

Effects of pH, organic acids, and inorganic ions on lead desorption from soils

J.Y. Yang^a, X.E. Yang^a, Z.L. He^{a,b,*}, T.Q. Li^a, J.L. Shentu^a, P.J. Stoffella^b

^a College of Natural Resources and Environmental Sciences, Huajiachi Campus, Zhejiang University, Hangzhou 310029, China

^b University of Florida, Institute of Food and Agricultural Sciences, Indian River Research and Education Center, Fort Pierce, FL 34945, USA

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The adsorption–desorption process is a basic and important reaction in soils controlling Pb²⁺ mobility and bioavailability.

Abstract

The desorption characteristics of lead in two variable charge soils (one developed from Arenaceous rock (RAR) and the other derived from Quaternary red earths (REQ)) were studied, and the effects of pH value, organic acid, and competitive ions were examined. Desorption of Pb²⁺ decreased from nearly 100.0 to 20.0% within pH 1.0–4.0 in both soils, and then the decrease diminished at pH > 4.0. Organic ligands at relatively low concentrations ($\leq 10^{-3}$ mol L⁻¹) slightly inhibited Pb²⁺ desorption, but enhanced Pb²⁺ desorption at higher concentrations. In this study, citric acid or acetic acid at higher concentrations ($> 10^{-3}$ mol L⁻¹) had the greatest improvement of Pb²⁺ desorption, followed by malic acid; and the smallest was oxalic acid. Desorption of the adsorbed Pb²⁺ increased greatly with increasing concentrations of added Cu²⁺ or Zn²⁺. Applied Cu²⁺ increased Pb²⁺ desorption more than Zn²⁺ at the same loading.

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1. Introduction

Concerns over the effects of heavy metals on ecosystem health have increased in recent years (Kham et al., 2000; Nigam et al., 2001). Waste disposals may accelerate the transport of potentially toxic metals to both surface and groundwater and also to animals through pathways such as crops grown on contaminated soils and direct ingestion of contaminated

soil. Metal availability is determined by its activity in the soil solution, which is controlled by both the solid and solution phase characteristics of the soil. As a result, metal availability may vary considerably depending on the nature of adsorption–desorption processes in the soils. Although, extensive research has been devoted to metal sorption in temperate soils, data on both sorption and desorption reactions in tropical and subtropical soils are limited (Naidu et al., 1997).

Variable charge soils (Oxisols, Ultisols, Andisols, and acid Alfisols) generally have low surface charge density with predominant pH-dependent charge, particularly at pH value of 4.0–5.0 (McBride, 1994), and heavy metals may become mobile in such soils under certain conditions (Naidu et al., 1994). Unlike soils with permanent charge where the charge arises from isomorphous substitution within the layer lattice of clay minerals, variable charge soils exhibit the property of being able to alter charge in response to changes in the ambient soil solution. The major factors determining this

Abbreviations: RAR, red soil developed on Arenaceous rock (clayey, mixed siliceous thermic typic Dystrachrept); REQ, red soil developed on Quaternary red earths (clayey, kaolinitic thermic plinthite Aquult); AAS, atomic adsorption spectrometry; CEC, cation exchange capacity; LMWOA, low molecular weight organic acid.

* Corresponding author. University of Florida, Institute of Food and Agricultural Sciences, Indian River Research and Education Center, 2199 South Rock Road, Fort Pierce, FL 34945-3138, USA. Tel.: +1 772 468 3922x109; fax: +1 772 468 5668.

E-mail address: zhe@mail.ifas.ufl.edu (Z.L. He).

variable charge include pH, ionic strength, nature of the electrolyte ion, and metals and ligands in the soil solution capable of specific sorption (Naidu et al., 1997).

Heavy metals including Pb pose great threats to soil quality and human health. They are used for a wide variety of industrial, urban, and agricultural production applications and can be toxic to humans (He, 1998). The persistence and mobility of Pb in the variable charge soils are dictated by the extent to which the metals are adsorbed/desorbed in the solid phase, which is a function of reactions affecting surface charge (i.e., pH and ionic strength). Understanding mechanisms of metal adsorption/desorption in soils is important as these reactions control the strength of the metal–soil surface interactions.

Previous studies indicated that pH is an important factor in Pb adsorption onto soil constituents. Increasing solution pH leads to a rapid increase in net negative surface charge and thus increases soil's affinity for metal ions (Wu et al., 2003b). There is a direct correlation between soil pH and metal retention (Reddy and Patrick, 1977). Harter (1983) assumed that adjusting the pH of any one soil had a major impact on soil's ability to retain heavy metals. Similarly, there is limited information about the correlation between pH and Pb desorption.

