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ORIGINAL PAPER

Interaction of organic acids and pH on multi-heavy metal extraction from alkaline and acid mine soils

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Abstract Vegetation at mining sites can produce increased heavy metal leaching by the organic acids and protons originating from root secretion and litter degradation. Batch experiments were conducted to investigate the effects of organic acids and pH on the extraction of Pb, Cd, Zn and Cu from an alkaline mine soil (sampled from a mining site of Chenzhou City, Hunan Province) and an acid mine soil (sampled from a mining site of Daxin county, Guangxi Province). The results showed that in the presence of organic acids (acetic, oxalic, malic, fumaric, tartaric and citric acids) at pH 7, the extraction of Pb, Cd, Zn and Cu from the acid mine soil was much higher than that from the alkaline mine soil, in which only citric acid with higher concentration was capable of extracting some heavy metals. Citric acid had the strongest ability in extracting heavy metals, followed by oxalic acid. Heavy metal extraction dramatically decreased with increasing pH. Moreover, at low pH, oxalic acid promoted the risk of Cu leaching; at high pH, the leaching of Pb, Zn, Cd and Cu was enhanced by both oxalic and citric acids. This indicated that those plants, which can produce substantial citric acid or oxalic acid by root secretion and litter degradation, should not be selected for the revegetation of mining sites.

Keywords Chelating · Contamination · Leaching · Mining · Trace metals · Revegetation

Introduction

The exploitation of mineral resources provides us with strategic resources, but also causes environmental pollution and ecological damage. In China, the total destroyed and occupied land due to mining has reached 7.43 million hm^2 and is estimated to increase annually by 40,000 hm^2 (Qiu et al. 2009). Multi-metal pollution in the soils within the vicinity of mines has become one of the most serious environmental issues (Conesa and Schulin 2010). These heavy metals may be released via the erosion of wind and water and can ultimately enter the food chain (Navarro et al. 2008). Today, great efforts are being made to remediate polluted mining sites, in which revegetation or phytostabilization is considered to be an efficient way to achieve long-term reclamation (Arienzo et al. 2004; Mendez and Maier 2008a, b). However, disadvantageous consequences after revegetation cover may arise due to organic acids excreted by the roots and/or decomposed by the litters of inhabiting plants. It was evidenced that organic acids could enhance the desorption of heavy metals from soils, resulting in more heavy metals leaching into the water body (Zhu et al. 1999). Lu et al. (2007) showed that exchangeable Cd was positively related to total organic acids in rhizosphere soils. Burckhard et al. (1995) found that organic acids, especially citric acid, promoted the leaching of Zn in mine tailings.

Low molecular weight organic acids, mainly originating from the decomposition of soil organic matter, plant root exudates and microbial metabolites (Jones 1998; Strobel 2001), play important roles in controlling the solubility of

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heavy metals and their subsequent uptake by plants due to the chelation or complexation between organic acids and heavy metals (Krishnamurti et al. 1997; Han et al. 2006). Naidu and Harter (1998) reported that organic ligands increased the extractability of Cd from soils. It was found that citric acid could significantly reduce Cd adsorption on soils due to the formation of soluble Cd–organic complexes (Zhou et al. 2003). Schwab et al. (2008) found that citric acid greatly enhanced the movement of Zn and Cd in soils, but had little influence on Pb movement. And some researchers also found that citrate had the most efficiency in releasing Cd, Pb and Zn than other organic acids (Wuana et al. 2010; Vesely et al. 2011). Low concentration of tartrate and citrate inhibited the desorption of Cd and Cu, but high concentration of tartrate and citrate promoted the desorption (Gao et al. 2003). Citric acid, malic acid and acetic acid more effectively desorbed Cu, Cd and Pb from soils than inorganic salts such as $CaCl_2$ and $NaNO_3$ (Qin et al. 2004). Increasing citric, oxalic or malic acid concentrations resulted in increases in Cd adsorption on acidic paddy and red soils at low pH, but citric acid dramatically increased Cd solubility at high pH (Ding et al. 2008). These results suggested that organic acids might stimulate either the solubility or the immobility of heavy metals in soils, depending upon the type and concentration of organic ligands, the type of metals, the soil properties and other environmental factors (Collins et al. 2003; Ding et al. 2008).

In order to choose suitable plant species for revegetation of mining sites, people must investigate the leaching risks of heavy metals affected by organic acids and protons from root exudates and litter degradation. Stresses to plants resulting from nutrient deficiency and heavy metal toxicities in mine soils often induce increased root exudates that are rich in organic ligands (Ryan et al. 2001). It is still unclear whether organic acids are exuded by roots as free acids or alkali metal salts (Jones 1998). In any case, the acidity of rhizosphere soil is usually different from that of bulk soil, and many plants can contribute to soil acidification (Zhu et al. 1999). Although the effect of organic acids on the solubility of heavy metals has been researched widely, people are still unclear about the interaction among organic acids, pH and heavy metals in mine soils. Better understanding the interactions will help to construct more environmentally friendly vegetative covers in mining sites and decrease the leaching of heavy metals into the ambient surroundings.

