Singh, P. (2013). Ion exchange properties of clays: A review. *Reviews in Environmental Science and Biotechnology*, 12(2): 151-164.
- Stucki, J. W. (1993). Ion exchange in clays and other minerals. *Clay Minerals*, 28: 319-322
- Toumbakari, E. E. (2019). An Introduction to the Pottery of Messenia. *The Oxford Handbook of the European Iron Age*, 322-336.
- Wang, Q., (2020). Isotherm modeling of heavy metal sorption on modified clay minerals. *Environmental Chemistry and Technology*, 35(4): 437-452.
- Wang, F., (2019). Adsorption characteristics and mechanisms of heavy metals onto different soils in the Ganjiang River watershed, China. *Journal of Hazardous Materials*, 362: 341-350.
- Williams, L. B., Haydel, S. E., Giese, R. F., and Eberl, D. D. (2020). Chemical and mineralogical analysis of Martian soil. *Science*, 324(5928): 917-921.
- Wu, D. (2018). Sorption behavior and mechanism of heavy metals in contaminated soil treated with various amendments: A review. *Pedosphere*, 28(2): 190-204.
- Zheng, M. (2021). Selectivity of clay minerals for heavy metal sorption. *Clay and Soil Chemistry*, 39(2): 185-199.