

Effects of pH and low molecular weight organic acids on competitive adsorption and desorption of cadmium and lead in paddy soils

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Abstract The bioavailability and ultimate fate of heavy metals in the environment are controlled by adsorption–desorption process. Batch equilibrium experiments were performed to assess the effects of pH and low molecular weight organic acids (LMWOAs) on competitive adsorption and desorption of cadmium and lead in paddy soils from China. The results indicated that both soils exhibited greater sorption capacity for lead (Pb) (1.37–1.61-fold) than cadmium (Cd) as estimated by the maximum sorption parameter (Q) from the Langmuir equation. The Langmuir bonding energy coefficient (b) and distribution coefficient (K_d) were greater for Pb than for Cd, furthermore, b_{binary} and $K_{d \text{ single}}$ were greater than b_{single} and $K_{d \text{ binary}}$, indicating that competition for sorption sites promote the retention of both metals on more specific sorption sites. Both Cd and Pb desorption as a function of solution pH was characteristic of “S” pattern. The presence of LMWOAs inhibited Cd or Pb desorption at the low concentrations ($\leq 0.1 \text{ mmol L}^{-1}$) but

promoted Cd and Pb desorption at higher concentrations ($\geq 0.5 \text{ mmol L}^{-1}$ for citric acid and $\geq 1 \text{ mmol L}^{-1}$ for malic and oxalic acid). The two paddy soils had a greater d_{Cd}^* than d_{Pb}^* in the presence of LMWOAs, indicating that Cd desorption was more affected by the presence of LMWOAs in binary metal system.

Keywords Cadmium · Competitive adsorption–desorption · Lead · pH · LMWOAs

Introduction

Soil contamination by heavy metals is increasingly concerned worldwide because of the potential threat to ecosystem functions and human health (Alloway 1995). Cadmium (Cd) and lead (Pb) are toxic metals, often occurring together at contaminated sites (Covelo et al. 2007; Khan et al. 2000). Anthropogenic activities in modern society including mining, smelting, land application of sewage sludge, fertilization, and reclaimed water irrigation have accelerated soil contamination by heavy metals (Khan et al. 2000; Nigam et al. 2001). The solubility and bioavailability of heavy metals in soil vary considerably, depending on the nature of adsorption–desorption processes (Krishnamurti et al. 1999). The study of adsorption–desorption processes is important for understanding the bioavailability, phytotoxicity, and the ultimate fate of the metals in the environment (Sparks 1995).

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Previous studies mainly focused on the sorption of these metals on various soil materials under different experimental conditions in a single metal system (Gomes et al. 2001; Saha et al. 2005; Serrano et al. 2005). Soil pH, temperature, ionic strength, time, and competing metals were reported to be important factors that influence the sorption and desorption of heavy metals in soils (Gurel 2006; Vega et al. 2006). The adsorption of metals is generally acknowledged to be directly proportional to soil pH. As soil pH increases, the retention of the heavy metal cations to soil surfaces increases via adsorption, inner-sphere surface complexation, and/or precipitation and multi-nuclear type reactions (Sparks 1995; Vega et al. 2006). The two empirical models that are most frequently used for describing heavy metal adsorption in soils are Freundlich and Langmuir isotherms (Atanassova 1999; Welp and Brummer 1999). In fields, soils are often simultaneously contaminated by several metals, which compete with each other for sorption sites. The competitive sorption–desorption has a profound effect on the bioavailability, phytotoxicity, and leachability of these metals (Covelo et al. 2004; Gomes et al. 2001). The effect of competitive sorption on individual metal behavior has been studied (Bradbury and Baeyens 2005; Christl et al. 2005; Serrano et al. 2005; Tsang and Lo 2006), but the development of consistent and predictive models that can be applied to describe multiple metal–soil systems is still lacking. Studies have been conducted to understand competitive adsorption of heavy metals on minerals (Saha et al. 2002), organic compounds (Saha et al. 2005), and acid soils (Gomes et al. 2001; Naidu and Harter 1998; Serrano et al. 2005); however, their practical applications are limited when applied to soils containing multiple competitive cations (Serrano et al. 2009). Limited effort has been made to model the adsorption–desorption of multiple heavy metals, especially in paddy soils. In addition, previous work mainly focused on adsorption process, with much less information available on the desorption process.