In order to clarify the interaction of organic acids and pH on the leaching of multi-heavy metals from mine soils, two typical mine soils (an alkaline soil and an acid soil) in South China were selected, and the effects of organic acids on the extractability of Pb, Cd, Zn and Cu were investigated under different concentrations and different acidity. The study was carried out in Agro-Environmental Protection Institute, Ministry of Agriculture, Tianjin, in August–September, 2010.

Materials and methods

Soil sampling

An alkaline mine soil (Chenzhou soil) and an acid mine soil (Daxin soil) were sampled from mining sites of Chenzhou City (112°13′–112°55′E, 25°27′–26°13′N), Hunan Province, and Daxin county (106°39′–107°29′E, 22°29′–23°05′N), Guangxi Province, respectively. Both soil samples were collected from the surface layer (0–20 cm) and were air-dried, ground to pass through a 60-mesh sieve (0.25 mm), and stored for analysis.

Soil pH was measured in distilled water at a soil-to-solution ratio of 1:2.5 (w:v). The content of soil organic matter (SOM) was determined by the method of Nelson and Sommers (1996). Cation exchange capacity (CEC)

Table 1 Properties of the mine soils studied

Item	Chenzhou soil	Daxin soil
pH (H_2O)	7.93 ± 0.01[a]	6.28 ± 0.02
CEC (cmol kg^{-1})	43.2 ± 0.28	11.2 ± 0.07
Organic matter (g kg^{-1})	3.89 ± 0.53	25.58 ± 1.61
Pb (mg kg^{-1})	7,200 ± 14.6 (350)[b]	829.5 ± 3.73 (250)
Zn (mg kg^{-1})	2,471 ± 12.7 (300)	4,130 ± 14.5 (200)
Cu (mg kg^{-1})	2,020 ± 13.5 (100)	29.2 ± 0.11 (50)
Cd (mg kg^{-1})	77.4 ± 0.91 (1.0)	45.87 ± 0.49 (0.3)

[a] Mean ± SD ($n = 3$)

[b] Values in brackets are the National Soil Environmental Quality Standard of China

was determined by the method of Bao (Bao 2000). Total concentrations of Pb, Cd, Zn and Cu in the soils were determined by HF–$HClO_4$ digestion (Tessier et al. 1979) and ICP-OES analysis (Optima 2000 DV, PerkinElmer, America). Accuracy was evaluated by the use of a certified reference material (Institute of Geophysical and Geochemical Exploration, NO. GBW07430). Multi-element standards, which were used as the certified reference material, were purchased from Sigma-Aldrich Co. LLC. All other reagents were analytical-reagent grade and were obtained from Sinopharm Chemical Reagent Beijing Co., Ltd. The physicochemical properties of both mine soils are listed in Table 1. Both mine soils were heavily polluted with Pb, Cd, Zn or Cu compared with the individual National Soil Environmental Quality Standard of China (GB 15618–1995). Although the Cu concentration in the Daxin soil was not high, the data are still shown in this study for comparison with that of the Chenzhou soil.

Organic acids tested

Acetic acid, oxalic acid, malic acid, fumaric acid, tartaric acid and citric acid were selected to extract heavy metals (Pb, Cd, Zn and Cu). These organic acids are commonly present in soils, and the tested concentrations ranging from 0 to 10.0 mmol L^{-1} are reasonable for soils, especially in the rhizosphere soils (Krishnamurti et al. 1997; Jones 1998). The organic acids were purchased from Sigma-Aldrich Co. LLC.

Extractability of Pb, Cd, Zn and Cu in mine soils by different organic acids with initial pH 7

Organic acid solutions were prepared, with the concentration of 0, 0.2, 0.5, 1.0, 2.0, 5.0 and 10.0 mmol L^{-1}, respectively. All solutions contained a background electrolyte of 0.01 mol L^{-1} $NaNO_3$, and solution pH was adjusted to pH 7 using diluted NaOH/HNO_3. A total of 1.5 g soil was placed in a 50-mL polypropylene centrifuge tube, 30 mL organic acid solution was added, and then 2 drops of toluene was added to inhibit microbial activity (Naidu and Harter 1998). The suspension was shaken end-over-end for 5 h at 25 °C, centrifuged at 3,000*g* for 15 min, and then filtered using 0.45-μm nylon membrane filters. The equilibrium pH was determined, and the concentrations of Pb, Cd, Zn and Cu in the filtrates were measured by ICP-OES. In this experiment, there were three replicates in each treatment.

