

Impacts of inorganic ions and temperature on lead adsorption onto variable charge soils

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ABSTRACT

The effect of inorganic ions and temperature on lead (Pb^{2+}) adsorption was evaluated on three acidic soils: yellow-brown soil (YBS), latosol soil (LS), and lateritic red soil (LRS). The results showed that the adsorption of Pb^{2+} in the presence of anions decreased in the order: $\text{SO}_4^{2-} > \text{NO}_3^- = \text{Cl}^-$, while in the presence of cations, it reduced in the order: $\text{K}^+ > \text{Ca}^{2+}$. Accordingly, the contamination of YBS, LS and LRS soils with Pb^{2+} was more noticeable when they contained more NO_3^- , Cl^- and Ca^{2+} than SO_4^{2-} and K^+ . The distribution coefficient (K_d) of Pb^{2+} declined in the order: $\text{YBS} > \text{LS} > \text{LRS}$ in the presence of anions. Adsorption and K_d values of Pb^{2+} were mainly dependent on ion types and altered surface properties caused by the adsorption and/or the formation of ion complexes. The K_d values enhanced slightly with increasing temperature up to 35 °C and then decreased at 45 °C. Based on the thermodynamic parameters, including the heat of reaction (ΔH), entropy change (ΔS) and the free energy change (ΔG), the adsorption process of Pb^{2+} on YBS, LS and LRS soils was endothermic and impetuous at low temperatures, whereas it was exothermic and non-spontaneous at high temperatures.

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1. Introduction

Contamination of soils by heavy metals such as lead (Pb^{2+}) is considered being a risk to human health when its concentration exceeds 400–500 mg kg^{-1} soil (US EPA, 2001). The toxicity of Pb^{2+} contaminated soils can primarily occur from direct ingestion of vegetables and crops. The concentration of Pb^{2+} in the soil solution is an important factor in all ecological considerations because the plants are expected to take up large amounts from it. Moreover, the mobility of Pb^{2+} in soils and groundwater depends on its concentration (Brummer et al., 1986). The fate and transportation of Pb^{2+} ions in the environment are generally controlled by adsorption and complexation reactions (Wang et al., 2009). Several studies were conducted to evaluate the adsorption of Pb^{2+} on soils, clay minerals and oxides (Adebowale et al., 2006; Lee et al., 1998; Sipos et al., 2005; Wang et al., 2009). These investigations showed that soil type, ionic strength, ion type and contact time were the most important factors in controlling the adsorption of Pb^{2+} on soils and clay minerals.

It is well known that tropical and subtropical regions have large areas of variable charge soils. These soils usually carry both positive and negative charges on their surfaces, so they can adsorb both anions

and cations (Yu, 1997). Inorganic ions and their ionic strength have essential effects on the adsorption of metals from aqueous solutions. Naidu et al. (1994) found that the increase of calcium (Ca^{2+}) and sodium (Na^+) concentrations decreased the adsorption of cadmium on variable charge soils. It has also been observed that the adsorption of metal ions enhanced due to the increase of soil pH, whereas it declined with rising ionic strength (Barrow and Ellis, 1986). Some strong evidences have indicated that cadmium (Cd^{2+}) and copper (Cu^{2+}) can react with chloride (Cl^-), sulfate (SO_4^{2-}) and low molecular weight organic ligands presenting in the soil solution (Smolders et al., 1998; Zhang et al., 2001). It was also shown that anions had different and frequent opposite effects on the exchange of heavy metals. Minkina et al. (2009) observed that the adsorption of Cu^{2+} enhanced in the presence of Cl^- ions, whereas it diminished in the presence of perchlorate (ClO_4^-) ions. Furthermore, the anionic composition of the soil solution also had marked effect on amounts of Ca^{2+} , potassium (K^+) and hydrogen (H^+), which desorbed from soil during Pb^{2+} adsorption. Many investigations have been carried out to examine the influence of many factors such as inorganic ions and temperature on the adsorption of Pb^{2+} on different soils. However, the effect of these factors is still only partially understood in acidic variable charge soils. Therefore, the aim of this work was to provide scientific information that will be helpful in the management of Pb^{2+} contaminated soils. We particularly studied the impact of inorganic ions and their ionic strength, temperature and initial metal concentration on the adsorption and affinity of Pb^{2+} on three variable charge soils.

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2. Materials and methods

2.1. Soil samples and basic properties

Three variable charge soils were used in this study: yellow brown soil (YBS) being Alfisol and Argosol in American and Chinese Taxonomy; latosol soil (LS) and lateritic red soil (LRS) being Oxisols and Ferralosols in American and Chinese Taxonomy. These soils (YBS, LS, and LRS) were obtained from Hubei, Hainan, and Guangxi provinces in P.R. China, respectively. All used soils were under forest land use. After collection at 0–20 cm depth, the soil samples were air-dried, ground, sieved through 2 mm, and homogenized prior to use.

