Organic acids influence on lead adsorption onto variable charge soils in China

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Abstract

Little information is available on influence of organic acid concentrations and addition sequence of organic acids/Pb on Pb adsorption onto variable charge soils. The influence of addition sequence of organic acids/Pb on Pb adsorption to soil is significant to evaluate the physicochemical behavior of Pb in the rhizosphere and natural environment. The influence of organic acid types and concentrations is important to evaluate the impact of organic acids on adsorption of lead, which will contribute to our knowledge of the impact of organic acids in alleviating environmental pollution resulting from lead in contaminated soils. Batch equilibrium experiments were conducted to investigate lead (Pb) adsorption onto four variable-charge soils, a Yellow brown soil (YBS), Red soil (RS), Latosol soil (LS), and Lateritic red soil (LRS) in the presence of different types and concentrations of organic acids. In order to check for the reversibility of the adsorption process, the adsorption of Pb in Pb- Organic acid – Soil systems for three addition sequence are investigated. Results showed that addition of organic acid increased adsorption of Pb onto soils. Pb adsorption decreased with increasing concentration of citric acid from 0.2 – 5 mmol/L. However, the least amount was higher than when no organic acid was added. The effect of addition sequence of organic acids/ Pb(II) on the adsorption of Pb(II) to soils were also studied. From our results the adsorption of Pb(II) was influenced by organic acid types, concentrations and addition sequence. Addition of organic acids after lead and addition of lead and organic acid at the same time resulted in higher adsorption than when organic acids were added before lead. At lower concentrations, adsorption of Pb in the presence of organic acids was almost the same, but at the highest concentration (5 mmol/L) adsorption percentage was least in the presence of citric acid.

Keywords: Adsorption of lead; Variable charge soils; Organic acids; Addition sequence

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1. Introduction

Heavy metal pollution in soils is a major environmental concern in the world and in China particularly as a result of the rapid industrialization of that nation (Chen et al., 2007). Considerable amounts of lead have accumulated in soils all over the world due to anthropogenic activities in the last decades. This metal is highly toxic for human and animals, hence recognizing its behaviour in soils is essential. In acidic soils, the complex or chelate formation may play an important role in the movement of lead (Sipos et al., 2005), primarily in colloidal form (Denaix et al., 2001).

The effect of lead in rhizosphere soil has received increased attention in recent years (Gao et al., 2003; Hu et al., 2007; Huang et al., 2010). Low molar mass organic acids (LMMOAs) such as acetic acid, tartaric acid, citric acid and oxalic acid, are widely spread in rhizosphere soil that are derived from the decomposition of plants and animal residues, microbial metabolism, canopy drip and root activity (Huang et al., 2003; Hu et al., 2007). LMMOAs function as ligands to increase the total amount of dissolved cations in soil solution by forming complexes with metal cations (Wang et al., 2009). LMMOAs are known to play an important role in the detoxification or phytoextraction of potentially harmful elements such as Al, Cd, Cu, Pb, Zn (Dytrtova et al., 2009). The acids are known to influence adsorption of non metal elements such as phosphorus by variable charge minerals and soils through proton and ligand-promoted reactions (Li et al., 2006; Wei et al., 2009). Since rhizosphere soil is a favorable habitat for acid-producing bacteria, the concentrations of LMMOAs in the immediate vicinity of plant roots are much higher than in the bulk soil (Chen et al., 2006; Hu et al., 2007). The abundance of non volatile aliphatic acids in rhizosphere soil also leads to an increase in negative charge and a decrease in positive charge in variable charge soils in the pH range 3.5 - 5.5. This phenomenon affects the adsorption, desorption, precipitation and dissolution reactions of heavy metals and hence their mobility in both soil and solution (Xu et al., 2003). Organic ligands do not always reduce adsorption of heavy metals to soil (Schwab et al., 2004). Adsorption of organic anions can increase negative charge on soil surface (Barrow, 1985), thus providing more sites for metal adsorption. In some cases, organic ligands have increased heavy metal adsorption to soils (Chairidchai and Ritcie1990).