Extractability of Pb, Cd, Zn and Cu in mine soils by citric acid and oxalic acid as a function of pH

Many plants can produce organic acids and protons from root exudation or litter degradation. Citric and oxalic acids were chosen to study the combined effects of pH and organic acids on heavy metal extraction because they have the highest chelating abilities with heavy metals according to the results of the above experiment. A total of 1.5 g soil was placed in a 50-mL polypropylene centrifuge tube, 30 mL organic

Table 2 Extraction of Pb, Cd, Zn and Cu (mg kg^{-1}) from Chenzhou soil by organic acids at initial pH 7

Organic acids	Heavy metals	Concentrations of organic acids (mmol L^{-1})						
		0	0.2	0.5	1.0	2.0	5.0	10.0
Acetic/Fumaric acid	Pb/Cd/Zn	nd[a]	nd	nd	nd	nd	nd	nd
	Cu	0.20 ± 0.01a[b]	0.20 ± 0.01a	0.20 ± 0.01a	0.20 ± 0.01a	0.20 ± 0.01a	0.20 ± 0.01a	0.20 ± 0.01a
Oxalic acid	Pb/Cd/Zn	nd	nd	nd	nd	nd	nd	nd
	Cu	0.20 ± 0.01c	0.23 ± 0.04c	0.25 ± 0.05c	0.24 ± 0.05c	0.31 ± 0.03c	2.42 ± 0.01b	12.5 ± 0.21a
Tartaric acid	Pb/Cd/Zn	nd	nd	nd	nd	nd	nd	nd
	Cu	0.20 ± 0.01e	0.22 ± 0.03e	0.22 ± 0.02e	0.31 ± 0.03d	0.44 ± 0.02c	1.09 ± 0.03b	2.19 ± 0.01a
Malic acid	Pb/Cd	nd	nd	nd	nd	nd	nd	nd
	Zn	nd	nd	nd	nd	nd	nd	0.67 ± 0.13
	Cu	0.20 ± 0.01e	0.21 ± 0.01e	0.33 ± 0.01e	0.69 ± 0.01d	1.59 ± 0.07c	3.48 ± 0.12b	8.41 ± 0.34a
Citric acid	Pb	nd	nd	nd	nd	nd	7.79 ± 1.19b	47.1 ± 3.20a
	Cd	nd	nd	nd	nd	0.74 ± 0.05c	4.20 ± 0.03b	9.19 ± 0.21a
	Zn	nd	nd	nd	0.51 ± 0.25d	7.95 ± 0.17c	47.1 ± 1.34b	102 ± 3.78a
	Cu	0.20 ± 0.01f	0.61 ± 0.04f	4.69 ± 0.18e	21.2 ± 0.65d	67.0 ± 0.82c	149 ± 3.02b	204 ± 1.71a

[a] nd = not detected; [b] values ± SD ($n = 3$), means in the same row followed by the same letters are not significantly different, whereas means by the different letters are significantly different at $p < 0.05$

acid (citric acid or oxalic acid) solution containing 0.01 mol L^{-1} $NaNO_3$ was added, and then 2 drops of toluene was added. The tested concentration of citric acid and oxalic acid was 0, 0.5, 1.0 and 5.0 mmol L^{-1}, respectively, and their solution pH was adjusted to different values using diluted $NaOH/HNO_3$. The subsequent procedure was the same as described above. Finally, the equilibrium pH was determined, and the concentrations of Pb, Cd, Zn or Cu in the filtrates were measured by ICP-OES. In this experiment, there were three replicates in each treatment.

Statistical analysis

The statistical analysis was performed in triplicate samples, and the mean values with standard error were recorded. The data were subjected to one-way analysis of variance (ANOVA) and Duncan's multiple range test using SPSS (version 16.0, SPSS Inc., USA). The significant differences between treatments were calculated at 5 % probability levels ($p < 0.05$).

Results and discussion

Extractability of heavy metals in mine soils by different organic acids

The extraction of heavy metals from both mine soils varied greatly (Tables 2, 3). Except citric acid with higher concentration, organic acids hardly extracted heavy metals from Chenzhou soil. Contrarily, all organic acids could extract well heavy metals from Daxin soil. The heavy metals of Daxin soil were much easily extracted than that of Chenzhou soil. Soil properties such as pH, CEC, OM, clay content and oxides of iron and manganese play important roles in controlling the solubility of heavy metals (Naidu et al. 1994). Chenzhou soil was a permanent charge soil with high surface negative charges, so its soil characteristics dominantly control the solubility of heavy metal solubility, and the extraction of heavy metals was hardly affected by environmental factors such as organic acids. On the contrary, Daxin soil was a variable charge soil where the charge could be regulated by the adsorption of

Table 3 Extraction of Pb, Cd, Zn and Cu (mg kg^{-1}) from Daxin soil by organic acids at initial pH 7