An understanding of metal speciation and the complex interactions between metals, organics, and sorbent surfaces is important to predict the fate and transport of metals in subsurface systems. Exudation of organic compounds by roots, microbial secretions, and plant and animal residues may influence ion solubility and uptake through their indirect effects on microbial activity, and root growth dynamics, and direct effects through acidification, chelation, precipitation and oxidation–reduction reactions (Mench et al., 1988; Strom, 1997; Uren and Reisenauer, 1988). Of these compounds, low molecular weight organic acids (LMWOA) are of particular importance due to their metal chelating and complexing properties for mobilization of heavy metals (Mench et al., 1988; Mench and Martin, 1991; Wu et al., 2003a). In recent studies, the LMWOAs have been implicated for altering the bioavailabilities and phytoremediation efficiencies of heavy metals in soils. Some earlier studies show that the formation of metal–organic complexes may increase or have no effect on sorption, depending on the nature of both the complex and the available sorbent surfaces. The contradictory results may be related to the concentration of heavy metals in soil solution, and subsequently to the desorption behavior of heavy metals from these soils (Gao et al., 2003). Different organic acids may affect differently the interaction between metal and soil. Hydrogen ions released by the carboxylic acid groups play a major role in metal dissolution. Functional group positions and types were most important in determining if an organic acid would complex metals and increase their potential leaching (Burckhard et al., 1995). Therefore, it is necessary to understand how and to what extent these organic acids may affect the behavior of heavy metals in soils. In addition, the slow desorption of heavy metals, especially Pb, in soils has been a major impediment in estimating the environmental hazard and the successful phytoremediation of contaminated sites (Mench et al., 1994; Salt et al., 1995; Wu et al., 2003b).

Understanding the processes governing the migration and plant availability of trace metals in soils is essential for predicting the environmental impact of spreading metal-containing wastes on agricultural land. The adverse effects of heavy metals are related to the soil's ability to adsorb and release these elements. Such information is needed to predict the environmental impact of Pb from anthropogenic sources, as well as to develop regulatory measures on the usage and disposal of Pb-containing materials on agricultural soils. Many environmental factors can interfere with the Pb adsorption and desorption process. Most studies have focused on the adsorption of heavy metals in soils, but desorption data are also needed to address contaminant-transport-model assumptions of reversibility, and to determine the feasibility of using chemical enhancement techniques for in situ removal of metals at hazardous waste sites.

The objectives of this study were to investigate the kinetics of Pb adsorption/desorption in variable charge soils and the impacts of pH, Cu^{2+} , and Zn^{2+} on Pb desorption. Acetic, malic, citric, and oxalic acids at various concentrations common in natural environments were also applied to investigate the effects of organic acids on desorption behavior of lead from the variable charge soils.

2. Materials and methods

2.1. Soil samples

Two representative variable charge soils were used in this study: RAR soil (clayey, mixed siliceous thermic typic Dystrachrept), derived from Arenaceous rock, and REQ soil (clayey, kaolinitic thermic plinthite Aquult), developed on Quaternary red earths. Soil samples were collected at depths of 0–20 cm from Longyou County (119°02'–120°20'E, 28°44'–29°17'N), Zhejiang Province, China. Composite samples of the soils were air-dried, ground, and passed through a 2-mm sieve prior to use. Some basic physicochemical properties of the soils were listed in Table 1.

Soil pH was measured using a pH meter (Thermo Orion 250, Orion Research, Inc. Boston, MA, USA) at a soil to solution ratio of 1:2.5 in both deionized water and 1 mol L⁻¹ KCl. Soil organic carbon was determined by the modified Tinsley method (Tinsley, 1950). Total exchangeable acidity and exchangeable Al³⁺ and H⁺ were determined by the 1 mol L⁻¹ extraction–titration method (Bao, 1999). Particle size distribution was measured by the hydrometer method (Liu et al., 1996). The cation exchange capacity (CEC) and exchangeable bases were determined using 1 mol L⁻¹ NH₄Cl (pH 7.0) following the procedure described by Bao (1999). Exchangeable Pb was extracted by 0.1 mol L⁻¹ HCl at a soil to solution ratio of 1:5 (Bao, 1999) and total Pb in the soil sample was determined by HF–HClO₄ digestion method (Tessier et al., 1979). The concentrations of Pb in the extract or digest were measured using atomic absorption spectrometry (AAS) in an acetylene-air flame (AA6800, Shimadzu, Kyoto, Japan). For the metals present in high concentrations, the supernatant solution was diluted with deionized water and the concentrations were obtained directly from appropriate calibration curves prepared with the components of the extraction solution diluted by the same factor.