Plants have been used for decades for stabilization of disturbed and contaminated sites, and plant – based remediation technologies are receiving broad acceptance (Lasat, 2002). One of the mechanisms by which plants are able to reduce toxicity from heavy metals in soils is the exudation of organic acids. Specific organic acids can sequester heavy metals and protect the roots from toxicity effects (Jones et al., 2003; Liao and Xie 2004). The concentration of organic acids in soil solution is normally less than 1 mM and variable (Jones et al., 2003). The most commonly reported organic acids exuded by plants are those that participate in the tricarboxylic acid cycle such as citric, succinic, malic, and cis-aconilic acids. Aliphatic acids including formic, acetic, propionic, butyric, oxalic, and tartaric acids. The concentration of organic acids is generally in the range of 1 - 0. 01 mM (Sposito, 1989), but higher concentrations of organic acids can be found under litter (Robert and Berthelin, 1986). Therefore, an understanding of the impact of organic acids that are found in the rhizosphere would contribute significantly to our knowledge of the impact of plants in polluted environments.

In vegetated soil, the effects of soluble organic ligands on the adsorption of heavy metals to soil may be important because plant roots and soil organisms continually produce organic acids throughout their life cycles. Some of these organic acids are very strong complexing agents for metals, but the influence of the organic ligands on heavy metal adsorption is not completely understood (Schwab et al., 2005). In heavy metal-contaminated soil, vegetation can significantly affect metal adsorption and hence mobility (Schmidt, 2003).

Adsorption is a major process responsible for accumulation of heavy metals. Therefore the study of adsorption process is of utmost importance for the understanding of how heavy metals are transferred from a liquid mobile phase to the surface of a solid phase (Bradl, 2004). Adsorption/desorption and precipitation/dissolution reactions control heavy metal accumulation in the soil profile, metal transport to groundwater, and bioavailability for plant uptake. Quantifying sorption is a critical aspect of predicting chemical behavior of a metal in soils (Schwab, 2005). Adsorption can be affected by many factors such as pH (Stahl and James, 1991), cation exchange capacity, insoluble organic matter and clay content (McBride and Blasaik, 1979), competition from other metal ions (Covelo et al., 2004), and soluble organic and inorganic ligands (McLean and Bledsoe, 1992; Bradl, 2004). The presence of soluble organic ligands in soil may significantly influence metal adsorption through the formation of stable complexes (Chairidchai and Ritchie, 1990; McLean and Bledsoe, 1992).

Humid tropic soils (Oxisols, Ultisols, Andisols and acid Alfisols) cover nearly 22 % of the earth's surface. These soils are mainly made up of minerals and amorphous colloids having amphoteric surfaces. This poses far-reaching implications in management of soils for agricultural purposes as well as retention of ionic soil contaminants (Naidu et al., 1997). Variable charge soils are dominant soils in tropical and subtropical regions. Variable charge soils are dominant soil in tropical and subtropical regions. To date, investigation on the effect of LMMOAs on adsorption of heavy metals ions have focused more on clay minerals such as vermiculite, montmorillonite and palygorskite (Sirvani et al., 2006; Abollino et al., 2007), iron (hydr) oxide minerals (Collins et al., 1999; Violante et al., 2003), while little information is available on variable charge soils (Hu et al., 2005; 2007; Schwab et al., 2005).

Despite the extensive investigations on influence of organic acids on the adsorption of heavy metals (Hu et al., 2005; 2007; Huang et al., 2010; Li et al., 2001; Schwab et al., 2005) onto soil and clay minerals, according to our literature survey, there is still little information with respect to influence of addition sequence on the adsorption of heavy metal ions. In addition, adsorption of heavy metals had been found to be influenced by addition sequence (Bryce et al., 1994). Contrarily, Tan et al. (2008) found that different addition sequence of nickel have no obvious influences on the adsorption of Ni(II) on oxidize multi-walled carbon nanotubes. This hypothesis has been tested only on a limited basis and has not been tested on natural soils like variable charge soils. However, it should be noted that either lead or organic acid may exist in the soil first before the other.

In this study we investigated the effects of organic acids on adsorption of Pb(II) onto variable charge soils by varying experimental conditions, viz. organic acid types, organic acid concentrations, addition sequence. Pb was chosen, which is among priority pollutants of the USEPA'S list and is also a major pollutant among

various toxic metals in China in particular and the world in general. Citric, tartaric, oxalic and acetic acids were chosen as the representative of organic acids commonly existing in the soils because they are the main components present in the rhizosphere microenvironment and plant exudates. (2) We checked the reversibility of the adsorption process.