Organic acids	Heavy metals	Concentrations of organic acids (mmol L^{-1})						
		0	0.2	0.5	1.0	2.0	5.0	10.0
Acetic acid	Pb	1.17 ± 0.22cd[a]	0.99 ± 0.01e	1.14 ± 0.08d	1.09 ± 0.02de	1.27 ± 0.07c	1.53 ± 0.10b	2.27 ± 0.02a
	Cd	2.46 ± 0.02c	2.66 ± 0.16b	2.69 ± 0.03b	2.66 ± 0.01b	2.76 ± 0.14b	2.76 ± 0.06b	2.95 ± 0.31a
	Zn	202 ± 0.71a	204 ± 1.10a	202 ± 2.78a	206 ± 1.56a	206 ± 11.8a	199 ± 4.61a	203 ± 2.46a
	Cu	0.44 ± 0.00d	0.47 ± 0.01cd	0.50 ± 0.01bc	0.52 ± 0.01b	0.52 ± 0.01b	0.53 ± 0.01b	0.77 ± 0.09a
Fumaric acid	Pb	1.17 ± 0.22e	1.11 ± 0.04e	1.23 ± 0.06e	1.46 ± 0.10d	1.76 ± 0.04c	2.69 ± 0.04b	3.86 ± 0.14a
	Cd	2.46 ± 0.02f	2.82 ± 0.04e	2.87 ± 0.05e	3.04 ± 0.02d	3.22 ± 0.02c	3.76 ± 0.08b	4.55 ± 0.07a
	Zn	202 ± 0.71d	230 ± 2.12c	225 ± 5.37c	226 ± 4.95c	231 ± 1.56c	251 ± 8.21b	274 ± 4.95a
	Cu	0.44 ± 0.00f	0.43 ± 0.00f	0.49 ± 0.02e	0.48 ± 0.01e	0.56 ± 0.02c	0.68 ± 0.04b	0.87 ± 0.01a
Oxalic acid	Pb	1.17 ± 0.22g	2.20 ± 0.03f	4.42 ± 0.06e	7.32 ± 0.05d	9.74 ± 0.10c	14.8 ± 2.10b	21.0 ± 0.09a
	Cd	2.46 ± 0.02a	1.98 ± 0.03b	1.62 ± 0.03c	1.49 ± 0.03d	1.14 ± 0.03f	1.05 ± 0.03g	1.23 ± 0.01e
	Zn	202 ± 0.71g	242 ± 0.35f	327 ± 4.24e	432 ± 10.2d	484 ± 18.3c	589 ± 10.2b	741 ± 20.3a
	Cu	0.44 ± 0.00g	0.64 ± 0.01f	1.26 ± 0.00e	2.34 ± 0.04d	4.48 ± 0.33c	7.41 ± 0.10b	10.1 ± 0.11a
Tartaric acid	Pb	1.17 ± 0.22f	1.13 ± 0.04f	1.55 ± 0.06d	2.42 ± 0.02c	3.61 ± 0.21c	9.51 ± 0.04b	21.4 ± 1.26a
	Cd	2.46 ± 0.02a	2.30 ± 0.02b	2.08 ± 0.06c	1.92 ± 0.01e	1.76 ± 0.03f	1.75 ± 0.04f	1.98 ± 0.01d
	Zn	202 ± 0.71d	184 ± 7.34f	192 ± 1.16ef	199 ± 0.95de	234 ± 12.4c	319 ± 2.69b	383 ± 15.0a
	Cu	0.44 ± 0.00d	0.54 ± 0.00d	0.54 ± 0.01d	0.59 ± 0.00d	0.81 ± 0.19c	1.13 ± 0.17b	1.90 ± 0.26a
Malic acid	Pb	1.17 ± 0.22f	1.26 ± 0.02f	2.35 ± 0.03e	5.47 ± 0.05d	7.21 ± 0.07c	12.6 ± 0.11b	18.3 ± 0.07a
	Cd	2.46 ± 0.02a	2.25 ± 0.03b	1.95 ± 0.04c	1.64 ± 0.03d	1.47 ± 0.03f	1.39 ± 0.02f	1.42 ± 0.02f
	Zn	202 ± 0.71g	223 ± 0.05f	265 ± 1.12e	286 ± 0.82d	337 ± 9.51c	426 ± 6.89b	532 ± 10.5a
	Cu	0.44 ± 0.00f	0.59 ± 0.03f	0.92 ± 0.23e	1.32 ± 0.15d	2.63 ± 0.37c	4.78 ± 0.12b	6.45 ± 0.32a
Citric acid	Pb	1.17 ± 0.22f	4.39 ± 0.08f	15.1 ± 0.35e	38.0 ± 0.02d	77.3 ± 1.77c	120 ± 7.09b	177 ± 2.40a
	Cd	2.46 ± 0.02f	2.17 ± 0.01f	3.88 ± 0.07e	6.45 ± 0.16d	9.88 ± 0.40c	12.8 ± 0.74b	16.2 ± 0.25a
	Zn	202 ± 0.71f	219 ± 3.68f	349 ± 8.85e	604 ± 15.4d	820 ± 16.9c	971 ± 50.1b	1,091 ± 59.7a
	Cu	0.44 ± 0.00g	1.60 ± 0.02f	2.91 ± 0.20e	3.36 ± 0.17d	4.86 ± 0.15c	6.44 ± 0.29b	8.27 ± 0.71a

[a] Values ± SD ($n = 3$), means in the same row followed by the same letters are not significantly different, whereas means by the different letters are significantly different at $p < 0.05$

potential-determining ions (H^+ and OH^-) on the surface. Subsequently, the adsorption of heavy metal ions on Daxin soils was easily affected by environmental factors such as chelating organic acids.