2.2. Adsorption of Pb²⁺

Portions of 2.0 g air-dried soil were placed into 100-mL polypropylene centrifuge tubes, and 50 mL of 0.01 mol L⁻¹ NaNO₃ (pH 5.0) solution containing different levels of Pb²⁺ [as Pb(NO₃)₂] was added to each tube. The final Pb²⁺ concentrations in the soils were 0.0, 62.5, 125.0, 250.0, 625.0, 1250.0, 2500.0, 3750.0, 5000.0, 7500.0, 10 000.0, 12 500.0 mg Pb²⁺ kg⁻¹. The suspensions were shaken at 200 rpm for 2.0 h at 25 °C and then equilibrated in a dark

Table 1
Basic properties of the tested soils

Items	RAR soil	REQ soil
pH (H ₂ O) (1 mol L ⁻¹ KCl)	5.31/3.69	4.77/3.42
Organic matter (g kg ⁻¹)	12.9	25.8
Total Pb (mg kg ⁻¹)	46.07	29.61
Available Pb (mg kg ⁻¹) (0.1 mol L ⁻¹ HCl, 1:5)	0.2232	0.445
CEC (cmol kg ⁻¹)	21.15	15.59
Exchangeable acidity (cmol kg ⁻¹)	1.097	2.9
Exchangeable H ⁺ (cmol kg ⁻¹)	0.856	0.789
Exchangeable Al (cmol kg ⁻¹)	0.24	2.11
Clay minerals (mm)	Kaolinite, Fe and Al oxides, chlorite, illite	Kaolinite, Fe and Al oxides
Particle composition (%)		
1–0.05 mm	56.97	9.86
0.05–0.01 mm	27.68	23.77
0.01–0.005 mm	4.07	13.92
0.005–0.001 mm	8.88	24.62
<0.001 mm	2.40	27.84

RAR soil = red soil developed on Arenaceous rock (clayey, mixed siliceous thermic typic Dystrochrept), REQ soil = red soil developed on Quaternary red earths (clayey, kaolinitic thermic plinthite Aquult).

incubator for an additional 22.0 h, a time previously found to be sufficient for equilibration. At the end of the designated time, the suspensions were centrifuged at 2000 × *g* relative centrifugal force for 10.0 min and filtered. Ten milliliters of the filtrate were transferred into a 10-mL polypropylene centrifuge tube for measuring Pb²⁺ concentration using the AAS. Total amounts of adsorbed Pb²⁺ were calculated by the difference between the total applied Pb²⁺ and the amount of Pb²⁺ in the equilibrium solution.

2.3. Desorption of Pb²⁺

Batch desorption of metals was accomplished by repeated replacement with metal-free NaNO₃ solution following adsorption. The tube with the soil residue separated from the supernatant solution by centrifugation was weighed to measure the residual Pb²⁺ in the solution. Fifty milliliters of 0.01 mol L⁻¹ NaNO₃ (pH 5.0) were added to each tube containing the Pb-enriched soil residue. The suspensions were shaken at 200 rpm for 2.0 h at 25 °C and equilibrated for an additional 22.0 h. The equilibrated suspensions were then centrifuged at 2000 × *g* relative centrifugal force for 10.0 min and filtered. Ten milliliters of the filtrate were transferred into a 10-mL polypropylene centrifuge tube for measuring Pb²⁺ concentration. In order to estimate the affinity of Pb²⁺ in soils, desorption process was repeated five times (D1–D5). The non-extractable fraction of the adsorbed Pb²⁺ was obtained by the difference between the total adsorbed Pb²⁺ and the total recovered Pb²⁺ by five successive extractions with the NaNO₃ solution (pH 5.0) (Yu et al., 2002).

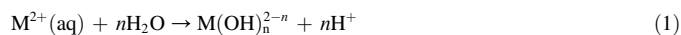
2.4. pH effects

The tube with the soil residue separated from the supernatant solution by centrifugation was weighed to measure the residual Pb²⁺ in the solution. Fifty milliliters of 0.01 mol L⁻¹ metal-free NaNO₃ (pH 5.0) with different pH levels was added to each tube containing the Pb-enriched soil residue. The initial pH of NaNO₃ solution was 1.0, 2.0, 3.0, 4.0, 5.0, 6.0, 7.0, 8.0 and 9.0 and the initial Pb concentration was 7500.0 mg kg⁻¹ soil. The process of desorption was the same as described above.

2.5. Organic acid effects

A pH level, at which heavy metal adsorption could be compared was selected. Low pH values (<4.0) were unsuitable because of weak metal retention for RAR and REQ soils. As pH increase, aqueous metal cations hydrolyze,

resulting in a series of soluble metal complexes according to the generalized expression for divalent metals:



This hydrolysis may be accompanied by precipitation of metal hydroxides, which is experimentally indistinguishable from removal of metals from solution by adsorption. This masking effect of precipitation precludes comparison of the relative sorption affinities at near-neutral conditions (Elliott et al., 1986). Thus, for the purposes of this study, a pH of 5.0 was selected for assessing a soil's metal selectivity preference and this pH is near the natural pH of the tested soils.