Low-molecular weight organic acids (LMWOAs) widely occur in water and soil as natural products of root exudates, microbial secretions, and decomposition of plant and animal residues. Low-molecular weight organic acids are of particular importance due to their metal chelating and complexing properties for mobilization of heavy metals (Mench et al. 1988;

Mench et al. 1994; Wang et al. 2009; Wu et al. 2003). They have been implicated for altering the bioavailability and phytoremediation efficiencies of heavy metals in soils. Amendment of contaminated soils with organic acids was reported to reduce (Khan et al. 2000) or increase metal bioavailability (Huang et al. 1997). Although effects of several organic acids on heavy metal sorption and desorption on various clay minerals and oxides have been studied (Gao et al. 2003; Glover et al. 2002; Yuan et al. 2007), there is limited information on the desorption behavior of heavy metals in natural soils, as affected by organic acids, especially in a multi-element system. The objectives of this study were to illustrate the competitive adsorption–desorption of Cd and Pb in paddy soils using Langmuir and Freundlich adsorption isotherms and to examine the effects of pH and low molecular weight organic acids on desorption behavior of Cd and Pb in the multi-element systems.

Materials and methods

Soil samples

The soil samples were collected from 0–20 cm depth in Deqing (Ultisol) and Jiaxing County (Inceptisol) of Zhejiang Province, China. The Ultisol developed on the Quaternary red earth, while the Inceptisol was derived from alluvial sediments. Both belong to Gleyi-Stagnic Anthrosols in FAO/UNESCO nomenclature. After collection, the composite samples of the soils were air-dried, ground, and passed through a 2-mm sieve prior to use. Physicochemical properties of soils (Table 1) were analyzed following standard procedures (Lu 1999). Soil pH was measured using a pH meter (Thermo Orion 250, Orion Research, Inc. USA) at a soil-to-solution ratio of 1:2.5 in both deionized water and 1 mol L⁻¹ KCl. Soil organic matter was determined by Walkley and Black wet dichromate oxidation method (Nelson and Sommers 1996). Cation exchange capacity (CEC) of soils was determined using 1 M NH₄OA_C. The particle size distribution was determined by a wet sieving and the pipette method. Total concentrations of Cd and Pb in the soils were determined by flame atomic absorption spectrometer (FAAS) (AA 6800, Shimadzu, Japan) after digestion in HF-HClO₄.

Table 1 Physical and chemical characteristics of the used soils

| Soils | pH ^a | OM (g kg ⁻¹) | Free Fe oxide (g kg ⁻¹) | Total Cd (mg kg ⁻¹) | Total Pb (mg kg ⁻¹) | CEC (cmol kg ⁻¹) | Sand ^b | Silt (g kg ⁻¹) | Clay |
|------------|-----------------|-----------------------------|--|------------------------------------|------------------------------------|---------------------------------|-------------------|-------------------------------|------|
| Inceptisol | 6.03 | 23.8 | 22.0 | 0.38 | 56.8 | 13.5 | 100 | 556 | 340 |
| Ultisol | 5.51 | 27.6 | 20.3 | 0.40 | 46.3 | 12.5 | 225 | 570 | 200 |

OM organic matter, CEC cation exchange capacity

^a 1:2.5 soil/water ratio

^b Sand (2–0.02 mm), silt (0.02–0.002 mm), and clay (≤0.002 mm)

Sorption experiments

Isotherm experiments of Cd and Pb from their single and binary mixed solutions were undertaken using batch experiments. Metal solutions were prepared from the nitrate salts of each metal using 0.01 mol L⁻¹ NaNO₃ (pH 5.0) as a background electrolyte. The initial concentrations of Cd and Pb added were 0, 5, 10, 50, 100, 200, 300, and 400 mg L⁻¹ in the single metal systems and 0, 5, 25, 50, 100, 150, and 200 mg L⁻¹ for both Cd and Pb in the binary metal systems. Batch experiments were performed by adding 50 ml of single (Cd or Pb) or binary metal (Cd + Pb) solutions to 2-g soil samples in 50-ml polypropylene centrifuge tubes. The soil suspensions were shaken on an end-over-end shaker at 200 rpm for 4.0 h at 25°C and then equilibrated in a dark 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 2,000×g relative centrifugal force for 10.0 min, filtered through a 0.45-µm filter paper, and the metal concentration in the filtrate was determined using FAAS (AA 6800, Shimadzu, Japan). The amount of sorbed metal was calculated from the difference between the initial and final concentration of the metal in the solution. All the measurements were performed in triplicate.

Sorption isotherm parameters were obtained by the least square analysis using the Langmuir and Freundlich isotherms described in Eqs. 1 and 2 (Sparks 1995), respectively,

$$C_e/q_e = 1/(bQ) + C_e/Q \tag{1}$$

$$\text{Log}q_e = \text{log}K_f + (1/n)\text{log}C_e \tag{2}$$

where C_e is amount of metal in the equilibrium solution (in milligrams per liter), q_e is the amount of

metal adsorbed (in milligrams per kilogram), Q is the maximum adsorption capacity (in milligrams per kilogram), b is the bonding energy coefficient, n is sorption intensity constant, and K_f is the Freundlich constant. In addition, the distribution coefficients (K_d) for each metal concentration in the studied soils were calculated according to the following formula (Vidal et al. 2009):

$$K_d = C_{\text{ads}}/C_{\text{aq}} \tag{3}$$

where C_{ads} is the amount of metal adsorbed on the soil surface (in milligrams per kilogram) and C_{aq} is the concentration of metal in the solution (in milligrams per liter) at equilibrium. An average K_d value (K_{d medium}) for each metal in the studied soils was used to compare the adsorption capacities of different soils for the metals.