Different organic acids showed different influences on the solubility of heavy metals in both mine soils (Tables 2, 3). For example, the extraction amounts of Cu from the Chenzhou soil by acetic acid, fumaric acid, oxalic acid, malic acid, tartaric acid and citric acid at a concentration of 10.0 mmol L^{-1} were 0.20, 0.20, 12.5, 2.19, 8.41 and 204 mg kg^{-1}, respectively, whereas from the Daxin soil, the values were 0.77, 0.87, 10.1, 6.45, 1.90 and 8.27 mg kg^{-1}, respectively. Elkhatib et al. (2007) also found that citric acid had higher Cu extraction ability than other organic acids. The Zn extraction amounts from the Daxin soil by these organic acids were 203, 274, 741, 383, 532 and 1,091 mg kg^{-1}, respectively, while from the Chenzhou soil, only a small quantity of Zn was extracted by citric acid. So, citric acid had the strongest ability to extract heavy metals, followed by oxalic acid.

In the presence of citric acid of 10.0 mmol L^{-1}, the desorption rate of metals from Daxin soil followed the order: Pb (21.3 %) <Zn (26.4 %) <Cu (28.3 %) <Cd (35.3 %) and that from Chenzhou soil followed the same order: Pb (0.7 %) <Zn (4.1 %) <Cu (10.1 %) <Cd (11.9 %). However, the common sequence of metal adsorption on soils is Pb > Cu > Zn > Cd, which it is related to the first hydrolysis equilibrium constant (Usman 2008). In the absence of citric acid, the desorption rate of heavy metals from Daxin soil followed the order: Pb (0.14 %) <Cu (1.5 %) <Zn (4.9 %) <Cd (5.4 %). Apparently, citric acid changed the desorption orders of Cu and Zn in both mine soils, which could be attributed to higher stability constant of Cu–citric acid complex than Zn–citric acid complex. Furthermore, for most metals, citric acid has the strongest chelating ability among low molecular weight organic acids.

Citric acid has the strongest ability to extract heavy metals because it has three carboxyl groups, which can form stable five- or six-member chelate rings (Qin et al. 2004). However, Cu extraction from Daxin soil by citric acid with higher concentration was less than that by oxalic acid under the same conditions (Table 3), perhaps because the equilibrium pH of soil citric acid was higher than that of soil oxalic acid, as shown in Table 4. Equilibrium pH plays another important role in controlling the solubility of heavy metals (Appel and Ma 2002). The acid-buffering capacity of mine soils had different response to organic acids (Table 4). The values of equilibrium pH of Daxin soil ranged from 5.77 to 7.23 when different organic acids with initial pH 7 were added, whereas that of Chenzhou soil ranged from 8.06 to 9.43, that is, Chenzhou soil had greater acid-buffering capacity than Daxin soil. This partly explained why the extraction of heavy metals from the former was much lower than that from the latter. Additionally, the different equilibrium pHs of the Daxin soil may partly explain why the extraction amounts of Cd decreased as the concentration of some organic acids (oxalic, tartaric and malic acid) increased (Table 3). Herein, it is necessary to consider the interaction effect of organic acids and pH on the extractability of heavy metals in mine soils.

Table 4 Equilibrium pH values after organic acids added to mine soils with initial pH 7

Soils	Organic acids	Concentrations of organic acids added to the soils (mmol L^{-1})						
		0	0.2	0.5	1.0	2.0	5.0	10.0
Chenzhou soil	Acetic acid	8.44 ± 0.02[a]	8.14 ± 0.01	8.15 ± 0.01	8.19 ± 0.01	8.21 ± 0.01	8.12 ± 0.00	7.97 ± 0.03
	Fumaric acid	8.44 ± 0.02	8.45 ± 0.03	8.47 ± 0.02	8.48 ± 0.03	8.51 ± 0.02	8.53 ± 0.02	8.55 ± 0.03
	Oxalic acid	8.44 ± 0.02	8.53 ± 0.01	8.66 ± 0.01	8.88 ± 0.01	9.18 ± 0.02	9.35 ± 0.01	9.43 ± 0.03
	Tartaric acid	8.44 ± 0.02	8.47 ± 0.01	8.51 ± 0.01	8.51 ± 0.02	8.48 ± 0.02	8.53 ± 0.01	8.55 ± 0.01
	Malic acid	8.44 ± 0.02	8.06 ± 0.02	8.14 ± 0.03	8.24 ± 0.01	8.27 ± 0.01	8.36 ± 0.04	8.40 ± 0.03
	Citric acid	8.44 ± 0.02	8.31 ± 0.02	8.40 ± 0.01	8.62 ± 0.02	8.79 ± 0.02	8.85 ± 0.02	8.90 ± 0.02
Daxin soil	Acetic acid	5.77 ± 0.02	5.84 ± 0.01	5.86 ± 0.01	5.90 ± 0.01	6.02 ± 0.00	6.07 ± 0.01	6.24 ± 0.00
	Fumaric acid	5.77 ± 0.02	5.87 ± 0.01	5.92 ± 0.01	5.91 ± 0.02	5.98 ± 0.04	6.04 ± 0.02	6.11 ± 0.01
	Oxalic acid	5.77 ± 0.02	5.87 ± 0.01	6.03 ± 0.05	6.14 ± 0.02	6.46 ± 0.06	6.70 ± 0.02	7.00 ± 0.05
	Tartaric acid	5.77 ± 0.02	5.87 ± 0.01	5.96 ± 0.01	5.99 ± 0.03	6.02 ± 0.04	6.11 ± 0.02	6.26 ± 0.01
	Malic acid	5.77 ± 0.02	5.87 ± 0.01	5.99 ± 0.02	6.07 ± 0.02	6.21 ± 0.03	6.56 ± 0.02	6.89 ± 0.03
	Citric acid	5.77 ± 0.02	5.90 ± 0.04	6.12 ± 0.03	6.30 ± 0.03	6.70 ± 0.07	7.07 ± 0.03	7.23 ± 0.01