Soil pH was measured in de-ionized water using the ratio of 1:2.5 (w/v) soil:water. Cation exchange capacity (CEC) and organic matter contents were determined by the method of Page et al. (1982). Particle size distribution was determined using the pipette method. The amounts of amorphous iron (Fe) and aluminum (Al) oxides were evaluated by oxalate extraction (McKeague and Day, 1966). The concentrations of crystalline Fe and Al oxides were determined by oxalate-ascorbic acid extraction method (Shuman, 1982). Both amorphous and crystalline Fe and Al oxide concentrations were measured by inductively coupled plasma atomic emission spectroscopy (ICP-AES). The mineralogical composition of the clay was examined with Cu K alpha-radiation on X-ray diffractometer (D8 Bruker Advance X-ray Diffractometer) (Fig. 1).

2.2. Effect of initial metal ion concentration

Sub-samples of 2.0 g air dried soil were placed into 100 mL centrifuge tubes containing 50 mL of 0.01 mol L⁻¹ KCl (pH 5.0 ± 0.1) solution with addition of different levels of Pb²⁺ as Pb(NO₃)₂. The initial concentrations of Pb²⁺ were 20, 50, 80, 100, and 250 mg L⁻¹. Solutions were adjusted to pH 5.5 ± 0.1 using 0.1 mol L⁻¹ NaOH or HCl. Suspensions were shaken at 230 rpm for 2 h at 25 °C ± 0.1, and then equilibrated in a dark incubator for additional 22 h without shaking. The use of 22 h was previously found to be sufficient for the equilibration process. At the end, the suspensions were centrifuged at 5000 g for 10 min followed by the filtration. The concentrations of Pb²⁺ in the filtrates were measured by atomic absorption spectrophotometer (computed-aided Varian AA 240FS). Total amounts of adsorbed Pb²⁺ were calculated by taking the difference between applied Pb²⁺ concentrations and the amounts of Pb²⁺ remaining in the equilibrium solution.

2.2.1. Adsorption equation

Two common expressions (Langmuir and Freundlich isotherm models) were used for describing the adsorption equilibrium of Pb²⁺. The Langmuir equation expresses in a mathematical form as follows:

$$C_e/q_e = 1/X_m * b + C_e/X_m$$

where C_e is the equilibrium concentration (mg L⁻¹), q_e is the amount adsorbed at equilibrium (mg g⁻¹), X_m is the maximum adsorption capacity (mg g⁻¹) and b is the adsorption energy (L mg⁻¹).

The Freundlich empirical equation takes the form as follows.

$$q_e = K_f C_e^{1/n}$$

The logarithmic form of the equation becomes as follows.

$$\log(q_e) = \log K_f + (1/n) \log(C_e)$$

where, K_f and n are indicators for the adsorption capacity and adsorption intensity, respectively.

2.2.2. Distribution coefficient

The tendency of heavy metals on soils can be determined by the solubility of the compounds in the soil solution. This solubility is known as the soil distribution coefficient. The high distribution coefficient values indicate strong attraction on soil particles. To determine the solubility of compounds, the distribution coefficient (K_d) was calculated using the following formula.

$$C_0 - C_e/q_e = V/m$$

where, C_0 is initial Pb²⁺ concentration (mg L⁻¹), C_e is equilibrium concentration of Pb²⁺ (mg L⁻¹), V is volume of the adsorbate solution (L), and m is adsorbent weight (g).

2.3. Effect of inorganic ions

2.3.1. Under nonadjusted pH

Volume of 25 mL of various electrolytes (KCl, KNO₃ or K₂SO₄) in three concentrations of 0.1, 0.01, and 0.001 mol L⁻¹ containing 150 mg L⁻¹ Pb²⁺ were separately added into 1 g soil samples. The pH of these solutions did not adjust to avoid their adverse effects. Solutions were agitated for 2 h, equilibrated for 22 h without shaking and centrifuged at 5000 rpm for 10 min.

2.3.2. Under adjusted pH

Volume of 25 mL of KCl or CaCl₂ in three concentrations of 0.1, 0.01, and 0.001 mol L⁻¹ containing 150 mg L⁻¹ Pb²⁺ were separately added into 1 g soil samples. The pH of these solutions was adjusted to 5.5 ± 0.1. These solutions were shaken for 2 h, equilibrated for 22 h and centrifuged at 5000 rpm for 10 min.

2.4. Effect of temperature

Soil samples of 1 g were placed into 50 mL polyethylene bottles and mixed with 25 mL of 0.01 KCl containing 100 mg L⁻¹ Pb²⁺. The solutions were adjusted to pH of 5.5 ± 0.1 with 0.1 mol L⁻¹ NaOH or HCl. Bottles were shaken at 230 rpm at different temperatures (5–45 °C) followed by centrifugation at 5000 rpm for 10 min. Supernatant solution was taken for Pb²⁺ analysis using atomic absorption spectrophotometer.