The tube with the soil residue separated from the supernatant solution by centrifugation was weighed to measure the residual Pb²⁺ in the solution. Fifty milliliters of 0.01 mol L⁻¹ metal-free NaNO₃ (pH 5.0) with different organic acids were added to each tube containing the Pb-enriched soil residue. Four organic acids were selected for study: acetic, malic, citric, and oxalic acids. The concentrations of each organic acid used were 10⁻⁶, 10⁻⁵, 10⁻⁴, 10⁻³, 10⁻², and 10⁻¹ mol L⁻¹ in 0.01 mol L⁻¹ NaNO₃. The initial Pb²⁺ concentration was 7500.0 mg kg⁻¹ soil. The initial pH of the desorption solution was adjusted to 5.0 with HNO₃ and NaOH. The process of desorption was the same as described above.

2.6. Copper and zinc effects

The tube with the soil residue separated from the supernatant solution by centrifugation was weighed to measure the residual Pb²⁺ in the solution. Fifty milliliters of 0.01 mol L⁻¹ NaNO₃ (pH 5.0) with different concentrations of Cu²⁺ or Zn²⁺ were added to each tube containing the Pb-enriched soil residue. Initial Pb²⁺ concentration was 7500.0 mg kg⁻¹ soil. Initial Cu²⁺ or Zn²⁺ concentrations were 0.0, 1.0, 2.5, 5.0, 10.0, 15.0, 20.0 mmol L⁻¹. The process of desorption was the same as described above.

All glassware and plastic-ware used in this study were previously soaked in 14% HNO₃ (v/v) and rinsed with deionized water. All reagents used were of analytical grade or better.

2.7. Statistical analysis

All experiments were replicated and only mean values were presented. All data were processed by Microsoft Excel, and the regression and other statistical analyses were conducted using the programs of Statistical Package SPSS 10.0.

3. Results and discussion

3.1. Adsorption–desorption of Pb²⁺

Adsorption isotherms of Pb²⁺ were constructed to compare metal adsorption capacity between two tested soils. In all cases, Pb²⁺ adsorption was greater in RAR than in REQ soil. Lead applied at low concentrations (0.0–250.0 mg kg⁻¹) was mostly adsorbed in both soils. Adsorption of Pb²⁺ increased steeply with concentration in the equilibrium solution at the low concentrations for both soils, then the increase diminished at the equilibrium solution of Pb²⁺ concentrations >750.0 mg kg⁻¹ soil (Fig. 1). At the highest level of added Pb²⁺ (12 500.0 mg kg⁻¹), RAR soil adsorbed 79.7% of the applied Pb²⁺, as compared with 43.5% for REQ soil, probably due to its higher CEC, pH, and the presence of chlorite and illite minerals (Table 1). These results are in agreement with a previous report, suggesting that metal adsorption was more affected by clay type than the amount of clay (Appel and Ma, 2002). Other soil properties that are associated with metal

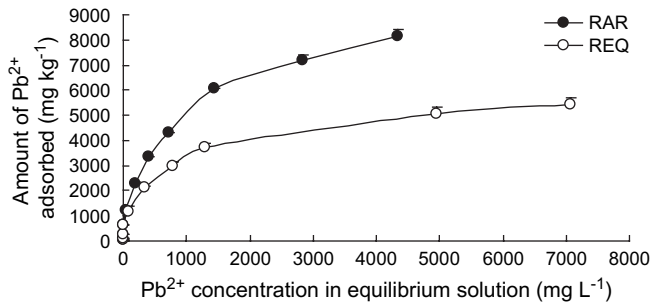


Fig. 1. Isotherms of Pb^{2+} adsorption in the two variable charge soils. Data are means of three replications.

adsorption (e.g., organic matter and clay content) may also influence metal adsorption through their relation to CEC (Hassett, 1974; Soldatini et al., 1976).

Lead adsorption in both soils may be described by the Langmuir, Freundlich, and Temkin equations (Table 2). The monolayer maximum adsorption (X_m) from the Langmuir equation is usually used for comparing potential adsorption capacity of different soils and soil components. The maximum adsorption (X_m) value was $10\,898.7\text{ mg kg}^{-1}$ for RAR soil and 6195.3 mg kg^{-1} for REQ soil.

Desorption of the adsorbed Pb^{2+} was very small in the $0.01\text{ mol L}^{-1}\text{ NaNO}_3$. Minimal desorption was detected even up to 625.0 mg kg^{-1} of Pb^{2+} applied. Lead desorption increased with increasing Pb^{2+} adsorption saturation for both soils, though with a lower rate. RAR soil desorbed less Pb^{2+} than REQ soil at the same Pb^{2+} concentrations. After five successive desorptions, the accumulative amounts of Pb^{2+} desorbed accounted for only 11.6% of the adsorbed Pb^{2+} for RAR soil and 18.7% for REQ soil.