[a] Values ± SD ($n = 3$)

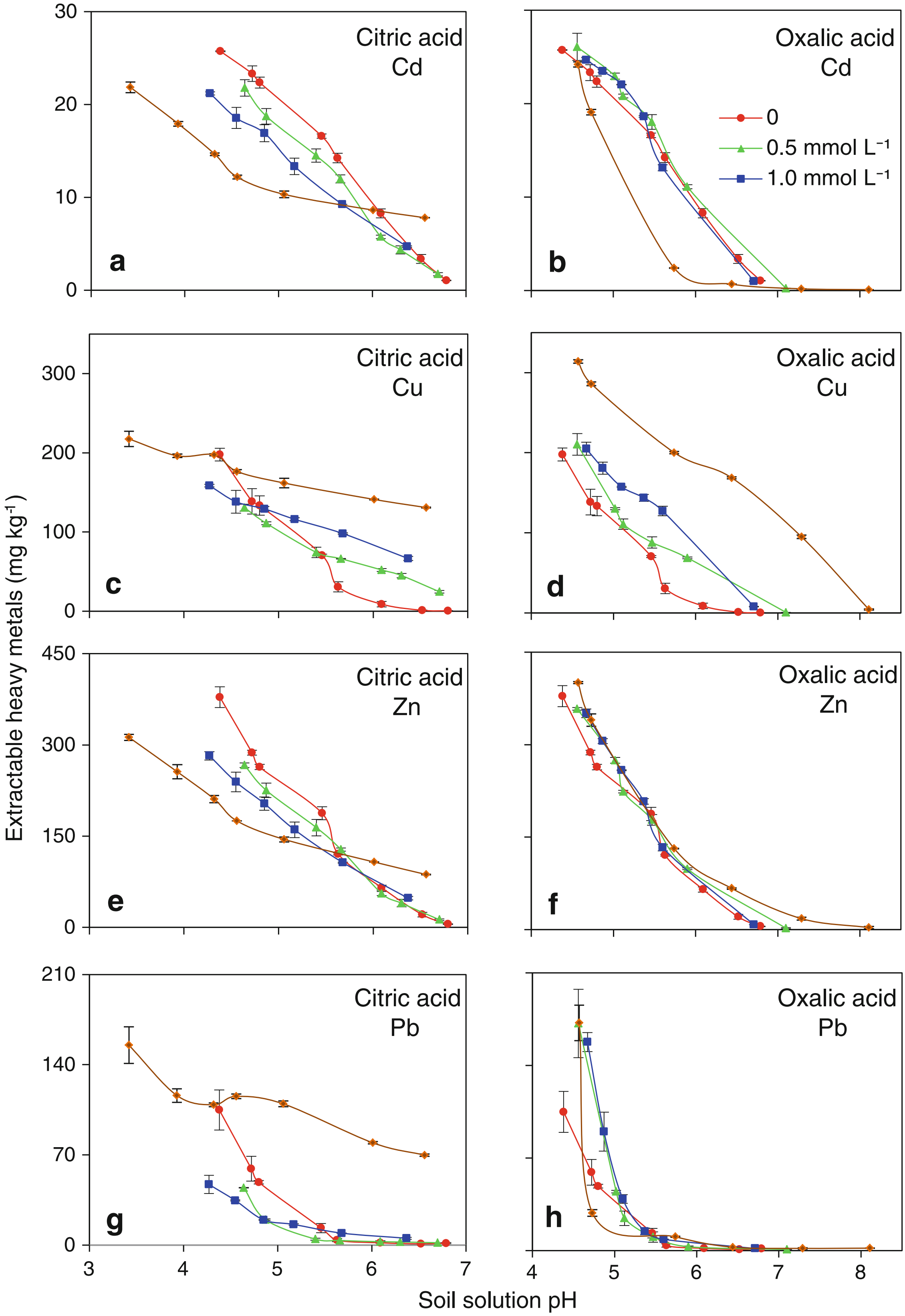

Fig. 1 Extraction of Pb, Cd, Zn and Cu from Chenzhou soil by citric acid and oxalic acid as a function of pH. *Error bars* represent standard deviations of triplicate measurements

