

Batch Studies for the Investigation of the Mechanism of Pb Sorption in Selected Acid Soils of China

Nkwopara U. N.^{1,2,*}, Emenyonu-Chris C. M.¹, Ihem E. E.¹, Ndukwu B. N.¹, Onweremadu E. U.¹, Ahukaemere C. M.¹, Egbuche C. T.³, Hu H.²

¹Department of Soil Science and Technology, Federal University of Technology, Owerri, Nigeria

²College of Resources and Environment, Key Laboratory of Subtropical Agricultural Resources and Environment, MOA, Huazhong Agricultural University, Wuhan, China

³Department of Forestry and Wildlife, Federal University of Technology, Owerri, Nigeria

Email address:

ugoiken2003@yahoo.com (Nkwopara U. N.)

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Abstract: The experiment focuses on mechanisms of Pb retention on acid soils. A batch experiment was conducted to investigate the effect of solution pH and ionic strength of electrolytes which will show the mechanisms of Pb retention on the soils. Result show that sorption of lead was affected strongly by solution pH and ionic strength of electrolytes. Retention of lead increased with increase in solution pH and decreased with increase in ionic strength of electrolytes. This suggests that surface complexation and ion exchange are the mechanisms of Pb retention on these acid soils. At pH above 6 there was precipitation of lead. SEM studies visualized the formation of white layers of Pb over the soil surface. Scanning electron microscopy (SEM) revealed that the adsorption of lead ions made the surface of the soil particles rougher than those without lead. This morphological change points to the formation of a surface coating on the soil particles.

Keywords: Sorption of Lead, Mechanism, Acid Soils, Solution pH, Ionic Strength of Electrolytes

1. Introduction

Heavy metals (such as lead) adsorption is usually described in terms of two basic mechanisms, specific adsorption e.g. surface complexation, and non specific adsorption such as ion exchange[1]. The chemistry of Pb in soils is affected by three main factors: specific adsorption to various solid phases, precipitation of sparingly soluble or highly stable compounds and formation of relatively stable complexes or chelates with soil components [2][3][4] [5] investigated the retention of Pb²⁺ ion by montmorillonites and found that cation exchange predominated in pH range 2 – 4, precipitation was the main mechanism at pH > 6, and a combination of both took place at intermediate pH 4 – 6. A strong dependence on ionic strength is typical for an outer- sphere complex, whereas insensibility of ionic strength is an indication for inner sphere surface complexation [6].

Scanning electron microscopy is widely used to study the morphological features and surface characteristics of the

adsorbent materials [7][8]. Scanning electron microscopy (SEM) has often been used to visually show the morphological changes of the adsorbents after adsorption with an adsorbate [9][10]. Scanning electron microscopy was used to assess morphological changes in the soils surface following adsorption of lead. This technique provides a deeper insight into the nature and the environment of the adsorbed species and lead to a sharper description of the surface involved [11].

The objective of this present work was to determine the mechanisms of Pb retention by the acid soils of eastern China. This study can give important information concerning the nature of selected samples of Chinese soil. The properties of these soils are usually not reported in the literature.

2. Materials and Methods

2.1. Soil Sample

Four representative variable charge soils were used in this study: Yellow brown soil (YBS), Red soil (RS), Latosol soil

(LS) and Latosolic red soil. They are Alfisol, Ultisol, and Oxisols in the American classification system. These soils were collected from Hubei, Hainan, and Guangxi provinces in China (Fig. 1). These soils with contrasting properties were

sampled at 0 – 20 cm depth. Samples of these soils were air-dried, ground, sieved through 2-mm mesh and homogenized prior to soil characterization and adsorption studies.



*= studied areas.

Fig. 1. Map of China showing the studied areas.

2.2. Effect of Solution pH on Sorption

A 100 mg L⁻¹ solution of Pb (NO₃)₂ was prepared from a stock solution of 1000 mg L⁻¹ using 0.01 mol L⁻¹ KCl as background electrolyte. Metal ion solutions (25 mL of 100 mg L⁻¹) were added to 1g of soils weighed into 50 mL polyethylene bottles. The solutions were adjusted to pH 3 -7 using either 0.1 M NaOH or HCl. The suspensions were agitated for 2 h. The pH of the solutions was checked and readjusted to the initial pH. The suspensions were equilibrated for 20 h and readjusted to the pH after equilibration. The supernatants obtained after centrifugations were analyzed for Pb²⁺ using an atomic absorption spectrophotometer (AAS) (computed-aided Varian AA 240FS). The amount adsorbed was calculated by the difference between the total applied Pb²⁺ and the amount of Pb²⁺ remaining in the equilibrium solution.

2.3. Effect of Inorganic Anions on Sorption

25 mL of the various background electrolytes (KCl, KNO₃, K₂SO₄) in three concentrations of (0.1, 0.01, and 0.001 mol L⁻¹) containing 150 mg L⁻¹ Pb²⁺ were separately added to 1 g soil. The pH of these solutions was not adjusted to avoid negating the pH effects of the electrolytes. These solutions were agitated in a shaker for 2 h, equilibrated for 22 h and centrifuged at 5000 rpm for 10 min. The supernatants obtained after centrifugation were analyzed for Pb²⁺ using an AAS. The amount adsorbed was calculated by the difference between the total applied Pb²⁺ and the amount of Pb²⁺ remaining in the equilibrium solution.