2. Materials and methods

The soil samples used in this study include four acidic soils, one Alfisol; yellow brown soil (YBS), one Ultisol; red soil (RS) and two Oxisols; latosol soil (LS) and lateritic red soil (LRS) classified as Argosol and Ferralosols in China Taxonomy, located in Hubei, Hainan and Guangxi provinces, China. They possessed lower content of organic matter and higher amounts of free iron oxide (Table 1). These soils with contrasting properties were sampled at 0 – 20 cm depth. Samples of these soils were air-dried, ground, and sieved through 2-mm mesh and homogenized prior to use.

Citric, tartaric, oxalic and acetic acids used were high-grade analytically pure reagents. Pb used was in the form of $Pb(NO_3)_2$.

Table 1. properties of the soils tested

soil	pH (H_2O)	O.M [z] g kg	CEC [y] g kg^{-1}	Clay (<0.002mm) g kg^{-1}	Clay minerals	Crystal Fe [x] g kg^{-1}	Crystal Al [w] g kg^{-1}	PZC [v]
YBS	5.19	10.84	27.42	256.5	I(45),V(25), K (30)	15.98	1.29	2.96
LS	4.46	13.14	15.89	415.9	K(75),HIV(15), GE	84.03	5.20	4.05
RS	4.19	6.22	20.89	359.6	V(35),K(40),I(25)	21.29	2.28	3.80
LRS	4.12	9.92	21.87	361.2	K(80),GE(20)	20.98	2.06	

YBS = yellow brown soil, LS = latosol soil, RS = red soil, LRS = lateritic red soil.

[z]O.M = organic matter, [y] CEC = cation exchange capacity, [x] crystal Fe = crystalline Iron, [w]crystal Al = crystalline aluminium.

I = illite, V = vermiculite, K = kaolinite, HIV=hydroxyinterlayer vermiculite, GE= goethite. Data in the parentheses are the contents (%) of the corresponding minerals.

[v] PZC = point of zero charge (Li et al., 2001; Hu et al., 2007)

2.1. Adsorption of lead in the presence of different types of organic acids

1 g of air-dried YBS soil was placed into 50 ml polypropylene centrifuge tubes, and 20 ml of 0.01 mol L^{-1} KCl (pH 5.5±0.1) solution containing 400 mg L^{-1} Pb and 0.2 or 5 mmol/L organic acid with pH adjusted to 5.5±0.1 was added to soil. The suspension was adjusted to 5.5±0.2. The suspensions were shaken at 230 rpm for 2 h, at 25℃±0.1. The suspensions were centrifuged at 5000g for 10 min and filtered through a 0.45 μm of cellulose nitrate membrane. The Pb^{2+} concentration in the filtrates were measured using the atomic absorption spectrophotometer (AAS) (computed- aided Varian AA 240FS). The amount of adsorbed Pb^{2+} was calculated by the difference between the total applied Pb^{2+} and the amount of Pb remaining in the equilibrium solution.

2.2. Adsorption of lead in the presence of different concentrations of organic acids

1 g of air-dried soil was placed into 50 ml polypropylene centrifuge tubes, and 20 ml of 0.01 mol L^{-1} KCl (pH 5.5±0.1) solution containing 400 mg L^{-1} Pb and organic acid with different concentrations (0 -5.0 mmol L^{-1}, with pH adjusted to 5.5±0.1) were added to soil samples using soil/solution=1:20.The suspensions were adjusted to 5.5±0.2. The suspensions were shaken, equilibrated, centrifuged, and Pb in the supernatant was determined as described above.

2.3. Adsorption of lead at different addition modes of organic acids

1 g of air-dried soil was placed into 50 ml polypropylene centrifuge tubes, and 10 ml of 0.01 mol L^{-1} KCl (pH 5.5±0.1) solution containing 400 mg L^{-1} Pb and 10 ml of organic acid solution of different concentrations (0, 0.2, 0.5, 1.0, 2.0, and 5.0 mmol L^{-1}) were added. Experiments were conducted as follows; (1) addition of organic acid after Pb adsorption (AO AF Pb); (2) addition of Pb after organic acid adsorption (Pb AF AO) and (3) addition as a mixture of Pb and organic acid (AO & Pb).