The thermodynamic parameters (ΔH , ΔS and ΔG) of Pb²⁺ sorption on the studied soils can be calculated from the temperature dependence.

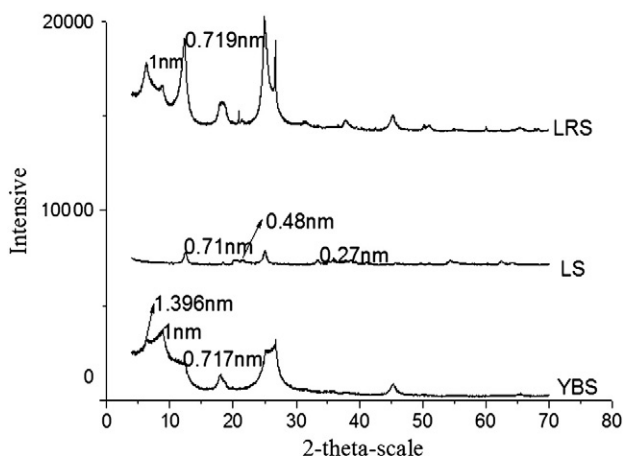


Fig. 1. X-ray diffraction patterns of three soils. YBS, LS, and LRS were abbreviations for yellow brown soil, latosol soil and lateritic red soil.

Free energy changes (ΔG) were calculated using the following formula:

$$\Delta G = -RT \ln k^0$$

where R is the universal gas constant ($8.314 \text{ J mol}^{-1} \text{ K}^{-1}$), T is the temperature in Kelvin and k^0 is the sorption equilibrium constant. Values of $1n k^0$ are obtained by plotting $1n k_d$ vs. C_{eq} and extrapolating C_{eq} to zero (Tan et al., 2008) and the intercept with the vertical axis gives the value of $1n k^0$.

The heat of reaction (ΔH) was determined using the formula: $\Delta H = q / 1000 \div \text{moles of reactant}$ (Anne, 2011), where q is mass in grams of reactant \times specific heat capacity \times change in temperature.

Standard entropy changes (ΔS) were calculated using the equation:

$$\Delta S = (\Delta G - \Delta H) / T.$$

2.5. Statistical analysis

All experiments were carried out in triplicate and only mean values are presented. All data were statistically analyzed by M-STATC for windows. The data was analyzed by ANOVA considering the soils, treatments and replicates as the independent variables. Duncan multiple range test was used to detect the significant difference between means of different soils at $p \leq 0.05$. The correlation coefficient (r) was performed to determine the relationship between different parameters.

3. Results

3.1. Physicochemical and mineralogical properties of soils

The results of physicochemical properties showed that YBS had higher CEC and pH ($27.4 \text{ cmolc kg}^{-1}$ and 5.2, respectively) than other soils, while LS had higher organic carbon, and crystalline Fe_2O_3 and Al_2O_3 (13.1 g kg^{-1} , 84.0 g kg^{-1} and 5.2 g kg^{-1} , respectively) than other soils (Table 1). The particle size analysis demonstrated that LS, YBS and LRS were clay (Oxisols), silt loam (Alfisol and Argosol) and clay loam (Ferralosols), respectively. Mineralogical composition indicated that LRS mainly consisted of kaolinite 60% and illite 40% characterized by diffraction peaks at 0.719 nm and 1.00 nm, respectively. The LS consisted of kaolinite 75%, hydroxyinterlayered vermiculite 15% and goethite characterized by diffraction peaks at 0.71 nm, 0.48 nm and 0.27 nm, respectively. The YBS consisted of illite 45%, vermiculite 25% and kaolinite 30% characterized by diffraction peaks at 1 nm, 1.396 nm and 0.717 nm, respectively (Fig. 1).

3.2. Effect of initial Pb^{2+} concentration on adsorption

An increase of initial Pb^{2+} concentrations in aqueous solution from 20 to 250 mg L^{-1} led to significant increase in the adsorption of Pb^{2+} on all examined soils (Fig. 2). However, the adsorbed percentages of Pb^{2+} decreased with increasing initial Pb^{2+} concentrations. Isotherms of Pb^{2+} adsorption on the soil could be well described by Langmuir and Freundlich models (Table 2). The Freundlich model gave good