Desorption experiments

Desorption of adsorbed Cd and Pb

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 Cd²⁺ or Pb²⁺ in the trapped solution. Fifty milliliters of 0.01 mol L⁻¹ NaNO₃ (pH 5.0) was added to each tube containing the Cd/Pb-enriched soil residue. The suspensions were shaken at 200 rpm for 2 h at 25°C and equilibrated for an additional 22 h. The equilibrated suspensions were then centrifuged at 2,000×g relative centrifugal force for 10 min and filtered. The metal concentration in the filtrate was determined using the FAAS. In order to estimate the affinity of Cd²⁺ or Pb²⁺ to soils, desorption process was repeated five times (D1–D5). The non-extractable fraction of

the adsorbed Cd^{2+} or Pb^{2+} was obtained by the difference between the total adsorbed Cd^{2+} or Pb^{2+} and the total recovered Cd^{2+} or Pb^{2+} by the five successive extractions with the NaNO_3 solution (pH 5.0) (Yu et al. 2002).

pH effects

The tube with the soil residue separated from the supernatant solution by centrifugation was weighed to measure the residual Cd^{2+} and Pb^{2+} in the trapped solution. Fifty milliliters of 0.01 mol L^{-1} metal-free NaNO_3 with different pH level was added to each tube containing the Cd/Pb-enriched soil residue. The initial pH of NaNO_3 solution was 2.0, 3.0, 4.0, 5.0, 6.0, 7.0, and 8.0. The initial Cd and Pb concentration for adsorption experiment was 200.0 mg L^{-1} for single metal systems and 100 mg L^{-1} for binary metal systems. The process of desorption was the same as described above.

LMWOAs effects

The tube with the soil residue separated from the supernatant solution by centrifugation was weighed to measure the residual Cd^{2+} and Pb^{2+} in the trapped solution. Fifty milliliters of 0.01 mol L^{-1} metal-free NaNO_3 (pH 5.0) with different low molecular weight organic acids were added to each tube containing the Cd/Pb-enriched soil residue. Three organic acids were selected for this study: malic, citric, and oxalic acids. The concentrations of each organic acid used were 0.01 – 100 mmol L^{-1} . The initial pH of desorption solution was adjusted to 5.0 with HNO_3 and NaOH . The initial Cd and Pb concentration for adsorption experiment was 200.0 mg L^{-1} for single metal systems and 100 mg L^{-1} for each metal in the binary metal systems. The process of desorption was the same as described above.

Statistical analysis

All experiments were triplicated and only mean values were presented. Data were analyzed statistically using analysis of variance ($P < 0.05$). The regression and other statistical analyses were conducted using the programs of Statistical Package SPSS 10.0.

Results and discussion

Adsorption isotherms

The adsorption isotherm parameters were determined for both single and binary adsorption using the Langmuir and Freundlich isotherm equations (Fig. 1, Table 2). Moreover, the values of the square of the correlation coefficient were employed to indicate the model fitness. The results indicated that the adsorption of Pb in both single and binary metal systems fits well to either the Langmuir or Freundlich model, whereas the adsorption of Cd in single metal system was well described by the Langmuir model only. Therefore, the maximum adsorption capacity (Q) from the Langmuir equation may be useful for comparing potential adsorption capacity of Cd and Pb in the two soils. Inceptisol had a greater sorption capacity for Cd and Pb than Ultisol in terms of the estimated maximum sorption Q for both single and binary sorption systems (Table 2). This could be attributed to the differences in pH and clay content between the two soils (Table 1). The two soils exhibited similar adsorption patterns, with a greater (1.37–1.61-fold) Q values for Pb than Cd regardless of sorption systems. This may be attributed to the higher affinity of Pb than Cd to the sorbent surfaces (Adhikari and Singh 2003; Appel and Ma 2002; Fontes and Gomes 2003). It is worth to point out that the Q values in single metal sorption system was greater than those obtained from the binary metal sorption for both Cd and Pb. These results indicated that competitive adsorption occurred between Cd and Pb, which reduced the sorption of Cd or Pb. In addition, the decrease in Q values of Cd in binary solutions was much greater than Pb, suggesting that Cd adsorption was more affected by the presence of a competing metal than Pb. This result is consistent with the previous work (Serrano et al. 2005).