2.4. Effect of Inorganic Cations on Sorption

25 mL of the various background electrolytes (KCl and CaCl₂) in three concentrations of (0.1, 0.01, and 0.001 mol L⁻¹) containing 150 mg L⁻¹ Pb²⁺ were separately added to 1 g soil. The pH of these solutions was adjusted to 5.5±0.1. These solutions were agitated in a shaker for 2 h, equilibrated for 22 h and centrifuged at 5000 rpm for 10 min. The supernatants obtained after centrifugations were analyzed for Pb²⁺ using an AAS. The amount adsorbed was calculated by the difference between the total applied Pb²⁺ and the amount of Pb²⁺ remaining in the equilibrium solution.

2.5. Scanning Electron Micrograph Studies

After adsorption, the soil residues were air-dried for 7 days and gold coated under vacuum in a JFC – 1600 sputter coater (JEOL, Japan) for 20 min. The SEM images obtained by a JSM 6390 scanning electron microscope (JEOL, Japan)

3. Results and Discussion

3.1. Physicochemical Properties and Mineralogical Properties of Soils

The results of the physicochemical properties showed that YBS had higher CEC and pH (27.4 cmol kg⁻¹ and 5.2), while LS had higher organic carbon and crystalline Fe₂O₃ and Al₂O₃ (13.1 g kg⁻¹, 84 g kg⁻¹ and 5.2 g kg⁻¹) respectively than the

other soils (Table 1). The particle size analysis showed that LS was clay, YBS was silt loam while RS and LRS were clay loam.

Mineralogical composition showed that LS mainly consisted of kaolinite 75 %, hydroxyinterlayered vermiculite 15 % and goethite characterized by diffraction peaks at 0.71nm, 0.48nm and 0.27nm respectively. YBS consisted of illite 45 %, vermiculite 25 % and kaolinite 30 % characterized by diffraction peaks at 1nm, 1.396nm and 0.717nm respectively. RS consisted of vermiculite 35 %, kaolinite 40 %, and illite 25 % characterized by diffraction peaks at 1.404nm, 0.723nm, and 0.493nm respectively. LRS consisted of kaolinite 60%, and illite 40% characterized by diffraction peaks at 0.719nm and 1nm respectively (Fig. 2). [12] reported that oxisols with high Fe oxide content are rich in clay;

however, the soils exhibit characteristics of sands. Considering the clay and organic matter content, CEC is very low in all soils, showing that they are low activity clay (LAC) soils because of strong weathering [13][14]. This is confirmed by the clay mineralogy, showing that kaolinite is the dominant clay mineral. The clay mineralogy is also in accordance with extractable Al and Fe. The high contents of crystal Fe and relatively low contents of amorphous Fe in the LS, RS and LRS are consistent with the weathering and dominance of goethite in these Oxisols and Ultisol [13][14]. On the other hand, the amount of amorphous Al exceeds crystal Al, i.e Al_{ox}/Al_{DCB} ratio > 1 (Table 1) showing substantial amounts of poorly ordered aluminum oxides in all soils. These observations agree with reports by [14] on variable tropical soils from Tanzania.