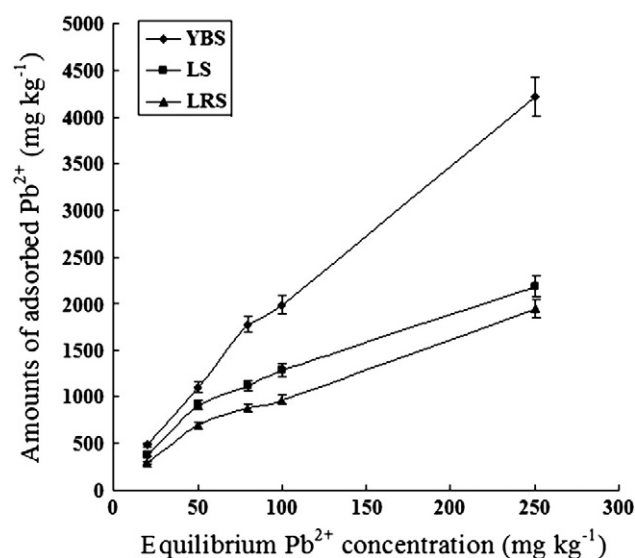


Fig. 2. Adsorption isotherm for the adsorption of Pb^{2+} onto soils. YBS, LS, and LRS are abbreviations for yellow brown soil, latosol soil and lateritic red soil.

representation for the experimental data based on fitting correlation coefficients (r^2). Freundlich parameters, K_f and n , which illustrated the capacity and intensity of adsorption are listed in Table 2. Values of K_f were 1.85, 1.67 and 1.50, while n values were 2.27, 2.13, and 1.64 for YBS, LS, and LRS soils, respectively. The monolayer maximum adsorption (X_m) value from Langmuir equation was 5000 mg kg^{-1} for YBS soil and 2500 mg kg^{-1} for both LS and LRS soils. Values of adsorption energy (b) were 0.06, 0.03 and 0.01 for YBS, LS, and LRS soils, respectively. Highest adsorptive capacity and intensity were recorded in YBS soil as indicated by X_m and b values (Table 2). From the Langmuir constant, dimensionless separation factor (K_R) can be calculated as:

$$K_R = (1 + C_0 * b)^{-1}$$

where C_0 is initial metal concentration (mg L^{-1}), and b is constant related to the adsorption energy. Values of K_R are related to the nature of adsorbent/adsorbate interaction and isotherm types: unfavorable ($K_R > 1$), linear ($K_R = 1$), favorable ($0 < K_R < 1$) or irreversible ($K_R = 0$). The calculated K_R values for various initial Pb^{2+} concentrations were $0.066 < K_R < 0.794$ in YBS soil, $0.133 < K_R < 1.587$ in LS soil, and $0.398 < K_R < 4.762$ in LRS soil (Fig. 3). An adsorption process of Pb^{2+} was favorable in YBS soil at all studied concentrations. In LS soil, the adsorption process was favorable only when the concentration of Pb^{2+} being higher than 20 mg L^{-1} , while in LRS soil, it was favorable only when the concentration of Pb^{2+} being 80 mg L^{-1} . The highest K_d value (713 mL g^{-1}) occurred in YBS soil, whereas the lowest one (11 mL g^{-1}) was recorded in LRS soil (Fig. 4).

3.3. Effect of ionic nature and strength on Pb^{2+} adsorption

During the equilibration period, no significant effect was observed for electrolyte pH. The pH values of solutions at equilibration were declined by less than one unit. Pb^{2+} ion adsorption did not show

Table 1
Some properties of the tested soils.

Soils	pH	OM (g kg^{-1})	CEC (cmolc kg^{-1})	Clay (g kg^{-1})	Clay minerals	Crystal Fe (g kg^{-1})	Crystal Al (g kg^{-1})
YBS	5.2	10.8	27.4	256.5	I (45), V (25), K (30)	16.0	1.3
LS	4.5	13.1	15.9	415.9	K (75), HIV (15), GE	84.0	5.2
LRS	4.1	9.9	21.9	361.2	K (80), GE (20)	21.0	2.1

I = illite, V = vermiculite, K = kaolinite, HIV = hydroxyinterlayered vermiculite, GE = goethite. Data in the parentheses are the contents (%) of the corresponding minerals. OM = organic matter and CEC = cation exchange capacity. YBS, LS, and LRS are abbreviations for yellow brown soil, latosol soil and lateritic red soil.

Table 2
Isothermal characteristics of Pb^{2+} adsorption on tested soils.

Soils	Langmuir equation			Freundlich equation		
	X_m ($mg\ kg^{-1}$)	b	r^2	Kf	n	r^2
YBS	5000	0.06	0.945	1.85	2.27	0.980
LS	2500	0.03	0.944	1.67	2.13	0.954
LRS	2500	0.01	0.939	1.50	1.64	0.986

YBS, LS, and LRS are abbreviations for yellow brown soil, latosol soil and lateritic red soil. X_m is the adsorption capacity ($mg\ g^{-1}$) and b is the adsorption energy ($L\ mg^{-1}$). The Kf and n are indicators for the adsorption capacity and adsorption intensity, respectively.

obvious difference according to the final pH values (Table 3). However, higher adsorption values of Pb^{2+} on the investigated soils were noticed in the presence of SO_4^{2-} as compared to NO_3^- and Cl^- (Table 4). Both NO_3^- and Cl^- led to same Pb^{2+} adsorption values.