(1) 10 ml of 0.01 mol L^{-1} KCl solution containing 400 mg L^{-1} Pb was added to soil and the solution was adjusted to 5.5±0.2. The suspensions were shaken at 230 rpm for 2 h, at 25℃±0.1. 10 ml organic acid solution (pH 5.5±0.1) was added and then equilibrated for additional 22 h. The suspensions were centrifuged at 5000g for 10 min and filtered through a 0.45 μm of cellulose nitrate membrane The Pb^{2+} concentration in the filtrates were measured using the atomic absorption spectrophotometer (AAS) (computed- aided Varian AA 240FS). The amount of adsorbed Pb^{2+} was calculated by the difference between the total applied Pb^{2+} and the amount of Pb remaining in the equilibrium solution.

(2) 10 ml organic acid solution was added to soil and the solution was adjusted to 5.5±0.2. The suspensions were shaken at 230 rpm for 2 h, at 25℃±0.1. 10 ml of 0.01 mol L^{-1} KCl (pH 5.5±0.1) solution containing 400 mg L^{-1} Pb was added and then equilibrated for additional 22 h. The suspensions were centrifuged at 5000g for 10 min and filtered through a 0.45 μm membrane. The Pb^{2+} concentration in the filtrates were measured using the atomic absorption spectrophotometer (AAS) (computed- aided Varian AA 240FS). The amount of Pb^{2+} adsorbed was calculated as previously stated.

(3) 10 ml organic acid solution and 10 ml of 0.01 mol L^{-1} KCl solution containing 400 mg L^{-1} Pb were added together to soil and the solution was adjusted to 5.5±0.2. The suspensions were shaken at 230 rpm for 2 h, at

25°C ±0.1 and then equilibrated for additional 22 h. The suspensions were centrifuged at 5000g for 10 min and filtered through a 0.45 μm membrane. The Pb^{2+} concentration in the filtrates were measured using the atomic absorption spectrophotometer (AAS) (computed- aided Varian AA 240FS). The amount of Pb^{2+} adsorbed was calculated as previously stated.

2.4. Organic acids

Citric, oxalic, tartaric and acetic acids are chosen as the representatives of low molecular weight organic acids (LMWOAs) present in the rhizosphere.

2.5. Statistical analysis

All statistical analyses were carried out with Microsoft Excel, SAS and sigmaplot10. The data was analyzed by ANOVA considering the soils, treatments and replicates as the independent variables. Duncan test was used to detect the significant difference between means of different soils.

3. Results

3.1. The effect of organic acid types on lead adsorption by acidic soils

When 0.2 or 5 mmol L^{-1} organic acids were added to YBS together with Pb, adsorption quantity increased from 6583 mg kg^{-1} (82.3 %) to 7878 mg kg^{-1} (98.5%) - 7943 mg kg^{-1} (99.3%) and 6706 mg kg^{-1} (83.8%) - 7961 mg kg^{-1} (99.5%), and the increment reached 16.2% -17.1% and 1.5 % - 17.2%, respectively (Figure 1). At 0.2 mmol L^{-1} the increment was the least in the presence of acetic acid among the four kinds of organic acid examined. The order of increment was: tartaric > citric > oxalic > acetic acid. However, there was no significant difference in the increment in the presence of all organic acids. At 5 mmol L^{-1}, the increment was the least in the presence of citric acid among the four kinds of organic acid examined. The order of increment was: tartaric > oxalic > acetic > citric acid. There was no significant difference in the increment in the presence of tartaric, oxalic and acetic acid.
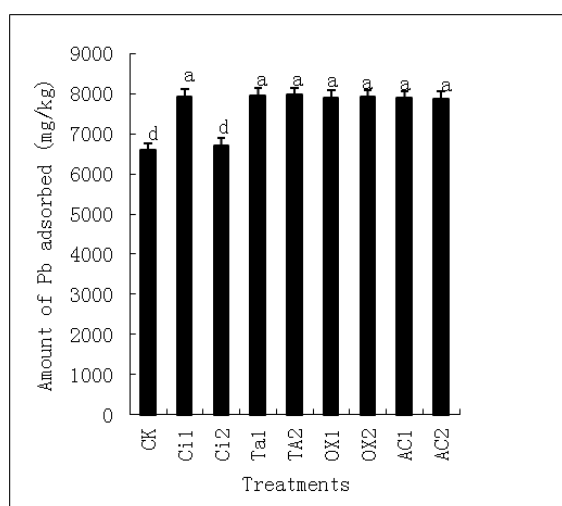