3.2. pH effects

The amount of Pb^{2+} desorbed from the two variable charge soils were greatly affected by pH (Fig. 2). Generally, an increase in pH reduced Pb^{2+} desorption. Desorbability (% of Pb desorbed of the total adsorbed) of Pb^{2+} was greater in REQ soil than in RAR soil in all cases. In this experiment, desorption edge for Pb^{2+} was in the pH range of 2.0–4.0. The two tested soils behaved similarly, although the pH desorption edge of REQ soil was shifted to slightly higher pH values, as compared with RAR soil. It was also found that the desorption of Pb^{2+} decreased from nearly 100.0 to 20.0% within a narrow pH range, and then the decrease

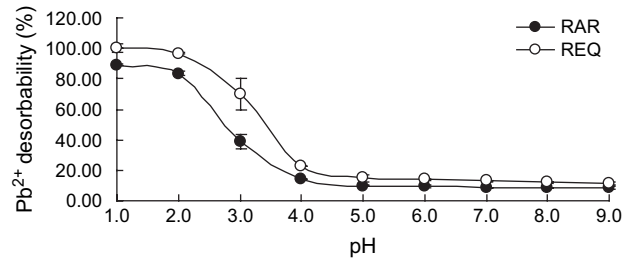


Fig. 2. Lead desorption as a function of pH. Data are means of three replications.

diminished at $pH > 4.0$ (Fig. 2). Approximately 50.0% of the adsorbed Pb^{2+} was desorbed at $pH < 4.0$. The desorbability of Pb^{2+} in RAR and REQ soils reached 50.0% at pH 2.9 and 3.4, respectively, reflecting that REQ soil needs less H^+ to desorb the same amount of adsorbed Pb^{2+} than RAR soil.

Lead desorption with increasing solution pH was characteristic of “S” pattern (Fig. 2). Desorption was maximum at low pH and decreased with the pH approaching a certain critical level. The desorption curve can be divided into three stages based on desorption rate: (1) the greatest desorption stage at $pH \leq 2.0$, with more than 80.0% of desorbability; (2) the desorption decreasing stage at $pH 2.0\text{--}4.0$, at which desorption of Pb^{2+} decreased considerably, with desorbability decreasing from 83.5 to 14.0% for RAR soil and 96.8 to 23.0% for REQ soil; (3) the precipitation and minimal desorption stage at $pH > 4.0$, at which the desorption rate leveled off. These results supported the previous findings in another aspect that increasing pH generally caused an increase in the metal adsorption (Elzahabi and Yong, 2001; Pagnanelli et al., 2003; Sun et al., 2001; Wang, 1991). It is reasonable to conclude that the magnitude of desorption varies with pH. There is no general agreement on a single mechanism responsible for this behavior, but strong adsorption of metal hydroxo complexes, hydrolysis of Al on exchange sites, competition of protons for adsorbing sites, and acid catalyzed dissolution of reactive oxide sites may be involved.

The difference in Pb^{2+} desorption behavior between these two soils can be interpreted in terms of the nature and properties of soil surfaces at low pH. This difference decreased with increasing solution pH, indicating that the nature of soil surface controls Pb^{2+} desorption at low pH, but with an increase in solution pH, other factors such as precipitation, may become dominant, rendering the difference in Pb^{2+} desorption between the two soils decreased.

Table 2
Isothermal characteristics of Pb^{2+} adsorption in the tested soils

Soils	Langmuir equation $1/X = 1/X_m + 1/(X_m K)1/C$			Freundlich equation $\log Y = \log K + 1/a \log C$			Temkin equation $Y = a + K \log C$		
	X_m (mmol kg^{-1})	K_L	r^2	a_f	K_F	r^2	K_T	a_t	r^2
RAR soil	52.6	2.1	0.98	2.3	250.6	0.98	3058.8	-3339.7	0.79
REQ soil	29.9	5.1	0.98	2.9	265.5	0.98	1791.7	-1934.3	0.94

RAR soil = red soil developed on Arenaceous rock (clayey, mixed siliceous thermic typic Dystrochrept), REQ soil = red soil developed on Quaternary red earths (clayey, kaolinitic thermic plinthite Aquult).