The bonding energy coefficient (b) is a useful parameter to characterize the soil affinity for metal (Kinniburgh 1986). Previous studies had shown that the binding energy coefficient varied with soil type and metal species (Serrano et al. 2005). Inceptisol showed a greater affinity for both Pb and Cd than Ultisol regardless of sorption systems (Table 2), probably due to its higher pH and clay content. This result is consistent with the maximum adsorption capacity. Both soils had a greater affinity for Pb than

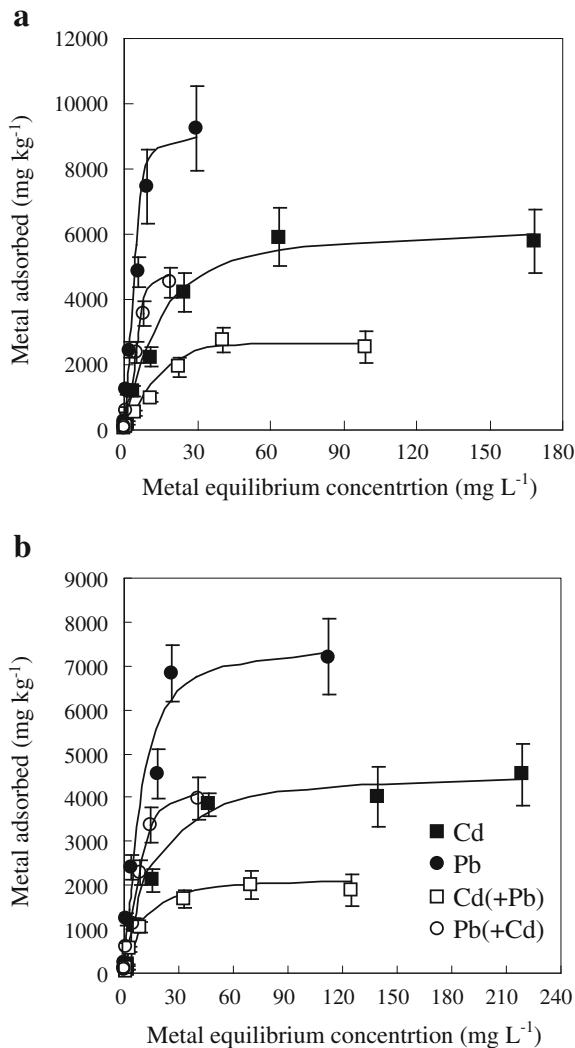


Fig. 1 Cadmium and Pb adsorption isotherms from both single (filled symbols) and binary metal (open symbols) system in Inceptisol (a) and Ultisol (b)

Table 2 Calculated Langmuir and Freundlich parameters of cadmium and lead adsorption isotherms

| Soils | Metal | Langmuir | | | Freundlich | | |
|------------|---------|------------------------------------|----------|-----------------------|---|----------|-----------------------|
| | | <i>Q</i> (mg kg ⁻¹) | <i>b</i> | <i>R</i> ² | <i>K_f</i> (L kg ⁻¹) | <i>n</i> | <i>R</i> ² |
| Inceptisol | Cd | 5,176.0 | 0.049 | 0.987 | 349.0 | 1.55 | 0.710 |
| | Pb | 8,333.3 | 0.212 | 0.996 | 1,186.4 | 1.71 | 0.975 |
| | Cd(+Pb) | 2,857.1 | 0.066 | 0.995 | 238.0 | 1.52 | 0.956 |
| | Pb(+Cd) | 4,545.5 | 0.260 | 0.964 | 710.5 | 1.41 | 0.985 |
| Ultisol | Cd | 4,621.1 | 0.034 | 0.970 | 245.0 | 1.64 | 0.769 |
| | Pb | 7,278.0 | 0.174 | 0.956 | 786.4 | 1.87 | 0.967 |
| | Cd(+Pb) | 2,631.6 | 0.045 | 0.989 | 201.0 | 1.82 | 0.857 |
| | Pb(+Cd) | 3,610.1 | 0.233 | 0.959 | 510.5 | 1.65 | 0.938 |

for Cd in both single and binary sorption systems, which is in agreement with previous work for single metal sorption (Adhikari and Singh 2003) and competitive sorption (Serrano et al. 2005). However, the *b* value was greater in binary than single sorption system for both soils ($b_{\text{single}} < b_{\text{binary}}$), for example, for Inceptisol, the *b* value of Cd in single and binary sorption systems were 0.049 and 0.066, respectively. Higher *b* values have been reported to relate to specific sorption of metals at high energy surfaces (Serrano et al. 2005).