Figure 1. The effect of organic acid types on lead adsorption ontoYellow brown soil. CK, Ci, Ta, Ox and AC were abbreviations for check, citric, tartaric, oxalic and acetic acids. The numbers 1 and 2 meant 0.2 and 5 mmol L^{-1} organic acid

3.2. The effect of concentration of organic acid on Pb adsorption by acidic soils

The degree of increment in Pb adsorption in the presence of organic acids depended on the concentrations of the organic acids. The greater the organic acid concentration added, the higher the increment in Pb adsorption in tartaric, oxalic and acetic acid in the tested soils except LRS. The greater the organic acid concentration added, the lesser the increment in Pb adsorption in citric acid in the tested soils (Figure 2).
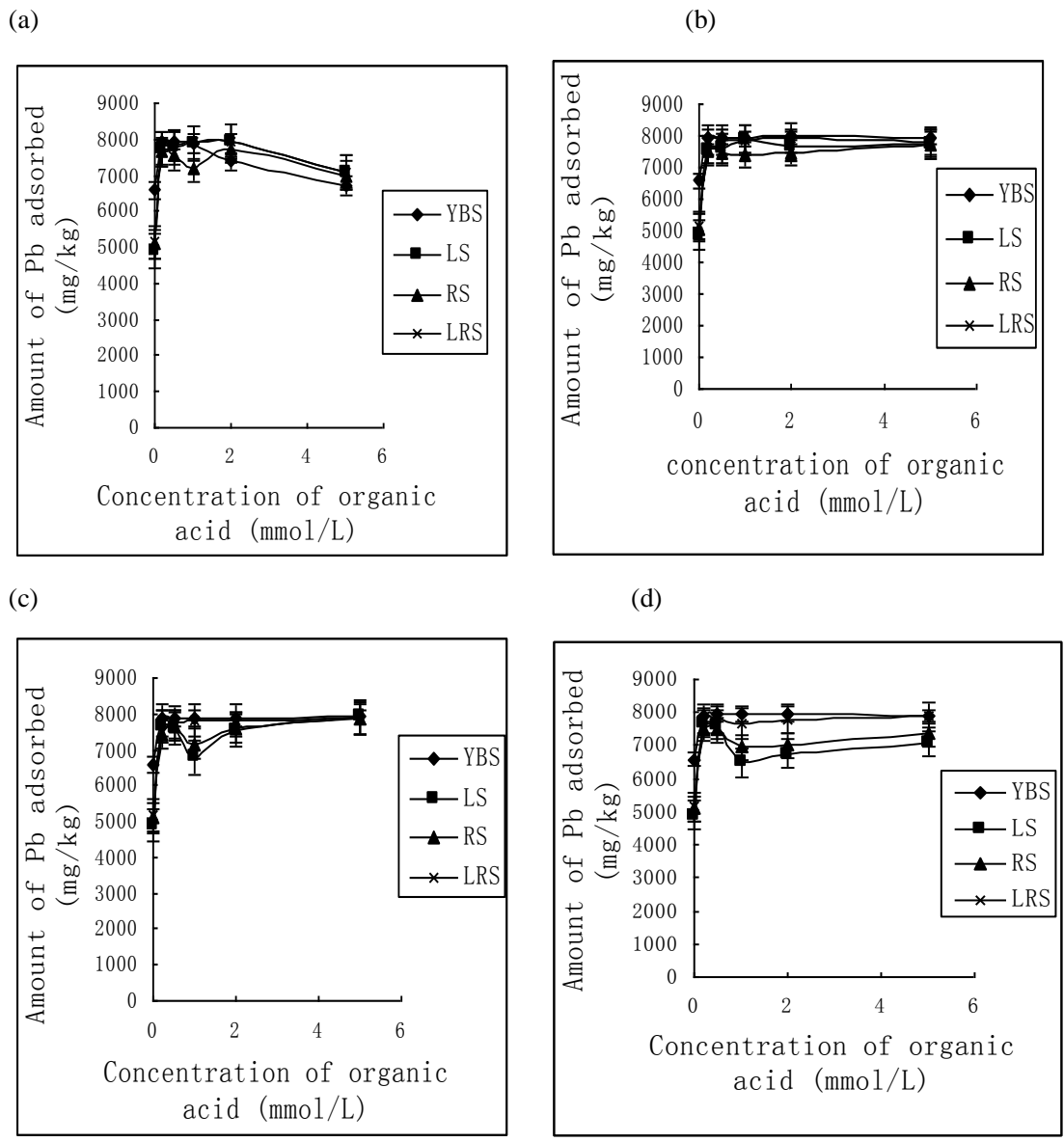