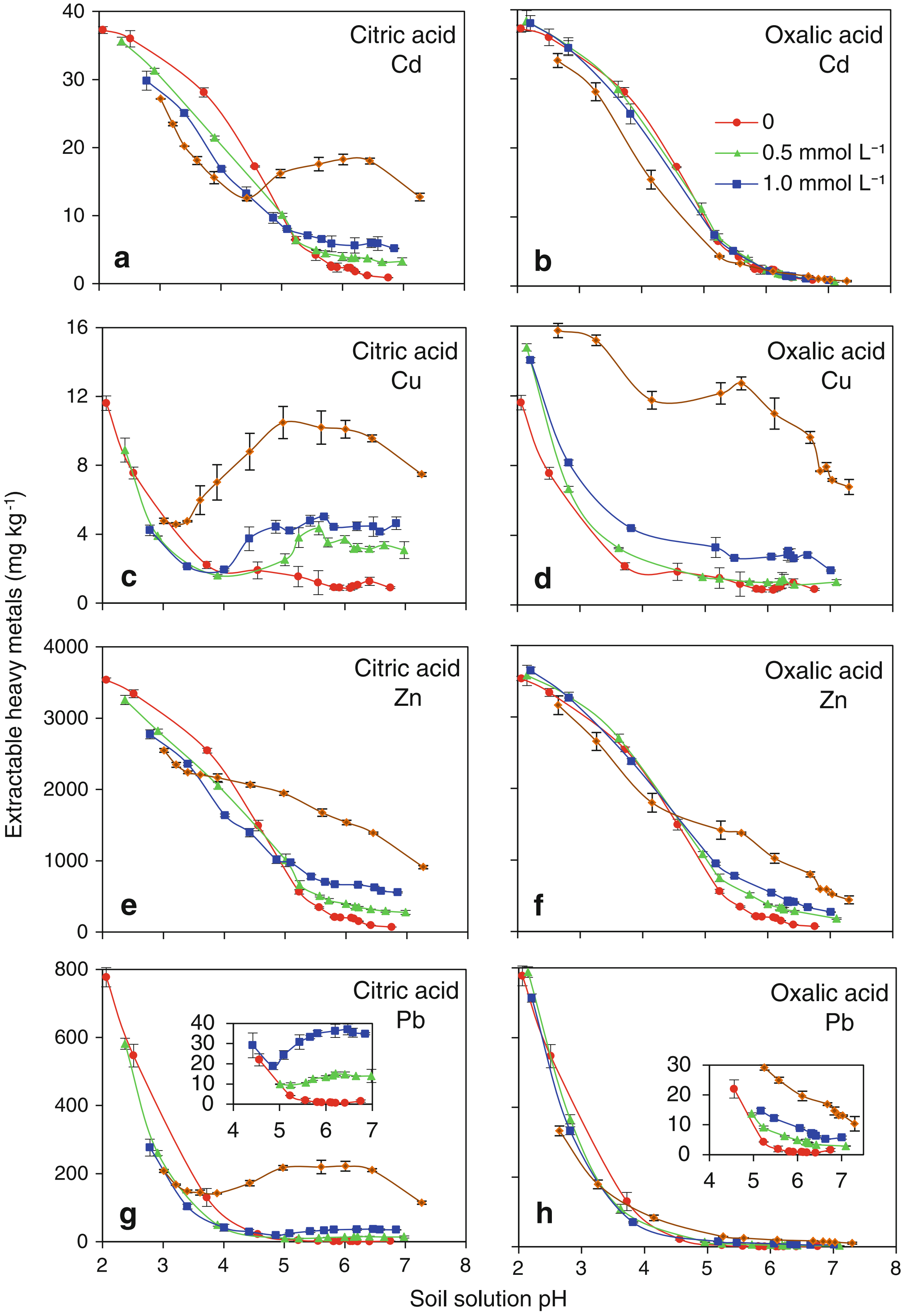

Fig. 2 Extraction of Pb, Cd, Zn and Cu from Daxin soil by citric acid and oxalic acid as a function of pH. *Error bars* represent standard deviations of triplicate measurements

Extractability of heavy metals in mine soils by organic acids as a function of pH

The extraction amount of heavy metals significantly decreased with increasing pH (Figs. 1 and 2). In the absence of organic acids, for Chenzhou soil, when equilibrium pH increased from 4.4 to 6.8, the extraction of heavy metals decreased as follows: Cd from 25.7 to 1.04 mg kg^{-1}, Cu from 198 to 0.34 mg kg^{-1}, Zn from 379 to 5.44 mg kg^{-1} and Pb from 105 to 1.50 mg kg^{-1}. For Daxin soil, when pH increased from 2.1 to 6.8, the corresponding decrease was: Cd from 37.3 to 0.88 mg kg^{-1}, Cu from 11.6 to 0.90 mg kg^{-1}, Zn from 3,538 to 80.0 mg kg^{-1} and Pb from 777 to 1.56 mg kg^{-1}, respectively. The dependency of heavy metals on soil pH was consistent with the results obtained by some previous researchers (Appel and Ma 2002; Qin et al. 2004). The net negative surface charge of soils increases with increasing pH, resulting in higher affinity between soil surfaces and heavy metal ions (Harter and Naidu 2001). Further, pH changes the ion forms of metals adsorbed on soil surfaces where the hydrolysis of metal cations increases with increasing pH. In addition, soil pH also affects the solubility of heavy metals by influencing the surface potential, clay edge charge, ion-pair formation, the solubility of organic matter and the stability of metal carbonates and phosphates (Appel and Ma 2002). In a word, due to these changes of heavy metals in adsorption, solubility, stability, etc., the extractability of heavy metals was affected strongly by soil pH, in which there is usually marked decrease in the extraction of heavy metals with the increase in soil pH.