The distribution coefficient (*K_d*) is a useful index for comparing the sorptive capacities of different soils or materials for a particular ion under the same experimental conditions (Alloway 1995; Usman 2008). A high *K_d* value indicates a high metal retention by the solid phase through adsorption and chemical reactions, leading to a low potential bioavailability of the metal. A *K_{d medium}* value was calculated to give one comparable coefficient for each metal and soil (Table 3). The data indicated that there was a great variation in the magnitude of *K_{d medium}* values among metals and soil types. The highest *K_{d medium}* value was found for Pb in single metal sorption system and followed by those of Pb in competitive sorption system, whereas the lowest *K_{d medium}* values were found for Cd in competitive sorption system. In general, the results obtained in this study agree with those reported by Elliott et al. (1986), Usman (2008), and Veeresh et al. (2003), which showed that Pb adsorption is much greater than Cd in single sorption system. This implies that under the competitive sorption conditions, Cd may pose more threat to plants and groundwater than Pb. In

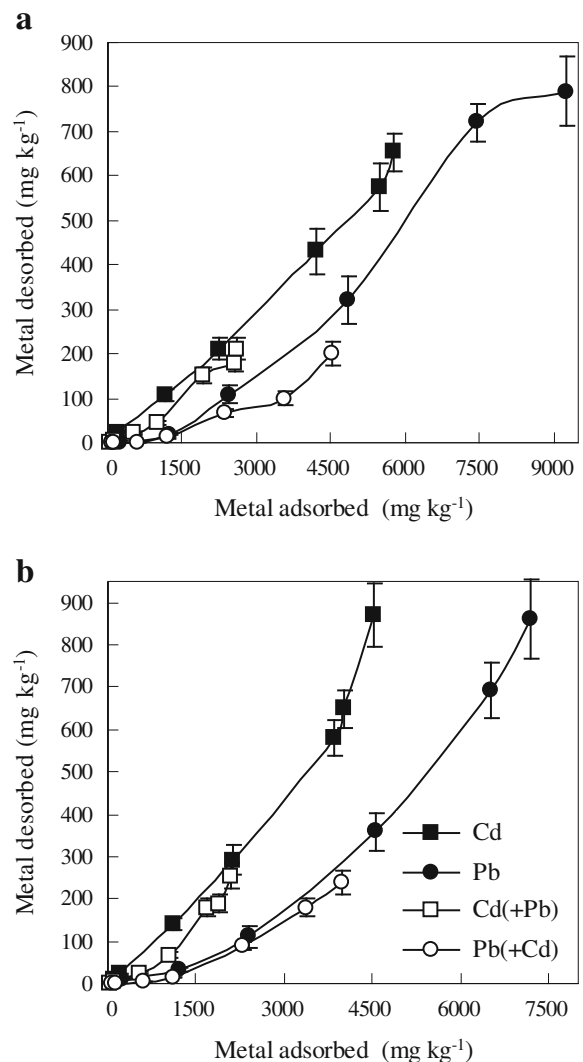
Table 3 The average distribution coefficients ($K_{d \text{ medium}}$) of each metal in studied soils

| Soils | $K_{d \text{ medium}}$ | | | |
|------------|------------------------|---------|---------|---------|
| | Cd | Pb | Cd(+Pb) | Pb(+Cd) |
| Inceptisol | 184.5 | 1,107.5 | 110.5 | 732.3 |
| Ultisol | 90.0 | 829.3 | 85.84 | 514.8 |

addition, the $K_{d \text{ medium}}$ of Cd and Pb was much greater in Inceptisol than in Ultisol for both single and competitive sorption systems, indicating that Inceptisol had a greater retention capacity for metals, and thus may result in a lower potential bioavailability of the metals (Veeresh et al. 2003; Vega et al. 2006).

Desorption of Cd and Pb

Desorption of Cd and Pb varied with soil type and sorption systems (Fig. 2). Cadmium and Pb desorption increased with increasing Cd and Pb adsorption saturation in both soils, Inceptisol desorbed less Cd and Pb than Ultisol at the same equilibrium concentration for both sorption system. After five successive desorptions, the accumulative amounts of Cd and Pb desorbed in both systems accounted for 0.8–19.5% of total adsorbed Cd and Pb in Ultisol and 0–11.9% in Inceptisol. This was consistent with the binding energy coefficient. For the two metals in different sorption system, the desorption ratio (defined as the ratio of the amount of metal desorbed to the total adsorbed: d_{Cd} and d_{Pb} for single sorption system and d_{Cd}^* and d_{Pb}^* for competitive sorption system) was much greater in single sorption system than competitive sorption system in both soils. For example, the d_{Cd} and d_{Cd}^* were 2.7–11.3% and 0.0–5.8%, for Inceptisol, whereas the corresponding values were 0.0–9.6% and 0.0–4.4% respectively for Ultisol. These results further confirmed that competition for sorption sites promotes the retention of both metals onto specific sorption positions. As a result, maximum sorption decreases, but the metals are held more strongly (Serrano et al. 2005). It is worth to point out that in competitive sorption system, the d_{Cd}^* was much greater than d_{Pb}^* . This implies that under the competitive sorption conditions, the adsorbed Cd is more readily desorbed from the soils than the adsorbed Pb.