Increasing the ionic strength of SO_4^{2-} , NO_3^- and Cl^- from 0.001 to 0.1 $mol\ L^{-1}$ affected the adsorption of Pb^{2+} . In the presence of SO_4^{2-} , adsorption of Pb^{2+} increased with increasing ionic strength, whereas NO_3^- and Cl^- decreased the Pb^{2+} adsorption (Table 4). Distribution coefficient (K_d) values decreased with increasing NO_3^- and Cl^- ionic strength. The K_d values of Pb^{2+} were 954, 587 and 489 $mL\ g^{-1}$ at ionic strength of 0.001 $mol\ L^{-1}$, and were 1827, 23 and 27 $mL\ g^{-1}$ at ionic strength of 0.1 $mol\ L^{-1}$ for SO_4^{2-} , Cl^- and NO_3^- in YBS soil, respectively (Fig. 5). This indicated that increasing the ionic strength of SO_4^{2-} improved the affinity of Pb^{2+} on soils, whereas the increase of Cl^- and NO_3^- ionic strength decreased the attraction of Pb^{2+} for soils.

Increasing the concentration of inorganic cation from 0.001 $mol\ L^{-1}$ to 0.1 $mol\ L^{-1}$ caused a drop in Pb^{2+} adsorption capacity on soils. Sorption of Pb^{2+} in the presence of K^+ was higher than that in the presence of Ca^{2+} at all concentrations and for all soils (Table 5). Calcium reduced the adsorption capacity of Pb^{2+} on the studied soils by 19.2–21.9% in comparison to K^+ . The K_d values of Pb^{2+} decreased from 1688 and 190 $mL\ g^{-1}$ to 747 and 87 $mL\ g^{-1}$ due to an increase in ionic strength of K^+ and Ca^{2+} from 0.001 $mol\ L^{-1}$ to 0.1 $mol\ L^{-1}$ (Fig. 6). The increase of ionic strength of K^+ and Ca^{2+} was responsible for major decreases in K_d values of Pb^{2+} . Addition of SO_4^{2-} and Ca^{2+} did not cause significant changes in adsorption percentages of Pb^{2+} under all used soils and concentrations. However, adsorption percentages of Pb^{2+} significantly altered in the presence of Cl^- , NO_3^- and K^+ (Tables 4 and 5). Moreover, there were no noticeable differences recorded in adsorption percentages of Pb^{2+} on LS and LRS soils in the presence of K^+ (Table 5).

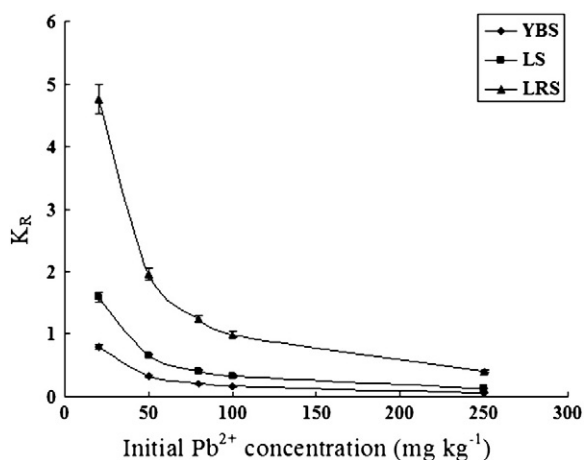


Fig. 3. Effect of initial Pb^{2+} concentration on separation factor (K_R). YBS, LS, and LRS are abbreviations for yellow brown soil, latosol soil and lateritic red soil.

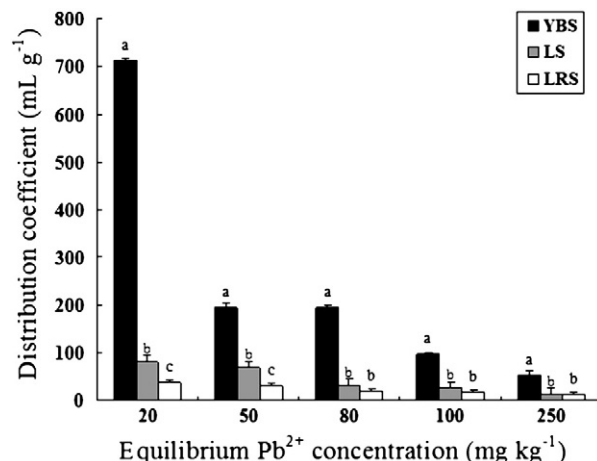


Fig. 4. Distribution coefficient (K_d) of Pb^{2+} as influenced by equilibrium Pb^{2+} concentration. YBS, LS, and LRS are abbreviations for yellow brown soil, latosol soil and lateritic red soil.