In the presence of organic acids, the extraction of heavy metals from mine soils also decreased with increasing pH (Figs. 1, 2). However, for Daxin soil, the extraction of Cd, Cu and Pb by citric acid had different trend with increasing pH, where the extraction amounts decreased sharply at first, then increased dramatically and then declined significantly again (Fig. 2). Ding et al. (2008) also found the similar behavior for Cd on red soil and paddy soil. The main form of citric acid (denoted as H_3L) changed from H_3L to H_2L^- to HL^{2-} and finally to L^{3-} with the increase in soil pH. Because the latter two forms had higher chelating ability to heavy metals and restricted stronger the hydrolysis of heavy metals than other formers, there was more extraction of heavy metals at higher pH (Qin et al. 2004). For Chenzhou soil, the extraction of heavy metals continually decreased with increasing pH (Fig. 1), it could be explained that there had higher affinity to heavy metals and soil pH played dominant role in controlling the solubility of heavy metals.

Different concentrations (0–5 mmol L^{-1}) of citric acid or oxalic acid exerted different effects on heavy metal solubility, depending on the soil solution pH and the specific organic acid. For example, citric acid promoted Cd adsorption at low pH, whereas it enhanced Cd desorption at high pH; oxalic acid had little effect except it enhanced Cd adsorption at high concentration (5 mmol L^{-1}). Some previous researchers (Naidu and Harter 1998; Ding et al. 2008) also found that Cd adsorption was enhanced in the presence of organic ligands at low pH. However, other studies have shown that Cd extraction increased with an increase in citrate concentration (Gao et al. 2003; Hu et al. 2006). Copper extraction increased as the concentration of citric or oxalic acid increased, indicating that dissolved citric and oxalic acids compete over soil adsorption sites for Cu. For Zn, the effect of citric acid was similar to Cd, whereas that of oxalic acid differed between both soils. The oxalic acid had similar effects as citric acid on the Daxin soil but had little effect on the Chenzhou soil. For Pb, the citric and oxalic acid enhanced desorption on the Daxin soil. In the Chenzhou soil, Pb was little affected by organic acids, but the strong complexing ligand, citrate, reduced Pb sorption at a high concentration (5.0 mmol L^{-1}). Overall, citric acid and oxalic acid could increase the leaching risk of heavy metals at high pH, whereas only oxalic acid could increase Cu leaching at low pH.

With the introduction of organic acids, the solubility of heavy metals could be changed due to the interaction among soil surfaces, soil solution pH, organic ligands and heavy metals. On the one hand, organic acids enhanced the mobility of heavy metals by forming stable metal–ligand complexes, or by directly competing for cation adsorption sites or by reducing the negative electrostatic potential of soil surfaces (Collins et al. 2003). On the other hand, organic acids could also decreased the mobility of heavy metals by co-adsorbing on soil surfaces and forming soil organic acid–metal bridge (ternary) complexes (Naidu and Harter 1998). In short, the effect of organic acids on the solubility of heavy metals in soils is not simple or constant. For example, in this study, organic acids at low concentration can extract more heavy metals than at high concentration in some cases (Figs. 1, 2), and weak organic acids can extract more heavy metals than strong organic acids (Fig. 2c, d). Therefore, more researches should be focused on the interaction among soils, organic acids, heavy metals and soil solution pH.

Conclusion

The effects of different organic acids on the extraction of Pb, Cd, Zn and Cu from an alkaline mine soil and an acid mine soil were conducted. Under alkaline conditions, citric acid could extract some heavy metals with high concentrations. Under acidic conditions, the extraction of heavy metals from both soils decreased with increasing pH. Citric and oxalic acids increased the risk of leaching of heavy metals at high pH, whereas at low pH, only oxalic acid increased Cu leaching. The risk of heavy metals leaching from the Daxin soil was higher than that from the Chenzhou soil, which had a higher acidic buffering capacity than the Daxin soil. The results indicate that the effects of organic acids on heavy metal dissolution depend on soil properties, the types of heavy metals, organic acids (types and concentrations) and the pH of the rhizosphere. Plants that produce substantial citric acid, oxalic acid or protons from root exudation or litter degradation should be avoided in the vegetative rehabilitation of mining sites, especially for acidic mine soils.

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