**Fig. 2** The relationship between adsorption and desorption of Cd and Pb from both single (filled symbols) and binary metal (open symbols) system in Inceptisol (a) and Ultisol (b)

Effect of pH on the desorption of Cd and Pb

It has been widely reported that pH highly affects the adsorption/desorption behavior of heavy metals in soils (Casagrande et al. 2004; Gao et al. 2003; Gurel 2006; Serrano et al. 2005; Vega et al. 2006; Yang et al. 2006). The amount of Cd and Pb desorbed from the two paddy soils was greatly affected by pH (Fig. 3). Generally, an increase in pH reduced Cd and Pb desorption in the soils. Desorption of Cd and Pb was greater in Ultisol (Fig. 3b) than in Inceptisol (Fig. 3a) at the same pH irrespective of sorption

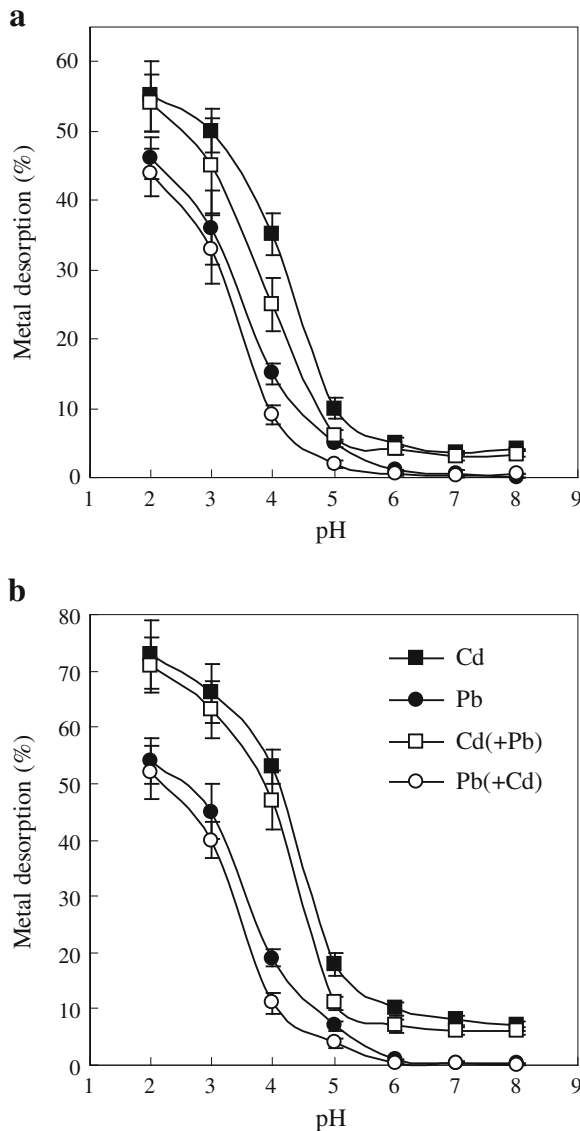


Fig. 3 Effect of pH on the desorption of Cd and Pb from both single (filled symbols) and binary metal (open symbols) system in Inceptisol (a) and Ultisol (b)

systems, which is in consistent with the previous work (Gao et al. 2003; Vega et al. 2006; Yang et al. 2006). Both Cd and Pb desorption with increasing solution pH was characteristic of “S” pattern, i.e., desorption was maximum at low pH and decreased with increasing pH before reaching a certain critical level. However, the pH desorption edge varied with soil type and sorption system. The desorption edge of Cd in both systems was shifted to slightly higher pH values as compared to Pb, implying that at the same

pH level, more Cd was desorbed from the soil than Pb. The desorption curve can be divided into three stages based on desorption ratio; however, the three pH range varied with soil and metal type: (1) the greatest desorption stage at pH<3.0, with more than 50.0% for Pb and 60% for Cd being desorbed; (2) the desorption decreasing stage at pH 3.0–5.0, at which desorption of both Cd and Pb decreased significantly; and (3) the precipitation and minimal desorption stage at pH>5.0, at which the desorption ratio was small but approached to a constant level. This result may be associated with the fact that at lower pH more protons are available for competition with metal ions in solution for sorption sites. Furthermore, metal cation desorption from oxide surfaces is more reversible at low pH as compared to high pH (Glover et al. 2002; Yang et al. 2006). At high pH, the preferential adsorption of hydroxy-metal species by soil organic matter and/or hydrous iron and aluminum oxide may be enhanced. In addition, pH affects surface charge, raising pH increased negative charge on soil surface, thus reducing desorption of adsorbed metals. It is interesting that when pH>6, no difference in desorption was observed between the single and competitive sorption system. This may be attributed to the fact that higher pH values resulted in the precipitation of insoluble metal hydroxide thus making adsorption irreversible. However, it is observed that d_{single} was greater than d_{binary} for both soils at pH 3–5, suggesting that at this pH range, the metals are held more strongly in competitive sorption system. It is worth to point out that $d_{Cd}^* > d_{Pb}^*$, indicating that in the competitive sorption system, more Cd was desorbed than Pb.