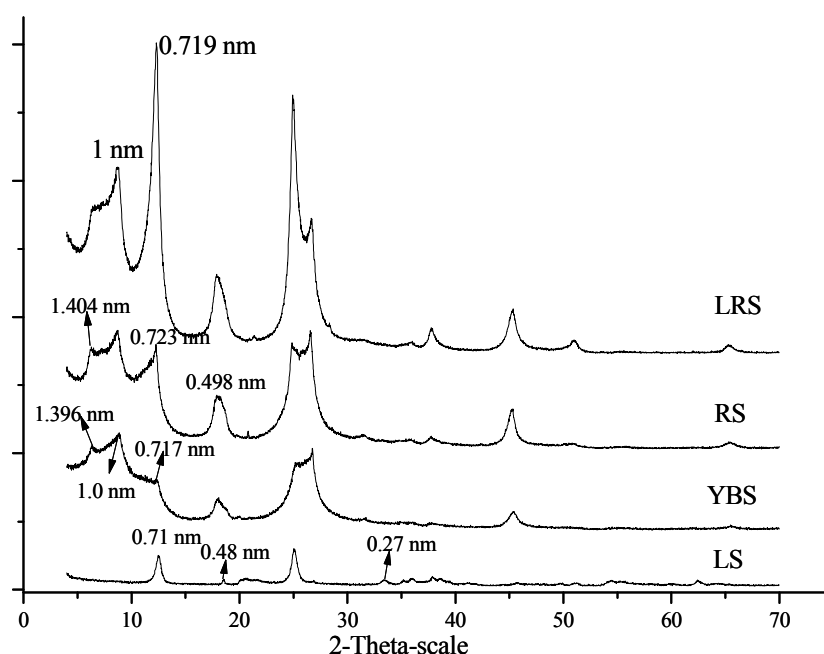


Fig. 2. X-ray diffraction patterns of studied soils

Table 1. Basic properties of the tested soils

Items	YBS soil	LS soil	RS soil	LRS soil
Sample site	Hubei	Hainan	Hubei	Guangxi
Order	Alfisol	Oxisol	Ultisol	Oxisol
pH (H ₂ O)	5.2	4.5	4.2	4.1
O.M (g/kg)	10.8	13.1	6.2	9.9
CEC (cmol/kg)	27.4	15.9	20.9	21.9
2-0.2mm Sand (g/kg)	64.8	270.7	304.4	279.2
0.2-0.02mm Silt (g/kg)	678.7	313.4	405.7	359.6
< 0.002mm clay (g/kg)	256.5	415.9	359.6	361.2
Crystal Fe (g/kg)	16.0	84.0	21.3	21.0
Amorphous Fe (g/kg)	13.8	8.7	5.9	3.5
Crystal Al (g/kg)	1.3	5.2	2.3	2.1
Amorphous Al (g/kg)	4.2	9.4	7.6	6.2
Clay minerals	I, V, K	GE, HIV,K	K, I, V	K, I
Background Pb (mg/kg)	Bdl	Bdl	Bdl	Bdl

YBS: Yellow brown soil, LS: Latosol soil, RS: Red soil, LRS: Latosolic red soil, O.M: Organic matter, CEC: Cation exchange capacity I: illite, K: kaolinite, V: vermiculite, GE: goethite, HIV: hydroxyinterlayered vermiculite, Bdl = below detection limit.

3.2. Effect of Solution pH on Sorption

The effect of pH on the adsorption of Pb^{2+} by soils is shown in Fig. 3. There was an increase in adsorption as the pH of metal ion solution increased. This result is consistent with previous findings that increasing pH generally causes an increase in the metal adsorption [4][15][16]. At pH 6.0, percent adsorptions of Pb^{2+} onto soils were 88.23 %, 31.17 %, 89 % and 88.88 % for YBS, RS, LS and LRS respectively. At pH 3.0, percent adsorptions of Pb^{2+} onto soils were 75.84 %, 7.71 %, 13.95 %, and 17.43 % for YBS, RS, LS and LRS respectively. [17] has reported 94 % adsorption of Pb^{2+} onto tripolyphosphate-impregnated kaolinite clay using 500 mg L^{-1}

solution of Pb^{2+} at pH of 7.0. Unlike the effect of the initial metal ion concentration, when the pH of the aqueous solution of metal ion increased, there was an increase in the equilibrium adsorption capacity as well as in the percentage of metal ion adsorbed (Table 2 and Fig. 3). There was significant difference in amount of Pb adsorbed at all pH and in all the soils (Table 2). At pH above 6 the pseudoequilibrium constant for adsorption (K) was 4.83×10^{-20} while the solubility product constant (K_{sp}) was 1.42×10^{-20} . The pseudoequilibrium constant for adsorption (K) was greater than solubility product constant (K_{sp}) which implies that there was precipitation of Pb at pH above 6 in this study.

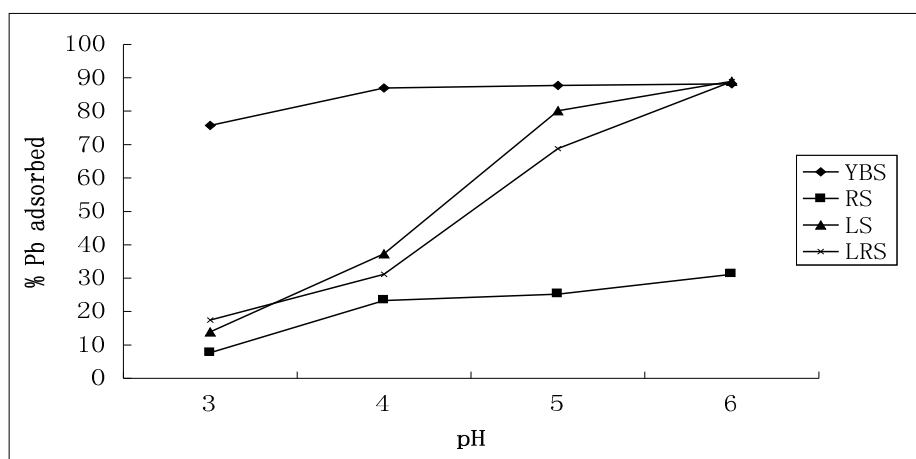


Fig. 3. Effect of pH on adsorption of 100 mg/L of Pb ion by soils

Table 2. Amount of Pb adsorbed at different pH (mg/kg)

pH	soils			
	YBS	RS	LS	LRS
3	1896d	193d	348d	436d
4	2173c	584c	933c	779c
5	2192b	631b	2003b	1720b
6	2206a	780a	2225a	2222a

All the values are means of three replicates. Within the same column, different letters (a-d) indicate significant difference ($p \leq 0.05$). YBS = Yellow brown soil, LS = Latosol soil, RS = Red soil, LRS = Latosolic red soil.