3.4. Effect of temperature on adsorption

In a series of adsorption experiments at temperature range from 5 °C to 45 °C, the K_d of Pb^{2+} increased slightly with increasing temperature up to 35 °C, and then decreased at 45 °C. The highest value of K_d (365 $mL\ g^{-1}$) was observed in YBS soil, whereas the lowest value (608 $mL\ g^{-1}$) was found in LS soil (Fig. 7). The heat of reaction (ΔH) and entropy change (ΔS) were positive at low temperatures (5–25 °C) but negative at high temperature (35–45 °C) (Table 6). Values of ΔH were 962, 544, 126, –293 and –711 $kJ\ mol^{-1}$, while ΔS values were 481.2, 90.70, 12.60, –20.90 and –39.50 $J\ mol^{-1}\ K^{-1}$ at 5, 15, 25, 35 and 45 °C, respectively. On the other hand, the free energy change (ΔG) was negative at low temperatures (5–25 °C) but positive at high temperature (35–45 °C). At 5, 15, 25, 35 and 45 °C, ΔG values were –1443.8, –815.8, –189, 440.3 and 1066.5 $kJ\ mol^{-1}$, respectively. Overall, the thermodynamic results indicated that the adsorption of Pb^{2+} was exothermic and non-spontaneous in nature at high temperatures but endothermic and spontaneous at low temperatures. To the best of our knowledge, this result has not been yet reported in the previous literatures.

4. Discussions

The YBS soil had higher adsorption capacity probably due to its higher CEC, pH and illite content (Table 1). Our results were in agreement with previous reports suggesting that the adsorption capacity of Pb^{2+} had a significant relationship with CEC of soils (Coles and Yong, 2002; Yang et al., 2006). Other properties that are associated with

Table 3
Changes of pH in initial and equilibrium solutions.

Electrolytes	Ionic strength ($mol\ L^{-1}$)	YBS		LS		LRS	
		Initial pH	Final pH	Initial pH	Final pH	Initial pH	Final pH
K_2SO_4	0.001	4.81	4.78	4.39	4.26	4.16	4.01
	0.01	5.02	4.94	4.74	4.68	4.30	4.22
	0.1	5.11	4.90	4.89	4.68	4.53	4.26
KNO_3	0.001	4.58	4.54	4.13	4.02	3.96	3.88
	0.01	4.46	4.42	4.12	4.06	4.03	3.94
	0.1	4.38	4.12	4.20	4.03	4.27	3.91
KCl	0.001	4.64	4.53	4.15	4.00	4.05	3.88
	0.01	4.48	4.37	4.15	4.09	4.06	3.89
	0.1	4.40	4.19	4.18	4.06	4.04	3.85

YBS, LS, and LRS are abbreviations for yellow brown soil, latosol soil and lateritic red soil.

Table 4
Adsorption percentage of Pb²⁺ on tested soils 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	97.5a	95.2a	96.0a	98.4a	82.1a	83.1a	98.7a	51.5a	48.3a
LS	91.5a	48.9b	52.5b	94.6a	32.7b	30.7b	98.5a	31.0b	30.1b
LRS	89.3a	43.6c	45.0c	91.2a	20.4c	18.4c	98.0a	17.0c	15.7c

Data are expressed as mean value of triplicates–duplicates. Different letters in a column indicate significant differences according to mean separation by Duncan's multiple range test at probability (p ≤ 0.05). YBS, LS, and LRS are abbreviations for yellow brown soil, latosol soil and lateritic red soil.

metal adsorption, e.g. clay content and organic matter may also influence Pb²⁺ retention through their relation to CEC (Yang et al., 2006).

In this study, the amount of adsorbed Pb²⁺ enhanced with the increase of its initial concentration. This could be explained by increasing the driving force of Pb²⁺ towards the active sites on soils. The adsorption was more favorable for higher initial Pb²⁺ concentrations with respect to low concentrations. It was similar to the findings obtained by Unuabonah et al. (2007), and Adebowale et al. (2006) on adsorption of Pb²⁺ on tripolyphosphate – impregnated kaolinite clay and kaolinite clay, respectively. The K_f values depicted greater adsorptive capacity for Pb²⁺ in YBS soil than the other soils. The increase of equilibrium Pb²⁺ concentration in aqueous solution caused decrease in K_d values. This indicated that Pb²⁺ had greater affinity on soils at lower than at higher concentrations (Fig. 4). Furthermore, K_d of Pb²⁺ for YBS soil was greater than for other soils, so Pb²⁺ had higher attraction on YBS soil.