Effect of LMWOAs on the desorption of Cd and Pb

The desorption of Cd and Pb in both soils varied with the type and concentrations of LMWOAs added (Fig. 4). More Cd and Pb were desorbed in Ultisol than Inceptisol in the presence of organic acid for both single and competitive sorption systems. Regardless of soil and sorption system, the desorption of Cd and Pb was higher in the presence of citric acid as compared with malic or oxalic acid, especially at the concentration ≥ 1 mmol L⁻¹. For instance, the amounts of Cd and Pb desorbed from Ultisol in single metal system in the presence of 10 mM citric acid were 2,130 and 1,898 mg kg⁻¹ respectively as compared

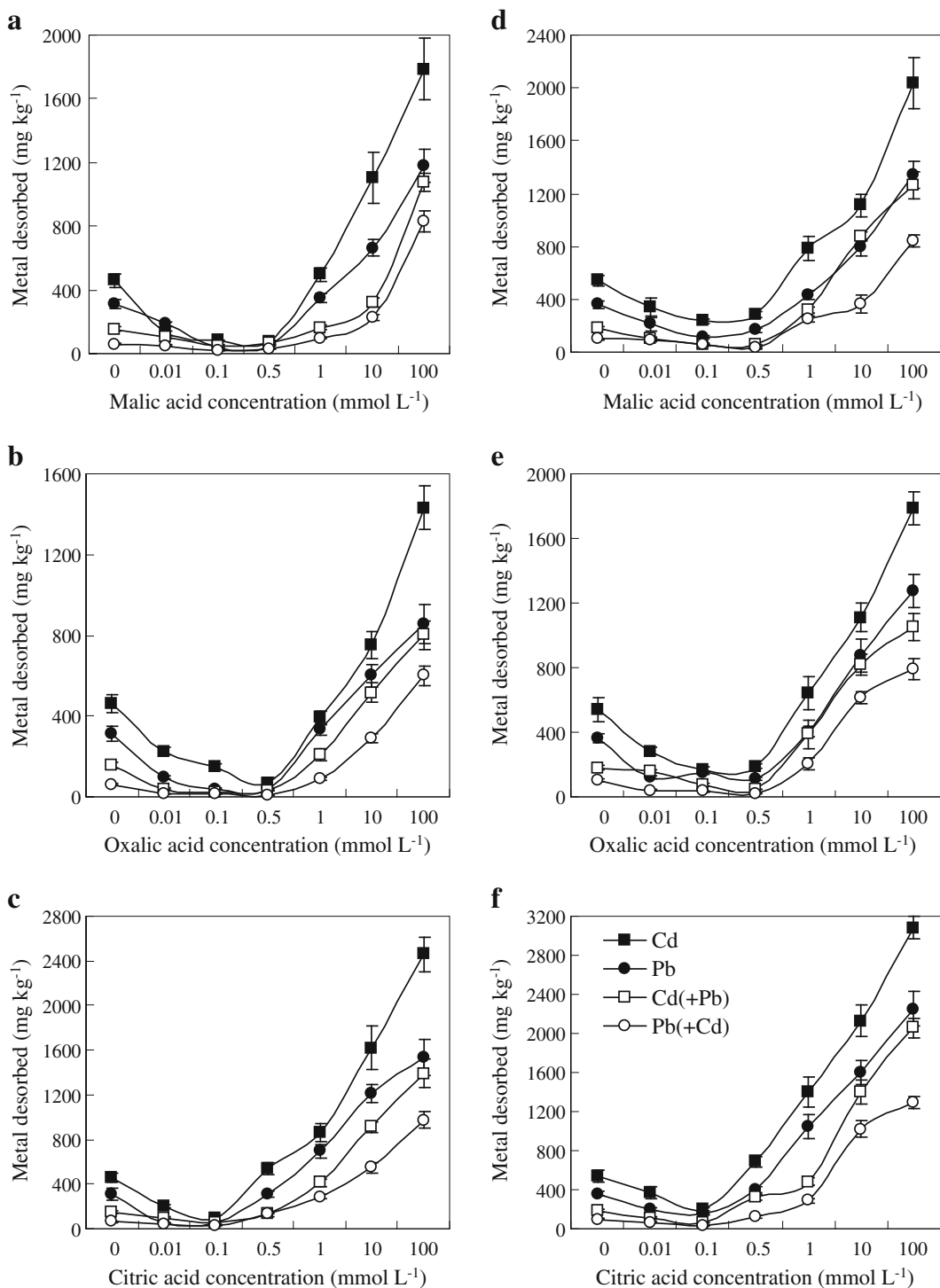


Fig. 4 Effects of LMWOAs on the desorption of Cd and Pb from both single (*filled symbols*) and binary metal (*open symbols*) system in Inceptisol (**a, b, c**) and Ultisol (**d, e, f**)