As expected, the adsorption of Pb increased with increasing solution pH. Several reasons may contribute to the increased adsorption of metal ion relative to soil solution pH. First, the soil surface which contains a large number of active sites may become positively charged at very low pH, thus increasing the competition between H^+ and the metal ions for available adsorption sites because of increased amount of H^+ in solution. However, as pH increases this competition decreases as these surface active sites become more negatively charged, which enhances the adsorption of the positively charged metal ions through electrostatic force of attraction. Second, increasing pH has been shown to decrease the solubility of Pb^{2+} . Third, increasing pH encourages metal ion precipitation from solution in the form of hydroxides. Fourth, It is known that Pb^{2+} is the dominant species at lower pH but as pH increases

the concentration of $PbOH^+$ species that has high affinity for oxides become significant. Finally, increase in adsorption can be attributed to the favourable change in surface charge and to the extent of hydrolysis of the adsorbing Pb^{2+} change with varying pH. At low pH, Pb^{2+} are present in the form of M^{2+} and $M(OH)^+$. This leads to an effective competition between H^+ and H_3O^+ [1].

As the surface charge becomes more negative with increasing pH, the surface attracts bivalent metal cations for adsorption. Furthermore, the proportion of hydrated ions increases with pH and these may be more strongly adsorbed than unhydrated ions. Therefore, both of these effects are synergistically enhancing the amount of adsorption at higher pH [18].

The four tested soils behaved similarly, although at lower pH (3 -5), YBS adsorbed more Pb while at higher pH 6, LS adsorbed more Pb. This could be attributed to the fact that at lower pH the nature and properties of the soil surface control the adsorption behavior of these soils, but with an increase in solution pH, other factors such as precipitation, may become dominant, causing the difference in Pb^{2+} adsorption between the four soils. [19] reported that above pH 5.5 both adsorption and precipitation are the effective mechanisms to remove Pb^{2+} in aqueous solution. This result supports the previous finding in another aspect that increasing pH caused a decrease in desorption of lead [20]. When the pH of the aqueous solution of lead ion increased, there was an increase in the equilibrium

adsorption capacity as well as in the percentage of lead ion adsorbed. Adsorption of Pb^{2+} ion onto soils was influenced by pH strongly. This suggests that the adsorption of Pb^{2+} ion onto soils is mainly dominated by surface complexation [21]. In general, surface complexation is mainly influenced by pH.

3.3. Effect of Inorganic Anion on Sorption

The effect of electrolyte anion on the adsorption of Pb^{2+} onto soils is shown in Table 3. During the equilibration period, no significant difference in electrolyte effect was observed (Table 4). The highest reduction occurred in LRS in the presence of NO_3^- (0.27), the lowest occurred in RS in the presence of Cl^- (0.11). No obvious pH changes were observed after equilibration (Table 4). The adsorption of Pb ion made no obvious difference to the final pH values. In the presence of K_2SO_4 , adsorption of Pb onto soils was more than 90%, with the highest rate being 98.7% in YBS and the lowest rate being 98% in LRS. While in the presence of KNO_3 and KCl , the highest adsorption rate of 51.5% and 48.3% were recorded in YBS and the lowest rate of 15.6% and 15.5% were recorded in RS (Table 3). It was observed that more Pb^{2+} was adsorbed in the presence of K_2SO_4 while KNO_3 and KCl gave almost equal adsorption. However, the adsorption rate of soils was reduced in the presence of Cl^- and NO_3^- anions. There was stronger attraction between Pb^{2+} and the soils in the presence of K_2SO_4 than the other anions which show almost equal attraction.

The distribution coefficient values (K_d) which indicate attraction to soil were higher in the presence of K_2SO_4 than in KNO_3 and KCl . In the presence of K_2SO_4 , at 0.1 mol L^{-1} YBS had the highest value of 1827 mL/g and LRS the lowest of 1215 mL/g, while in the presence of KNO_3 and KCl , the values were low, with the highest values of 27 mL/g and 23 mL/g occurring in YBS and the lowest of 5 mL/g in RS and LRS (Fig. 4). Higher K_d value indicates stronger attraction to the soil solids and lower susceptibility to leaching loss.

The solution pH after equilibration decreased by less than one pH unit. This observation is contrary to [22] on adsorption of Cu by clinoptilolite that solution pH after equilibration increased by more than one pH unit in the presence of KCl and KNO_3 but less than one unit in the presence of K_2SO_4 . The lack of pH dependence in the soil that has highest permanent charge clay indicates that the silicate clay may form the predominant sites for Pb adsorption in this soil. For other soils it seems that the Fe and Al oxyhydroxides and organic matter are providing most sites for adsorption. It is suggested that Pb sorption enhancement due to sulfate is as a result of reduction of oxide surface charge caused by anion adsorption and could not be attributed to formation of ternary complexes. The finding agrees with the assumption of [23] that chloride and nitrate metal ion species are not significantly adsorbed. Thus, when these anions form charged complexes with metal ions, they reduce the amount of metal ions adsorbed and hence the adsorption equilibrium capacity of the adsorbent, especially Cl^- which has the ability to form charged and uncharged species (e.g. MCl_2^0 , MCl_3^- and MCl_4^{2-}) with metal ions [17]. Similar results were reported by [24][4] for adsorption of Pb^{2+}

and Cd^{2+} onto phosphate – modified and unmodified kaolinite clay and adsorption of Cd^{2+} onto goethite respectively. Besides, Cl^- adsorption on the surface of soils changes the surface state of soils and decreased the availability of binding sites [25].