Figure 2. Effects of organic acid concentrations on adsorption of Pb onto soils (a) citric acid; (b) tartaric acid; (c) oxalic acid; (d) acetic acid.

YBS, LS, RS, LRS were abbreviations for yellow brown soil, latosol soil, red soil, and lateritic red soil

When the solution containing organic acids with pH 5.5 and 400 mg L^{-1} Pb was added to the tested soils, if the organic acid concentration was 0.5 mmol L^{-1} in the solution, the increment of Pb adsorption on five soils would range from 17.1 % - 36% for citric acid, 17.1% - 33.8% for tartaric acid, 16.3% - 33.8% for oxalic acid and 17.3 - 34.2% for acetic acid respectively. Most increment occurred with LS, the least on YBS for the same kind and concentration of organic acid, probably positively related to the content of crystal iron and negatively to the CEC and pH (Table 1). However when their concentrations were increased to 5 mmol L^{-1}, the increment were 1% - 27.3% for citric acid, 17.7% -35.8% for tartaric acid, 16% - 37.7% for oxalic acid and 15.6% - 34.1% for acetic acid. These results imply that there was competition between organic acid and Pb for soil surface. Generally, at lower concentration of organic acid adsorption of Pb in the presence of organic acid was almost the same.

3.3. The influence of addition way of lead and organic acids

The amount of Pb adsorption by YBS, LS, RS, and LRS were 6583 mg kg^{-1} (82.3 %), 4895 mg kg^{-1} (61.2 %), 5097 mg kg^{-1} (63.7 %), and 5154 mg kg^{-1} (64.4 %) when 400 mg/L Pb was added alone. When 0.2 and 5 mmol/L organic acids were added, the amount of Pb adsorption increased, and the increment percentage was influenced by the way in which Pb and organic acids were added. Figure 3 shows the adsorption of Pb by soils in different ways of addition. There was no significant difference in Pb adsorption in LS, RS and LRS (Figure 3). In YBS in the presence of citric acid at lower concentration (0.2 mmol L^{-1}), when organic acid was added after Pb the percentages of Pb adsorption by soil was 99.1%. However when Pb was added after organic acid the percentages of Pb adsorption by soil was 97.2%. When Pb was added together with organic acids the percentages of Pb adsorption by soil was 99.1%. Generally, when organic acids were added after Pb the percentages of Pb adsorption by soil were higher than when Pb was added after organic acids. When Pb was added together with organic acids, the percentages of Pb adsorption by soils were almost the same with that of when organic acids were added after Pb. At all concentrations of organic acid and in all the soils, the adsorption percentage of Pb was lowest when Pb was added after organic acids (Figure 3).