We assumed that the higher Pb²⁺ sorption in the presence of SO₄²⁻ than in the presence of other anions was due to larger reduction of oxide surface charge caused by anion adsorption and could not be attributed to formation of ternary complexes. This was similar to the results of Adebowale et al. (2006) and Bradl (2004) who evaluated the adsorption of Pb²⁺ and Cd²⁺ on phosphate modified and unmodified kaolinite clay and adsorption of Cd²⁺ on goethite, respectively. However, the assumption of Neal and Sposito (1986) showed that Cl⁻ and NO₃⁻ had weak effects on metal ion adsorption. Thus, the adsorption of metal ions and the adsorption capacity of adsorbents become more noticeable when the previous anions (Cl⁻ and NO₃⁻) formed charged complexes with metal ions, especially Cl⁻ that had high ability to form charged and uncharged species (e.g. MCl₂⁰, MCl₃⁻ and MCl₄²⁻) with metal ions (Cotton and Wilkinson, 1972). The ionic strength of anions could be responsible for the change in adsorbent-suspension pH through its effect on the diffuse

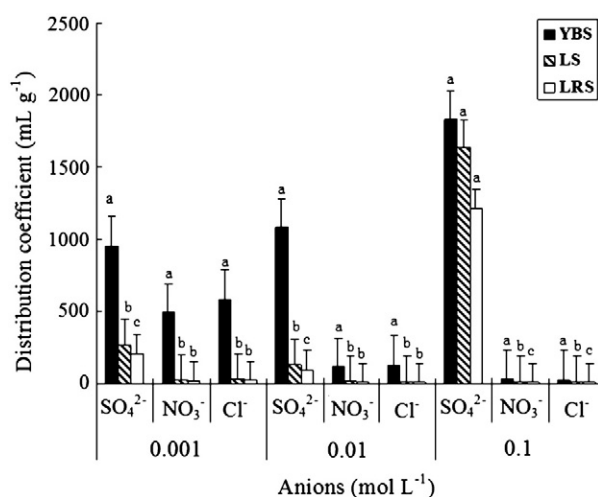


Fig. 5. Distribution coefficient of Pb²⁺ at different ionic strength of anions. YBS, LS, and LRS are abbreviations for yellow brown soil, latosol soil and lateritic red soil.

Table 5
Adsorption percentage of Pb²⁺ on tested soils 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
LRS	89.1a	96.0b	77.3a	90.9b	66.2a	70.1b

Data are expressed as mean value of triplicates. Different letters in a column indicate significant differences according to mean separation by Duncan's multiple range test at probability (p ≤ 0.05). YBS, LS, and LRS are abbreviations for yellow brown soil, latosol soil and lateritic red soil.

double layer. An increase in ionic strength of anions led to obvious decrease in the adsorption of Pb²⁺ due to its effect on the electrostatic potential and surface charges (Schofield and Samson, 1954). The highest adsorption of Pb²⁺ in the presence of SO₄²⁻ could be attributed by the greatest increase in negative charges. It should be noted that the adsorption of Pb²⁺ in the presence of K₂SO₄ could have been resulted from the combination of adsorption and precipitation processes. It was not easy to distinguish the adsorption from precipitation reactions by conventional techniques. However, it was possible to mention that the adsorption was the dominant process.

The high effects of cations on the adsorption of Pb²⁺ were probably resulted from an increase in the competition between cations and Pb²⁺ for adsorption sites on soils and also to their great effects on thickness of the double layer (Naidu et al., 1994; Unuabonah et al., 2007). It had been shown that potential of Pb²⁺ adsorption was related to the cation valences through their effects on surface charge densities (Unuabonah et al., 2007). The enhancement of cation valences caused significant reductions in the adsorption of Pb²⁺ (Li and Li, 2000). Similar trends had been observed by Naidu et al. (1994) for the adsorption of Cd²⁺ on soils; Adebowale et al. (2006) for the adsorption of Pb²⁺ and Cd²⁺ on orthophosphate-modified and unmodified kaolinite, and Spark et al. (1995) for the adsorption of Cu²⁺, Zn²⁺, Co²⁺ and Cd²⁺ on kaolinite. More concentration of Cl⁻ in CaCl₂ than KCl led to marked decreases in the Pb²⁺ adsorption. The effect of ionic strength of cations on metal ion adsorption was often attributed to changes in adsorbent-suspension pH effect on the diffuse double layer (Barrow and Ellis, 1986). Naidu et al. (1994) found that the pH of soil suspensions decreased by 0.4–1.0 unit on average due to the increase of ionic strength of cations. This might explain in part the decrease of metal ion adsorption. Barrow