Heavy metals have more affinity for sulphur group and sulphide than other anions as can be seen from the natural occurrence of most of the metals in their sulphide form [26]. Chemical affinity of lead towards sulphur groups is higher. Since, lead chemical species show a high affinity toward sulphur, adsorption capacity of the soils could be enhanced by introduction of sulphur materials into the soils. Sulfate ions are attracted by the positive charges that characterize acid soils containing iron and aluminum oxide and 1:1 type silicate clay. They also react directly with hydroxyl groups exposed on the surfaces of these clays. However much sulfate may be held by the iron and aluminum oxide and 1:1 type silicate clays that tends to accumulate in the subsoils horizons of the Ultisols and Oxisols of the warm, humid regions [27]. There is extensive ion pairing of SO_4^{2-} with multivalent cations, no ion pairing of cations with Cl^- and small amount with NO_3^- [22].

Also there could be precipitation of lead in the presence of potassium sulfate. The greater distribution coefficient values (K_d) in YBS than the other soils indicate that Pb^{2+} has a greater affinity for YBS than the other soils. The interpretations mentioned above are reasonable in principle.

3.3.1. Effect of Nature and Ionic Strength of Different Anions on Adsorption

The effect of inorganic anion on the adsorption of Pb^{2+} onto soils is shown in Table 3. It was observed that more Pb was adsorbed in the presence of SO_4^{2-} while NO_3^- and Cl^- gave almost equal Pb adsorption. However, the adsorption rate of soils was reduced in the presences of Cl^- and NO_3^- anions compared to SO_4^{2-} anion. There was stronger attraction between Pb^{2+} and the soils in the presence of SO_4^{2-} than the other anions which show almost equal attraction.

Increasing the ionic strength of the anions (from 0.001 – 0.1 mol L^{-1}) affected the adsorption of lead. In the presence of SO_4^{2-} , Pb adsorption increased with increasing ionic strength but the reverse was the case in the presence of Cl^- and NO_3^- (Table 3). In the presence of anions, the K_d values decreased with increase in ionic strength with the exception of SO_4^{2-} . At ionic strength of 0.001 mol L^{-1} SO_4^{2-} , Cl^- and NO_3^- had 954 mL/g, 587 and 489 mL/g in YBS respectively, while at 0.1 mol L^{-1} , SO_4^{2-} , Cl^- and NO_3^- had 1827 mL/g, 23 and 27 mL/g in YBS respectively (Fig.4). It was observed that increasing the ionic strength of SO_4^{2-} increased the affinity of Pb^{2+} for soils while increasing the ionic strength of Cl^- and NO_3^- decreased the affinity of Pb^{2+} for soils. There was no significant difference in percent Pb^{2+} adsorbed in the presence of SO_4^{2-} in all the soils and at all concentrations, while there was significant difference in the presence of Cl^- and NO_3^- (Table 3).

Ionic strength of anions effects can be attributed to changes in adsorbent-suspension pH through its effect on the diffuse double layer. However, the negative effect of increasing ionic strength of anion on adsorption of metal ion operates through

its effect on electrostatic potential in the plane of adsorption, rather than through its effect on surface charge. It is also suggested that increasing anion concentration can cause screening of surface negative charge by the anion leading to a drop in the adsorption of the Pb ion [28]. More adsorption of Pb ion in the presence of SO_4^{2-} than the other anions can be attributed to increase in the negative charge in the presence of SO_4^{2-} than the other anions. Among anionic ligands, sulfate is believed to form inner-sphere complexes with surface active sites [29] and to increase the net negative surface charge,

increasing metal adsorption. On the contrary, it was stated that Cl^- and NO_3^- form outer-sphere complexes and enhance metal adsorption indirectly [29]. It should be noted that higher adsorption in the presence of potassium sulfate was not entirely due to the adsorption on the soils but, likely, involved precipitation of lead. It is not possible to distinguish adsorption from precipitation by conventional techniques. However, we may make a reasonable assumption that adsorption was the dominant process.

Table 3. Percent Pb^{2+} adsorption in the presence of anions

soils	0.001 (mol L ⁻¹)			0.01 (mol L ⁻¹)			0.1 (mol L ⁻¹)		
	SO_4^{2-}	NO_3^-	Cl^-	SO_4^{2-}	NO_3^-	Cl^-	SO_4^{2-}	NO_3^-	Cl^-
YBS	98.5a	95.2a	96a	98.5a	82.2a	83.2a	98.7a	51.5a	48.3a
LS	91.5a	49.4b	52.5 b	94.7a	32.7b	30.7b	98.5a	31b	30.1b
RS	92.5a	59.6c	60.9c	96.6a	27.6c	27.7c	98.4a	15.6c	15.5c
LRS	89.3a	43.6b	45b	91.2a	20.4c	18.4c	98a	17c	15.7c

All the values are means of three replicates. Within the same column, different letters (a- c) indicate significant difference ($p \leq 0.05$). YBS = Yellow brown soil, LS = Latosol soil, RS = Red soil, LRS = Lateritic red soil, SO_4^{2-} = sulphate, NO_3^- = nitrate, Cl^- = chloride