3.3. Organic acid effects

The batch desorption behavior of Pb^{2+} in RAR soil was similar to that of REQ soil (Fig. 3). The desorption of Pb^{2+} in two soils in the presence of 10^{-6} and 10^{-5} mol L^{-1} of different organic acids was almost the same. However, Pb^{2+} desorption was higher in the presence of citric or acetic acids than malic or oxalic acid at increased concentrations of each organic acid. This implied that desorption behavior of Pb^{2+} was related to the type and concentration of organic acid. The desorption of Pb^{2+} in the two soils decreased initially and then increased with the increase of citric, acetic, malic or oxalic acid concentration from 10^{-4} to 0.1 mol L^{-1} . A valley-like curve was shown for Pb^{2+} desorption as a function of organic acid concentration in desorption solution (Fig. 3). The amount of Pb^{2+} desorbed was 599.4 and 682.9 mg kg^{-1} , respectively, for RAR and REQ soils without organic acid. When citrate concentration in the

desorption solution increased from 10^{-6} to 10^{-5} mol L^{-1} , then to 10^{-1} mol L^{-1} , the amount of Pb^{2+} desorbed changed from 527.9 to 470.0 mg kg^{-1} , and then sharply increased to 5886.0 mg kg^{-1} for RAR soil. The same trend was found for REQ soil under the effect of citrate. Similarly, Pb^{2+} desorption initially decreased to 542.0 and 413.3 mg kg^{-1} , and then sharply increased to 5668.0 and 4301.2 mg kg^{-1} when acetic acid concentration in the desorption solution increased from 10^{-6} to 10^{-5} (for RAR soil) and 10^{-4} mol L^{-1} (for REQ soil), then to 10^{-1} mol L^{-1} for RAR soil and REQ soils, respectively. Greater inhibition of malic acid on Pb^{2+} desorption was found even at 10^{-4} mol L^{-1} for RAR soil and 10^{-3} mol L^{-1} for REQ soil, and the desorption of Pb^{2+} was still less than that without organic acid. As to oxalic acid, the amount of Pb^{2+} desorbed ranged from 468.2 to 522.0 mg kg^{-1} when oxalic acid concentrations in the desorption solution were $<10^{-2}$ mol L^{-1} , and then sharply increased to 2497.0 mg kg^{-1} , for RAR soil. Pb^{2+} desorption behavior of REQ soil was slightly different in the presence of oxalic acid. The amount of Pb^{2+} desorbed was less than that without oxalic acid when oxalic acid concentrations were $<10^{-4}$ mol L^{-1} , and increased at 10^{-4} and 10^{-3} mol L^{-1} oxalic acid, then decreased to 761.6 mg kg^{-1} at 10^{-2} mol L^{-1} oxalic acid. When oxalic acid concentration attained 10^{-1} mol L^{-1} , the amount of Pb^{2+} desorbed remarkably increased to 2404.0 mg kg^{-1} .

These results indicate that the presence of citric, acetic, malic, or oxalic acids at low concentrations ($\leq 10^{-3}$ mol L^{-1}) in desorption solution inhibits Pb^{2+} desorption in variable charge soils, whereas the presence of organic acids at higher concentrations ($\geq 10^{-3}$ mol L^{-1} for citric, acetic, or malic acid for both soils, and $\geq 10^{-2}$ mol L^{-1} for oxalic acid in RAR soil, but 10^{-4} mol L^{-1} for oxalic acid in REQ soil) enhances Pb^{2+} desorption. Most of the adsorbed Pb^{2+} was desorbed in the presence of 10^{-1} mol L^{-1} citric, acetic, and malic acids, and approximately half of the adsorbed Pb^{2+} was desorbed with oxalic acid.

Small amounts of organic acids added to soil are mostly adsorbed by organic and inorganic components in the soil, which may increase negative charge or CEC of the soil. Moreover, Pb^{2+} in desorption solution may be bound by organic ligands adsorbed on the surfaces of the soil (Huang and Bethelin, 1995), which leads to the reduction of Pb^{2+} desorption in the presence of low concentrations of organic acid. However, with the continuously rising organic acid concentrations in desorption solution, the ratio of organic ligand concentration in solution to the organic ligand adsorbed by the soil increases. An increased competitive ability of organic ligands in the solution for adsorbing sites with Pb^{2+} results in enhanced desorption with increasing organic acid concentrations above a certain level. The net effect on Pb^{2+} desorption is controlled by the relative binding strengths between the soil surface sites and the metal and the complex reactions between the organic acid and the metal (Wu et al., 2003a).

Krishnamurti et al. (1997) demonstrated that various LMWOAs were able to influence the release of heavy metals from different soils and increase their solubility in bulk soil through the formation of soluble metal–LMWOA complexes.