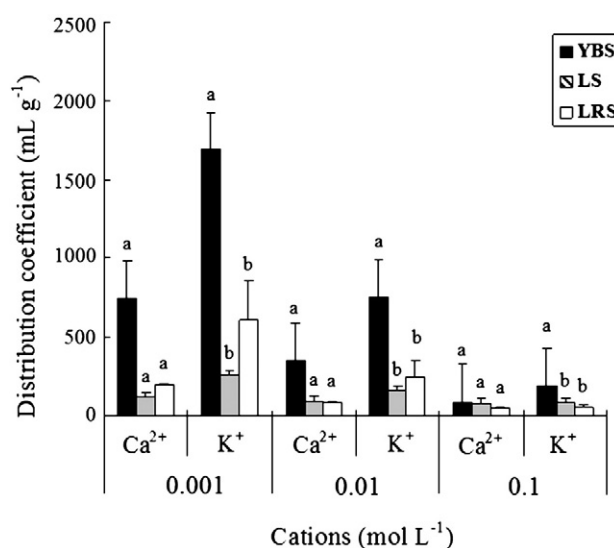


Fig. 6. Distribution coefficient of Pb²⁺ at different ionic strength of cations. YBS, LS, and LRS are abbreviations for yellow brown soil, latosol soil and lateritic red soil.

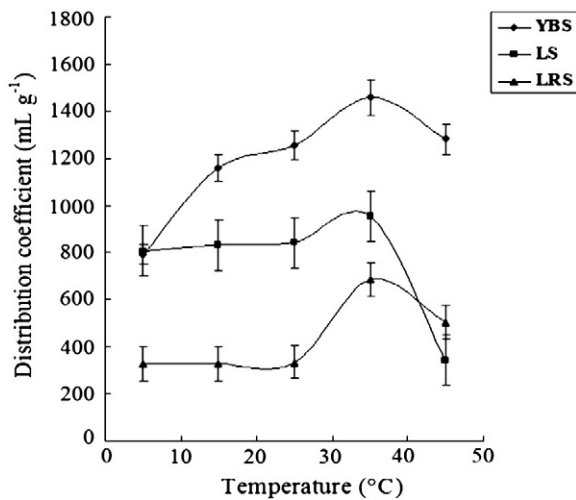


Fig. 7. Distribution coefficient of Pb^{2+} at different temperatures. YBS, LS, and LRS are abbreviations for yellow brown soil, latosol soil and lateritic red soil.

(1985) showed that the adsorbent surface charges became more positive as a result of increasing ionic strength of inorganic cations. This led to significant decrease in the adsorption of metal ions. In addition, the effect of ionic strength could be ascribed to: (1) the competition of high concentrations of cations in electrolyte with Pb^{2+} for adsorption sites on the soil surface; (2) the decrease of activities of Pb^{2+} due to an increase in ionic strength; (3) the formation of ionic pairs or chelating compounds (Chen, 1996). The presence of salts might compress the electric double layer surrounding the negative charged surfaces (Philips et al., 2004).

The adsorption of Pb^{2+} enhanced with an increase in temperatures up to 35 °C. However, the mobility of Pb^{2+} become more noticeable with increasing temperatures more than 35 °C, and the adsorption process was endothermic and spontaneous. At high temperature due to bond rupture of functional groups on adsorbent surface there may be an increase in number of active sorption sites, which may also lead to enhance sorption with rise in temperature up to 35 °C (Erentürka and Malkocb, 2007).

5. Conclusions

In the presence of SO_4^{2-} , more Pb^{2+} was adsorbed which increased with the increasing ionic strength unlike in the presence of Cl^- and NO_3^- . The presence of SO_4^{2-} reduced the surface potential of soil colloids so that the surface became more attractive for Pb^{2+} . The increase of K^+ and Ca^{2+} concentrations reduced the amount of Pb^{2+} adsorption by soils. Comparatively, increment of Pb^{2+} adsorption in the presence of inorganic ions was more pronounced on YBS soil than on LS and LRS soils (YBS > LS > LRS). Furthermore, the adsorption of Pb^{2+} was greater in the presence of SO_4^{2-} than the other anions, and greater in the presence of K^+ than Ca^{2+} .

The Pb^{2+} adsorption onto soils was more favorable at lower temperatures 5–25 °C than higher temperatures 35–45 °C. The positive value

Table 6

Values of thermodynamic parameters for the adsorption of Pb(II) on soils.

Temperature (°C)	ΔH (kJ mol ⁻¹)	ΔS (J mol ⁻¹ K ⁻¹)	ΔG (kJ mol ⁻¹)
5	962	481.2	-1443.8
15	544	90.70	-815.80
25	126	12.60	-189.00
35	-293	-20.90	440.30
45	-711	-39.50	1066.5

YBS, LS, and LRS are abbreviations for yellow brown soil, latosol soil and lateritic red soil. ΔH , ΔS and ΔG are the heat of reaction, entropy change and free energy change, respectively.

of ΔG indicated that the adsorption of Pb^{2+} was non-spontaneous and unfavorable at high temperatures, whereas their negative values showed that the adsorption of Pb^{2+} was spontaneous and favorable at low temperatures. We conclude that the clay could be responsible for major sites of Pb^{2+} adsorption on YBS soil, while Fe and Al oxyhydroxides, and organic matter could provide the most important sites of Pb^{2+} adsorption on LS and LRS soils.

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