Table 4. Changes in solution pH at initial and equilibrium solution

Electrolyte	Ionic strength (mol/L)	YBS		LS		RS		LRS	
		Initial	Final	Initial	Final	Initial	Final	Initial	Final
K_2SO_4	0.001	4.81	4.78	4.39	4.26	4.37	4.29	4.16	4.01
	0.01	5.02	4.94	4.74	4.68	4.60	4.47	4.30	4.22
	0.1	5.11	4.90	4.89	4.68	4.65	4.43	4.53	4.26
KNO_3	0.001	4.58	4.54	4.13	4.02	4.27	4.22	3.96	3.88
	0.01	4.46	4.42	4.12	4.06	4.23	4.17	4.03	3.94
	0.1	4.38	4.12	4.20	4.03	4.17	3.98	4.27	3.91
KCl	0.001	4.64	4.53	4.15	4.00	4.21	4.14	4.05	3.88
	0.01	4.48	4.37	4.15	4.09	4.21	4.18	4.06	3.89
	0.1	4.40	4.19	4.18	4.06	4.21	3.98	4.04	3.85

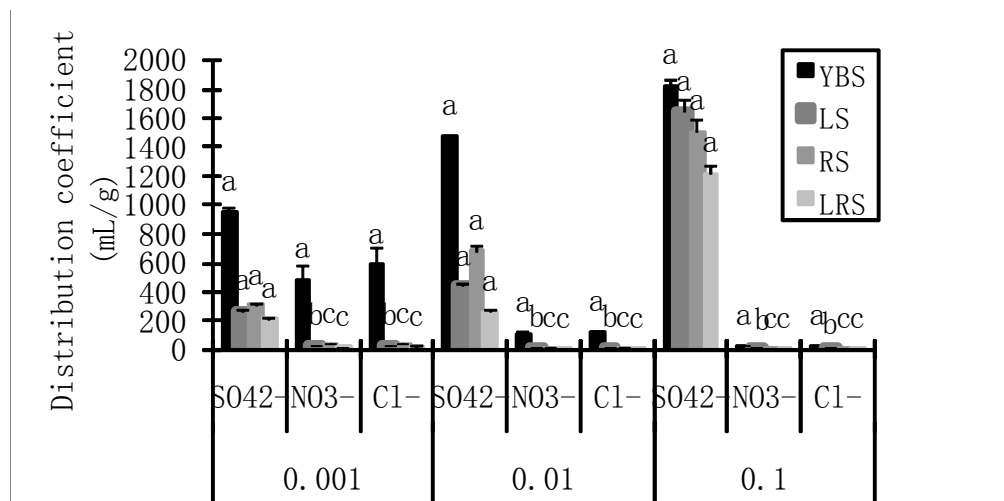


Fig. 4. Distribution coefficient of Pb^{2+} at different ionic strength of anions

3.3.2. Effect of Nature and Ionic Strength of Different Cations on Adsorption

Sorption of Pb^{2+} in the presence of K^+ was more than that observed in the presence of Ca^{2+} solutions at all concentrations and in all the soils (Table 5). Increasing the concentration of

inorganic cation from 0.001- 0.1 mol L⁻¹ caused a drop in adsorption capacity of soils, which suggests that the cations greatly affects Pb^{2+} adsorption. Ca^{2+} had a more negative effect than K^+ . It reduces the adsorption capacity of the soils by 19.2 – 21.9 %. Fig. 5 shows the distribution coefficient value (K_d) of Pb in the presence of inorganic cation. The

values were higher in K^+ than Ca^{2+} and decreases as the ionic strength increase. At ionic strength of 0.001 mol L^{-1} K^+ had 1688 mL/g in YBS and Ca^{2+} had 747 mL/g while at 0.1 mol L^{-1} , K^+ had 190 mL/g in YBS and Ca^{2+} had 87 mL/g. This indicates that increasing ionic strength decreased the affinity of Pb^{2+} for the soils and that affinity of Pb^{2+} for soil was greater in the presence of K^+ than Ca^{2+} cation. There was no significant difference in percent Pb^{2+} adsorbed in the presence of Ca^{2+} in all the soils and at all concentrations, while there was significant difference in the presence of K^+ . However, in the presence of K^+ there was no significant difference in percent Pb^{2+} adsorbed in LS, RS and LRS (Table 5).

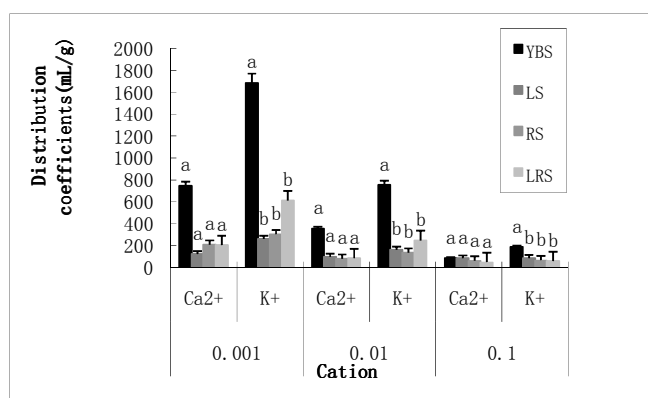


Fig. 5. Distribution coefficient of Pb^{2+} at different ionic strength of cations

Table 5. Percent Pb^{2+} adsorption in the presence of cations

soils	0.001 mol L ⁻¹		0.01 mol L ⁻¹		0.1 mol L ⁻¹	
	Ca ²⁺	K ⁺	Ca ²⁺	K ⁺	Ca ²⁺	K ⁺
YBS	96.8a	98.5a	93.5a	96.8a	77.6a	88.4a
LS	83.2a	91.3b	79.8a	86.8b	77.1a	77.6b
RS	89.4a	92.4b	76.5a	84.6b	71.3a	72.3b
LRS	89.1a	96b	77.3a	90.9b	66.2a	70.1b