4. Discussion

Lead adsorption by the soils in the presence of citric, tartaric, acetic and oxalic acids as well as different addition sequence namely; addition of organic acid after Pb adsorption, addition of Pb after organic acid adsorption and addition of organic acid and Pb together showed noticeable differences. Increase in adsorption in the presence of organic acids compared to absence of organic acids could be attributed to increase in the negative charge on soil surfaces which provide more sites for metal adsorption. This result is consistent with Barrow (1985) and Chairidchai and Richie (1990) that adsorption of organic anions increased the negative charge on soil surfaces. Variable charge soils, however, had both positively and negatively charged surfaces, depending on the pH of the solution.
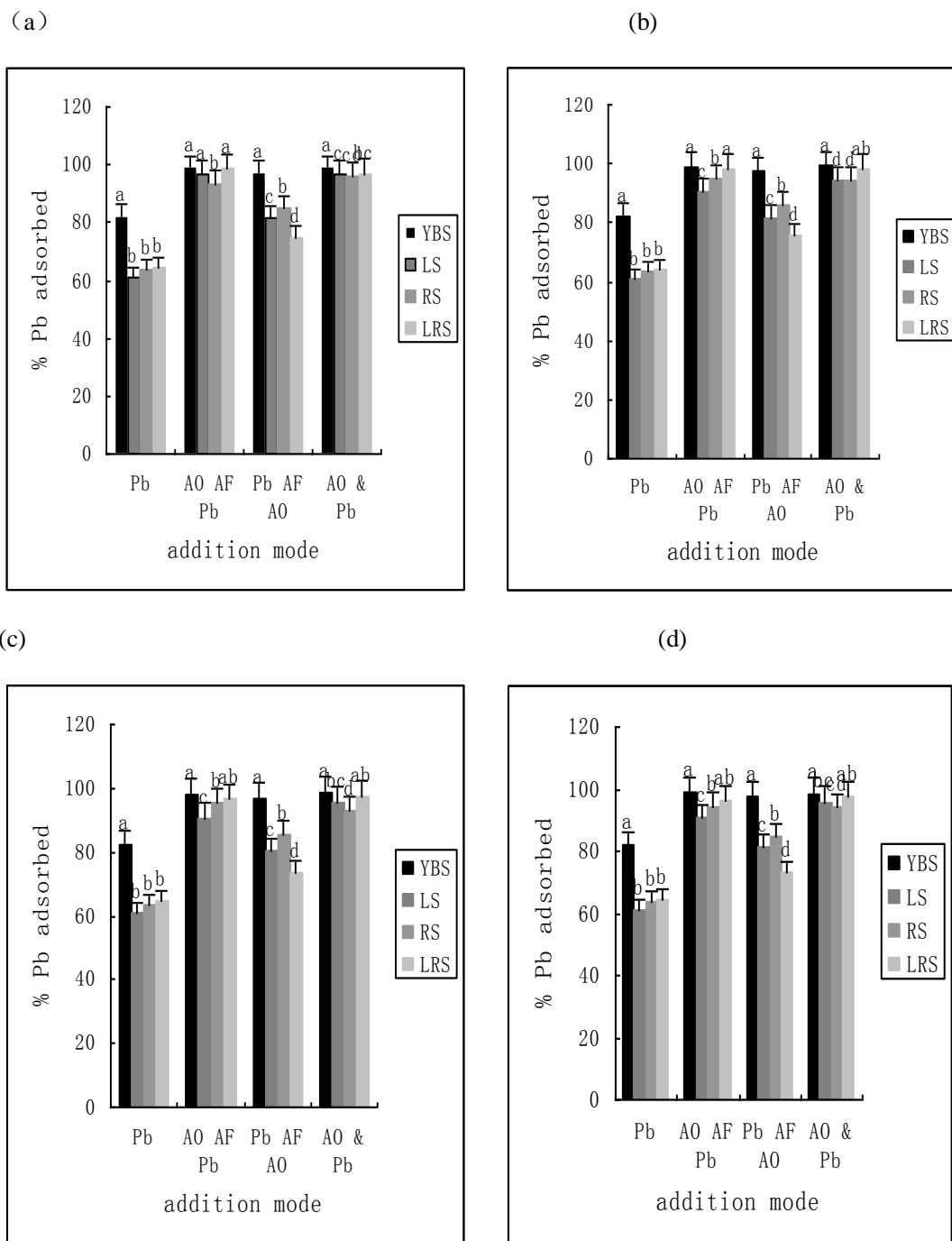
（a）

（b）

(c)

(d)

Figure 3. Effect of different addition mode of Pb and organic acids on Pb adsorption onto soils at 0.2mmol/L. (a) citric acid; (b) tartaric acid; (c) oxalic acid; (d) acetic acid.