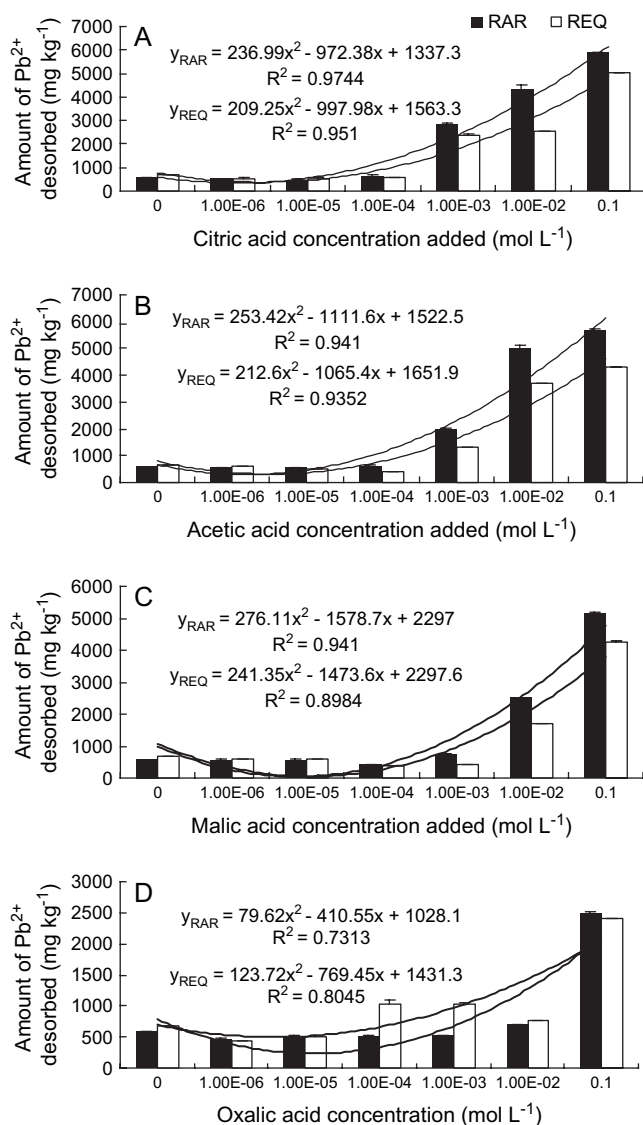


Fig. 3. Lead desorption as a function of organic acid concentrations. (A – citric acid; B – acetic acid; C – malic acid; D – oxalic acid). Data are means of three replications.

The organic ligands are not only adsorbed on the external surface, but also incorporated into the structural network of the soil. All of these factors significantly changed the kinetics of Pb^{2+} adsorption in variable charge soils. Hence, addition of organic acids, which chelate with Pb^{2+} and PbOH^+ , may result in smaller amounts of Pb^{2+} adsorbed onto soil surface. The stronger the chelator, the less Pb^{2+} is adsorbed, and correspondingly, more Pb^{2+} is desorbed. The $\log K$ of the four organic acids change in the order: citric acid (7.98) > oxalic acid (6.16) > malic acid (5.40) > acetic acid (1.6) (Xu et al., 2002). As the capacity of organic acid chelating with Pb^{2+} is parallel with the $\log(K)$, is the more stable of the complex, the more Pb^{2+} is desorbed. In this study, citric acid or acetic acid at high concentrations ($>10^{-2}$ mol L^{-1}) had the greatest improvement of Pb^{2+} desorption, followed by malic acid, and the smallest improvement of Pb^{2+} desorption was with oxalic acid. At low concentrations ($\leq 10^{-3}$ mol L^{-1}), each of the four organic acid provided a minimal increase in Pb^{2+} desorption.

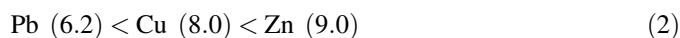
3.4. Copper and zinc effects

Some common trends were observed of Pb^{2+} desorption in the presence of Cu^{2+} or Zn^{2+} as a competitive cation. The desorption of Pb^{2+} increased greatly with the increase of added Cu^{2+} or Zn^{2+} (Fig. 4), from 9.9 and 15.9% to 83.8 and 98.2% with Cu^{2+} concentration increasing from 0 to 20 mmol L^{-1} for RAR and REQ soils, respectively. The corresponding value of Pb^{2+} desorption was 81.2 and 89.9%, respectively, for RAR and REQ soils in the presence of Zn^{2+} . Applied Cu^{2+} increased Pb^{2+} desorption more than Zn^{2+} at

the same concentration levels, implying that ion characteristic is a factor affecting metal adsorption and desorption.

Since Cu^{2+} and Zn^{2+} are bivalent cations at the same original solution levels, a correlation between ionic size and adsorption selectivity may be expected. For the ion exchange process, the strength with which cations of equal charge are held is generally inversely proportional to the unhydrated radii. Thus, the predicted order of selectivity based on unhydrated radii is Pb^{2+} (0.120 nm) > Zn^{2+} (0.074 nm) > Cu^{2+} (0.072 nm). Although the unhydrated radii of Cu^{2+} and Zn^{2+} are similar, the complexation of Cu^{2+} with soil is more stable than Zn^{2+} . Therefore, Cu^{2+} is more readily adsorbed onto soil surface and occupies more adsorption sites than Zn^{2+} , and as a result, more Pb^{2+} was desorbed by Cu^{2+} . The selectivity sequences observed for these soils support previous findings that the unhydrated radius may serve as a predictive index of metal adsorption.