All the values are means of two replicates. Within the same column, different letters (a- c) indicate significant difference ($p \leq 0.05$). YBS = Yellow brown soil, LS = Latosol soil, RS = Red soil, LRS = Lateritic red soil, Ca^{2+} = calcium, K^+ = potassium

The effect of cation may be attributed to increased competition between Pb^{2+} and Ca^{2+} for adsorption sites on the surface of soils and to the greater specificity of the divalent Ca^{2+} and its effect on the thickness of the double layer [17][30]. It has been shown by [17] that the potential in the plane of adsorption is related to the valence of the ion through its effect on surface charge density. Increasing the valence of the cation makes the potential in the plane of adsorption less negative thereby reducing Pb^{2+} adsorption. The valence of the cation has a dominant influence on the case of displacement of ions from a charged surface. The higher the valence of the cation, the higher the displacing ability of the ion [31]. Therefore, Pb^{2+} ions displace H_3O^+ and other monovalent ions from soil surface in the presence of K^+ . This explains why Ca^{2+} had greater negative impact on the equilibrium adsorption capacity of soils than K^+ . The difference in the adsorption capacities of the soils for lead ion in the presence of K- and

Ca- electrolytes is due to the difference between K^+ and Ca^{2+} with respect to competition with Pb ions sorption sites. This indicates that the soils show stronger preference for Ca^{2+} (a divalent cation) than for K^+ (a monovalent cation) with the resultant effect of a further drop in monolayer adsorption capacities of the soils for the lead ion when Ca-electrolyte was used. Similar trends have been observed by [30] for adsorption of Cd^{2+} on soils; [24] for the adsorption of Pb^{2+} and Cd^{2+} on orthophosphate-modified and unmodified kaolinite and [32] for the adsorption of Cu^{2+} , Zn^{2+} , Co^{2+} and Cd^{2+} on kaolinite.

The effect of ionic strength on metal ion adsorption is often attributed to changes in adsorbent-suspension pH effect on the diffuse double layer [33]. [30] found that pH of soil suspension decreased by 0.4 – 1 unit on the average, with increase in ionic strength of cation. This may explain in part the decrease in metal ion adsorption. However, the negative effect of increasing ionic strength of inorganic cation on the adsorption of metal ion operates through its effect on electrostatic potential in the plane of adsorption, rather than through its effect on surface charge. According to [34], if increasing ionic strength of inorganic cation decreases metal ion adsorption, then this implies that increasing ionic strength is making the potential of the adsorbent surface less negative (the potential in the plane of adsorption is getting increasingly positive) and this would decrease metal ion adsorption. In addition, the effect of ionic strength could be ascribed to: (1) the competition of high concentrations of cations in electrolyte with lead for the adsorption sites on soil surface. An increase of ionic strength will supply more K^+ or Ca^{2+} ions which compete with lead for the adsorbing sites on soil surface (2) the decrease of activities of lead due to the increase of ionic strength; (3) the formation of ionic pairs or chelating compounds [35][36]. An increase in ionic strength will supply more K^+ or Ca^{2+} ions which compete with lead for the adsorption sites on soil surface. This resulted in a decrease of exchangeable adsorption. Additionally, the presence of salts may compress the electric double layer surrounding negative charged surfaces which contributed to the release of adsorbed lead [37][38]. Beside, the cations in solution may influence the double layer thickness and interface potential, and thereby affect the binding of the adsorbed species. The observed variation in Pb sorption with ionic strength may be explain by the formation of outer-sphere complexes since K^+ and Ca^{2+} in the background electrolyte could compete with the Pb^{2+} ion adsorbed on the outer-sphere sorption sites and reduced the adsorption. Whereas K^+ and Ca^{2+} would not have competed for the inner-sphere sites, as independence of sorption with background electrolyte concentration has been interpreted to indicate that the sorption process is primarily non-electrostatic in nature [39]. Ion exchange and outer-sphere complexes are affected by the variations of ionic strength more easily than the inner-sphere complexes, since the background electrolyte ions are placed in the same plane as outer-sphere complexes [25]. [40] studied the adsorption of Pb(II) onto montmorillonite and found that increasing ionic strength from 10 to 100 mM sensibly decreased lead adsorption at the pH below the Pb hydrolysis point. [41] investigated the

adsorption of Pb(II) onto oxidized multiwalled carbon nanotubes (MWCNTs) and found that the adsorption was independent of ionic strength. The present results showed that the adsorption of Pb^{2+} ion onto soils was influenced by ionic strength strongly. This suggests that the adsorption of Pb^{2+} ion is mainly dominated by ion exchange [21]. Adsorption was dependent on ionic strength, suggesting that they were mainly adsorbed on the outer-sphere sites [42].