The surface of negative-charge minerals was favorable for Pb, but in the presence of lower concentrations of organic acids, adsorption of organic acids may produce new adsorption sites for Pb and increase the negative charge (Hu et al., 2005), all of which would increase adsorption of Pb by the soils. This explains the higher adsorption percentage of Pb in the presence of citric acid as it is a strong complexing agent. However at higher concentrations of organic acids, the organic acids remaining in solution might compete with Pb for soil surface sites thus explaining the decline in adsorption percentage of Pb in the presence of citric acid a strong complexing agent. Presence of tartaric, oxalic, and acetic acids increased adsorption percentage slightly at higher concentrations. This could be due to their adsorption in the soils, which increased the negative charge of the soil surface, or production of adsorption sites for Pb. Increased Pb adsorption with increasing concentration of tartaric, oxalic, and acetic acids suggests that these organic acids tends to form a tertiary surface complex that successfully compete for Pb against any tendencies to form solution complexes. The adsorption of oxalic acid onto soils is great. The adsorbed oxalic acid may increase the content of organic matters, which could enhance adsorption of heavy metals (Stobel et al., 2001). The ability of Pb to remain relatively immobile in soil even in the presence of a strong complexing agent such as citric acid was also observed by Schwab (2005). In other aspect, the little amount of organic acids added to soils would be mostly sorbed by soil organic matter and soil clay minerals. Moreover, Pb ion in adsorption solution would be bound by organic ligands sorbed to the soil, which on the whole, will lead to the increment of Pb adsorption in the presence of low concentrations of organics (Huang and Bethelin, 1995).

According to the amount of Pb adsorbed in the presence of different organic acids, the organic acids examined could be divided into two types. One type, such as citric acid reduced the amount/percentage of Pb adsorption with increased concentration; the others such as tartaric, oxalic and acetic acids increased slightly the amount/perecentage of Pb adsorption with increasing concentration. This implies that the ability of organic acid for reducing Pb adsorption was related to the number of carboxylic functional group in each organic acid molecule, i.e tricarboxylic acid > dicarboxylic acid > monocarboxylic acid. There was also a similar effect on Pb adsorption among carboxylic acids with different molecular weight and different number of carboxylic functional group in a molecule such as oxalic and tartaric acids. In general dicarboxylic acids show the same chemical behavior and reactivity as monocarboxylic acid. Strong adsorption and limited mobility for Pb is commonly reported (McLean and Bledsoe, 1992; Camobreco et al., 1996). Citric acid has been reported to be the most effective in mobilizing heavy metals (Schwab et al., 2008). Although Pb can form soluble complexes with organic acids, these complexes may be strongly adsorbed by soil matrix and have little mobility (Schwab et al., 2005). Lead adsorbed strongly to soil particles, and complexing agents and low pH do not significantly enhance its mobility.

The way of organic acid addition was able to influence Pb adsorption due to the competition for surface site between organic acids and lead ion. If lead was added first, Pb could occupy surface site more easily. In this case, the addition of organic acids only resulted in the desorption of lead which was adsorbed weakly to the surface, so the maximum adsorption of lead ion occurs. On the contrary, if Pb was added after organic acid adsorption, organic acid would have occupied surface sites first, then Pb was adsorbed through desorption of some organic acid, so that a maximum reduction of Pb adsorption occurs. If Pb was added together in combination with organic acid, either of them could arrive at the adsorption sites at a different

speed. The binding sites could also trap these ligand ions in a different or similar way. Therefore, the amount of Pb adsorbed depended on the concentration ratio of organic anion to Pb and the relative affinity.

The reason for the difference between the effect of organic acids on Pb^{2+} ion sorbed by soils may be as follow: The molecular weight, functional groups, ability of forming complexes with heavy metals and the complex stable constant of citric acid is stronger than that of the other organic acids. Secondly, more ligands of citric acid added remain in solution than the other organic acids did, the competition of Pb^{2+} ion with citric acid was stronger than that of other organic acids (Li et al., 2001).

5. Conclusions

The present study showed that the effect of organic acids on Pb^{2+} ion adsorption was influenced by organic acid kinds, concentration and way of organic acid addition. The adsorption behavior of Pb was correlated with organic acid types, and concentration, although soil properties were different. Adsorption of Pb^{2+} ion and organic acid depended on the relative affinity in the surface group at different conditions. It seemed that the soil surface for adsorbing Pb^{2+} ion and organic acid could be similar, although the surface sites might have different energy states. The study suggested that the presence of citric acid in soil at higher concentration (≥ 5 mmol L^{-1}) may mobilize Pb whereas the presence of other organic acids would not. The adsorption of Pb^{2+} is dominated by the interaction of Pb^{2+} with surface sites of soils, by the interaction of Pb^{2+} with surface adsorbed organic acids on soils surface and by interaction of with organic acids in solution.

In order to reduce the availability of Pb in the environment and alleviate environmental pollution resulting from Pb^{2+} ion, the competition between Pb^{2+} ion and organic acids should be considered.

Acknowledgement

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