with 1,823 and 1,294 mg kg⁻¹ for malic acid of the same concentration. The addition of oxalic acid

resulted in least desorption increase as compared to the other two organic acids. This difference may be

attributed to the difference in molecular weight and structure of the three organic acids. Organic acid that has a higher molecular weight such as citric acid can attract and/or chelate more metals since it carries more negative charge and has a larger surface area than a smaller organic acid such as oxalic acid. Previous studies also demonstrated that organic acids with more carboxylic and hydroxyl groups have a greater influence on metal desorption owing to its higher complexing capability (Jing et al. 2007). In this study, citric acid has more functional groups than malic and oxalic acids and thus it is more effective in the desorption of Cd and Pb.

The desorption of Cd and Pb with increasing concentration of organic acid was characteristic of a “V” pattern, the desorption of Cd and Pb decreased initially and then increased with the increase of organic acid concentration. For example, the amount of Cd desorbed from Ultisol in single metal system without organic acid was 540.5 mg kg^{-1} . When citric acid concentration in the desorption solution increased from 0.01 to 0.1 mmol L^{-1} and then to 100 mmol L^{-1} , the amount of Cd desorbed changed from 540.5 to 382.8 mg kg^{-1} , and then sharply increased to $3,081 \text{ mg kg}^{-1}$. The same trend was found for both Cd and Pb in the two soils under the effect of citric acid. These results are in agreement with previous work on Pb desorption from variable charge soils using single metal system (Yang et al. 2006), indicating that the presence of malic, citric, or oxalic acids inhibits Cd and Pb desorption at low concentrations ($\leq 0.1 \text{ mmol L}^{-1}$) but enhances their desorption at higher concentrations ($\geq 0.5 \text{ mmol L}^{-1}$ for citric acid and $\geq 1 \text{ mmol L}^{-1}$ for malic and oxalic acid). This can be explained by the fact that small amounts of organic acids added to soil are mostly adsorbed by the soil, which may increase negative charge or CEC of the soil. Moreover, Cd and Pb in desorbing solution may be bound to the organic ligands that were adsorbed on the surfaces of the soil (Huang 2004), which leads to the reduction of Cd and Pb desorption. At higher organic acid concentrations, the ratio of organic ligands remaining in solution to the organic ligand adsorbed by the soil rapidly increases and consequently increased the competitive ability of the organic ligands for adsorbing sites with Cd and Pb, thus resulting in enhanced desorption with increasing organic acid concentrations above a certain level.

There was a difference in metal desorption between the single and binary metal system in the presence of organic acids. The desorption ratio in single metal system was much greater than in the binary metal system for the two soils in the presence of organic acids ($d_{\text{single}} > d_{\text{binary}}$). This is especially for Ultisol in the presence of citric acid. In addition, our study found that d_{Cd}^* was greater than d_{Pb}^* for both soils in the presence of organic acids, which is in consistent with the result of pH, indicating that in the binary metal system, Cd desorption was more affected by the presence of organic acids than Pb desorption.

Conclusions

This study investigated the adsorption–desorption behavior of Cd and Pb in soils using both single and binary metal systems. The sorption isotherms of Cd and Pb in the single and binary metal system of the same ionic strength were adequately described by Langmuir equation. Inceptisol with higher pH and clay content had a greater sorption capacity for both metals as estimated by the maximum sorption parameter (Q) from the Langmuir equation. The coexistence of both metals reduces their tendency of sorption but the effect was more on Cd than Pb. The Langmuir bonding energy coefficient (b) and distribution coefficient (K_d) were greater for Pb than for Cd; furthermore, b_{binary} and $K_{d \text{ binary}}$ were greater than b_{single} and $K_{d \text{ single}}$, indicating that competition for sorption sites promote the retention of both metals onto more specific sorption sites. Cadmium and Pb desorption increased with increasing Cd and Pb adsorption saturation for both soils; however, the desorption ratio in single metal system was greater than that in binary metal system. An increase in pH reduced Cd and Pb desorption. Both Cd and Pb desorption with increasing solution pH was characteristic of “S” pattern. When the concentration of LMWOAs in desorption solution was relatively low ($\leq 0.1 \text{ mmol L}^{-1}$), the presence of LMWOAs inhibited Cd or Pb desorption but promoted Cd and Pb desorption at higher concentrations ($\geq 0.5 \text{ mmol L}^{-1}$ for citric acid and $\geq 1 \text{ mmol L}^{-1}$ for malic and oxalic acid). The two paddy soils had a greater d_{Cd}^* than d_{Pb}^* in the presence of LMWOAs, indicating that Cd desorption was more affected by the presence of LMWOAs in binary metal system.

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