3.4. Scanning Electron Microscopy Analysis

The morphology of the soils with Pb^{2+} ion showed some important observations. Typical SEM photographs are shown in Fig. 6(a–h). Coverage of the surface of the soil due to adsorption of Pb^{2+} ion presumably leading to formation of

layer of lead molecules over the soil surface. It is evident from the formation of white layer (molecular cloud). There was higher surface coverage of lead in YBS, RS and LRS than LS. It is noticed that soils have bigger pore structures, 1 – 5 μm and after adsorption, the pore size have been reduced to 0.4 – 0.6 μm . There was spherical like structures attached in bundles. This could be due to adsorption of Pb^{2+} ion on soils. Surface adsorbed spherical shaped Pb particles on the soil could be found. There was increase in the roughness of the soil surface after adsorption of lead ions, indicating that the adsorption reaction occurred on the surface of the soil particles (Fig.6 (a–h)). The increase of roughness may be attributed to the formation of lead ion complexes on the surfaces [9].

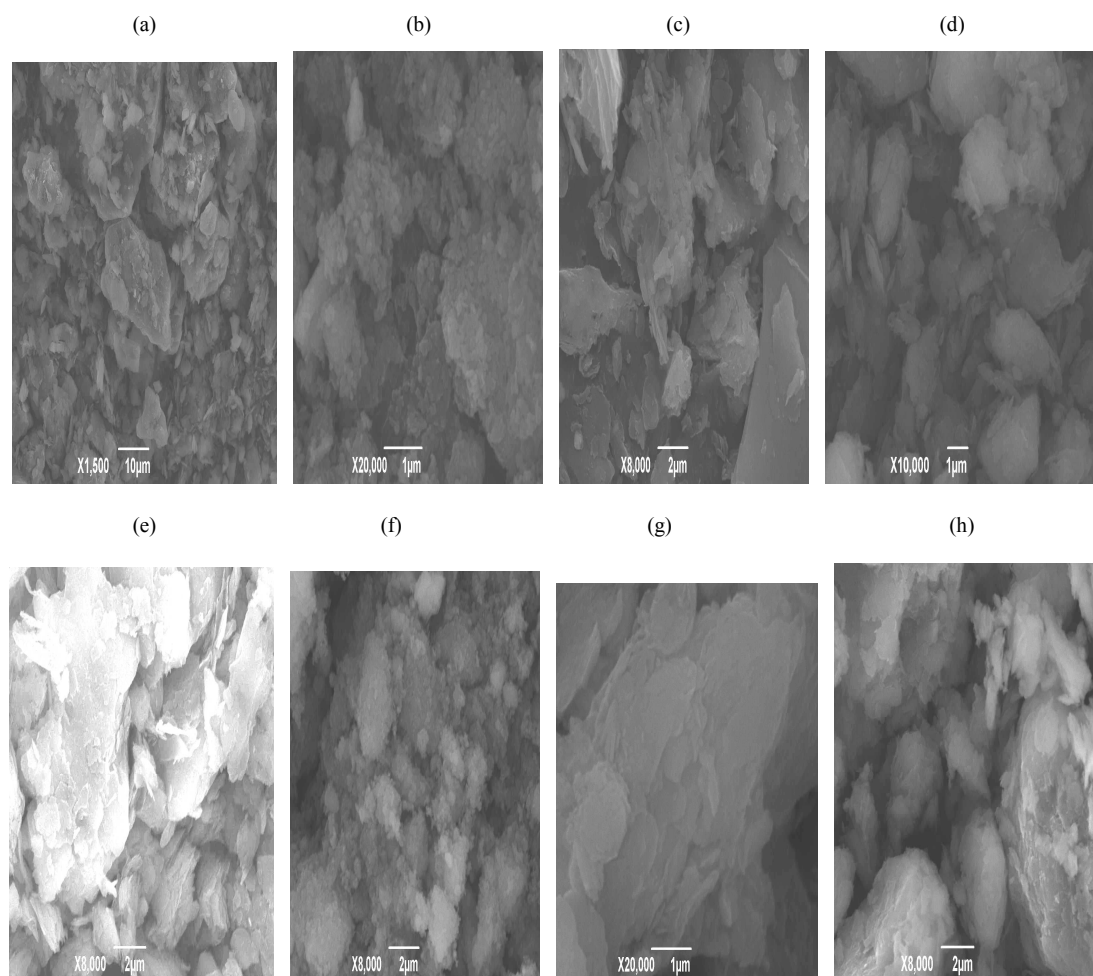


Fig. 6. Scanning electron microgram of soils without and with Pb adsorption a. LRS, b. LS, c. YBS, d. RS without Pb, e. LRS, f. LS, g. YBS, h. RS with Pb

4. Conclusion

The greater content of illite and the moderate content of vermiculite provide YBS with greater exchange capacity than the other soils, as this minerals have larger net surface than kaolinite. In YBS cations will be commonly adsorbed than anions compared to other soils. In general, the soils are acid, of low fertility and poor in organic matter. Low 2:1 clay mineral is attributable to the high weathering of the soils. Adsorption

of Pb^{2+} ion onto soils was influenced by pH strongly. This suggests that the adsorption of Pb^{2+} ion onto soils is mainly dominated by surface complexation. Scanning electron microscopy (SEM) revealed that the adsorption of lead ions made the surface of the soil particles rougher than those without lead. The present results showed that the adsorption of Pb^{2+} ion onto soils was influenced by ionic strength strongly. This suggests that the adsorption of Pb^{2+} ion is mainly dominated by ion exchange and was mainly on the

outer-sphere sites. In general, ion exchange is mainly influenced by ionic strength.

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