For adsorption of hydrolysable metals onto various oxides, the pH at which the extent of adsorption is determined may be related to the pK of the first hydrolysis product of the particular metal. The studied metals are in order of increasing pK values (Baes and Messmer, 1976):



This suggests that at the same pH, there is more CuOH^- than ZnOH^- . This agreed with the previous finding that metal ion characteristic is the main factor determining the soil's affinity for the metal, and the sequence was $\text{Pb}^{2+} > \text{Cu}^{2+} > \text{Zn}^{2+}$ (Pagnanelli et al., 2003; Elliott et al., 1986).

4. Conclusion

Even in contaminated soils, most of the Pb^{2+} present as insoluble forms, precipitated or bound to the soil surfaces. In our study, Pb^{2+} was almost completely adsorbed in both RAR and REQ soils at low concentrations, and the results indicate that the variable charge soils have high fixation ability for Pb^{2+} . However, recent study indicates that although heavy metal such as Pb^{2+} was tightly adsorbed in the soil with very limited mobility, its activation may be caused by increased input and inadequate utilization of the soils.

The adsorption–desorption process is an important reaction in soil controlling Pb^{2+} mobility and bioavailability. The adsorption characteristics of lead in two tested soils (RAR soil and REQ soil) were well described by the Langmuir equation and Freundlich equation. Only a small percent of adsorbed Pb^{2+} was desorbed. At the highest Pb^{2+} loading, 11.6 and 18.7% of the total adsorbed Pb^{2+} was desorbed in RAR and REQ soils, respectively. pH was an important factor controlling Pb^{2+} desorption. Acidic environment (pH < 5.0) was favorable for Pb^{2+} desorption, and the desorbability of Pb^{2+} decreased with increasing solution pH. Organic acids can also remarkably influence the desorption behavior of Pb^{2+} in both soils. Low concentrations of organic ligands inhibited Pb^{2+} desorption, whereas at higher concentrations enhanced Pb^{2+} desorption. In this study, citric acid or acetic acid at

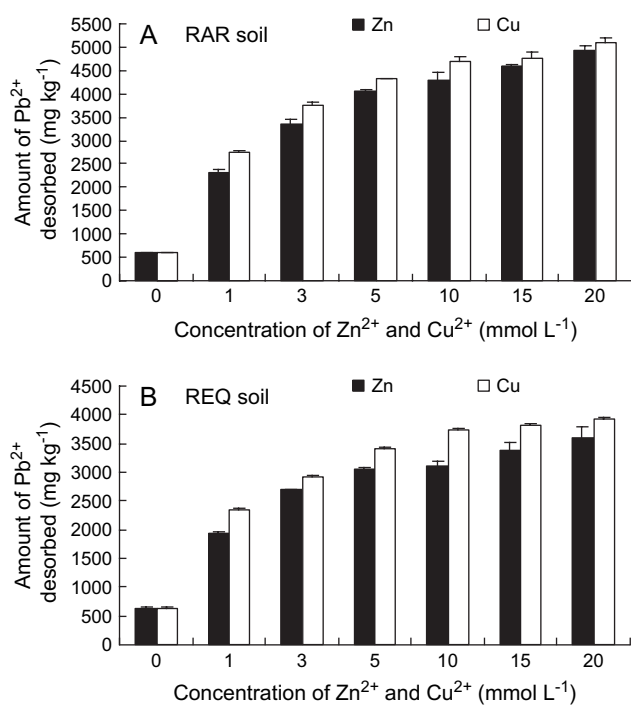


Fig. 4. Lead desorption as a function of competitive ion concentrations. (A – RAR soil; B – REQ soil). Data are means of three replications.

high concentrations had the greatest improvement of Pb^{2+} desorption, followed by malic acid and oxalic acid. And desorption of Pb^{2+} can also be effected by the presence of Cu^{2+} or Zn^{2+} . The results show that the desorption of adsorbed Pb^{2+} increased greatly with increasing concentrations of added Cu^{2+} or Zn^{2+} , and applied Cu^{2+} increased Pb^{2+} desorption more than Zn^{2+} at the same concentration levels.

Finally, it should be realized that these data apply only for acid soil conditions where adsorption is more important than precipitation processes in removing metal ions from solution. For near neutral and alkaline soils, solubility and complexation reactions may be superimposed on adsorption processes, thereby complicating the prediction of relative retention of heavy metals.

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