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The Role of Organic Acids in the Mobilization of Heavy Metals from Soil

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Abstract

Batch laboratory experiments were performed to determine the effectiveness of organic acids in mobilizing heavy metals (Cu, Pb, Zn) from contaminated soils. Because the direct measurement of all of the species that are extracted by an organic acid is not possible, we calculated the speciation of Cu, Pb, and Zn in the presence of oxalate with regard to the primary distribution of metals and oxalate in solution using GEOCHEM-PC. Significant amounts of copper and zinc were removed from contaminated soil at higher initial concentrations of oxalic and succinic acids in solution. For the viewpoint of lead immobilization in soil, citric acid was the most effective among organic acids. Our speciation calculations by GEOCHEM-PC for metal-oxalate complex imply that significant amounts of the Cu, Pb and Zn that was extracted from the soil existed as oxalate complexes and free metal ionic form.

Keywords: *copper, mobilization, lead, oxalic acid, succinic acid, zinc*

1. Introduction

The concentrations of heavy metals at industrial and municipal waste sites with contaminated soils are generally several orders of magnitude higher than such concentrations in nature (Travel, 1989; Rautengarten *et al.*, 1995; Ahmad *et al.*, 2005). Because heavy metal contaminated soils contain high heavy metal contents and suffer serious acid deposition by acid rain, we can opine on the potential consequences for the ecosystem.

Heavy metals that contaminate soil react with soil components in many ways (Evan, 1989; Murray *et al.*, 1997; Evangelou and Marsi, 2001; Covelo *et al.*, 2004). The reaction mechanisms and rates depend on the type and amount of organic matter, clay, and hydroxides that are in the soil. Other factors include the concentration of exchangeable cations, pH, oxidation-reduction potential, and moisture content of the soil.

Many Low-Molecular-Weight (LMW) aliphatic organic acids, which exist naturally, have been identified, including acetic, citric, formic, oxalic, and succinic acid (Stevenson, 1982; Fox, 1990; Bolan *et al.*, 1994; Cozzarelli *et al.*, 1994; Cieslinski *et al.*, 1998). Organic acids, such as citric, oxalic, and succinic acid, which form relatively stable complexes with metals, have greater potential to mobilize metals from soil than those that do not, such as acetic and formic acid (Stevenson, 1985; De Wit *et al.*, 1993; Hedges and Oades, 1997; Ravichandran, 2004).

The adsorption of LMW organic compounds onto soil surfaces affects the dissolution of heavy metals from the soil surface. Anionic organic compounds adsorb onto most structural metals in soils, endowing a net negative charge to the soil surface. Complexation of metal centers on soil surfaces by organic compounds can accelerate heavy metal dissolution rates (Furrer and Stumm, 1983; Jones, 1998; Duckworth and Martin, 2001; Lumsdon and Farmer, 2005). Because LMW organic anions function as organic ligands, they increase the mobilization of heavy metals from contaminated soil by (i) replacing adsorbed metals at the soil surface through ligand-exchange reactions, (ii) dissolving metal-oxides from surfaces that have adsorbed metals, and (iii) forming metal-organic complexes in solution (Stone, 1988; McColl and Pohlman, 1986; Pohlman and McColl, 1986; Banks *et al.*, 1994; Burckhard *et al.*, 1995).

Several authors have investigated the effects of organic acids on metal dissolution from well-characterized silicate minerals and contaminated soils (Elliott *et al.*, 1989; Elliott and Brown, 1989; Wasay *et al.*, 2001; Lim *et al.*, 2004). Other studies have discussed the importance of the type and position of the functional group in organic acids in metal complexation reactions from primary minerals (Tan *et al.*, 1986; Linn and Elliott, 1988; Martin and Ruby, 2004; Kakitani *et al.*, 2007; Yuan *et al.*, 2007). Therefore, based on their properties, LMW organic acids can be used as agents in washing or flushing soil to develop an innovative technology for the remediation of soil that has been contaminated with heavy metals. This study discusses the feasibility of soil remediation using low-molecular-weight organic acids, such as acetic, citric, oxalic, and succinic acid, especially, in soil con-

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taminated with copper, lead, and zinc. The objective of this study is to determine quantitatively the role of organic acid in the mobilization of heavy metal from contaminated soil.

2. Materials and Methods

2.1 Soil Samples

The soil used in this study was collected from electroplating industrial complex in Ansan, Korea. This area is contaminated by metals due to leakage from electroplating wastewater operations. The soil samples were collected from the surface (0~20 cm) and transported to our laboratory in plastic barrels. The soil was spread out onto sheets of brown paper. When sufficiently air-dried, the soil was ground with wooden roller, passed through a 2-mm sieve, sealed in a plastic bag, and stored in a refrigerator for designed experiments. Metal concentrations in the soil were determined by a nitric–perchloric acid digestion following the procedure recommended by Association of Official Analytical Chemists (AOAC) (1990). One gram of sample was placed in a 250 mL digestion tube and 10 mL of concentrated HNO_3 was added. The mixture was boiled gently for 30~45 min to oxidize all easily oxidizable matter. After cooling, 5 mL of 70% $HClO_4$ was added and the mixture was boiled gently until dense white fumes appeared. After cooling, 20 mL of distilled water was added and the mixture was boiled further to release any fumes. The solution was cooled, further filtered through Whatman No. 42 filter paper and <0.45 μm Millipore filter paper.

2.2. Experimental Procedures

Batch experiments were conducted to determine the effect of organic acids (acetic, succinic, oxalic, and citric acid) on the mobilization of heavy metals, such as Cu, Pb, and Zn, from contaminated soil at various concentrations of organic acids (1, 10, and 100 mM) and initial pHs (3.5, 4.5, 5.5, and 6.5). The pH was controlled with HCl and NaOH. For each condition, we added 2.5 g of soil to 25 mL of organic acid solution in a centrifuge bottle and covered with a Teflon cork in darkness to avoid photooxidation. Each bottle was then shaken by hand for 1 min to ensure full saturation of the soil with the solution and then the bottles were shaken on an orbital shaker at room temperature and 250 rpm for 24 hr. The pH was measured after the soil was removed by centrifugation at 10,000 rpm for 30 min.

2.3. Analyses

The Cation Exchange Capacity (CEC) and Organic Matter (OM) of soil used in this study were determined by an ammonium-acetate method and $FeSO_4$ titration method, respectively (US EPA, 1995). The total concentration of each metal in the supernatant was measured on an inductively coupled plasma mass spectrometer (IRIS Intreoid II XDL Duo, Dongil Science, Korea).

The percents of each metal removed were calculated using an equation similar to one earlier reported by Reddy and Chinthamreddy (2000) as:

$$\text{Percent metal removed (\%)}\ \frac{C_L V_L}{C_S m_s} \times 100 \qquad (1)$$

Where C_L and C_S are the concentrations of metal in supernatant (in mg L^{-1}) and soil (mg kg^{-1}), respectively; V_L is the volume of supernatant (in L) and m_S is the dry mass of the soil (in kg).

3. Results and Discussion

3.1 Characteristics of Contaminated Soil

The textural analysis of contaminated soil showed the preponderance of sand fraction (81.2%), followed by silt (10.1%), then clay (8.7%). The pH of soil is slightly acidic as 6.2. Also, the soil had relatively lower OM content (5.6%) and CEC (4.1 cmol kg^{-1}) than soil with high sand content. The relatively low levels of silt, clay, OM and CEC indicate the high permeability, hence leachability of heavy metals in soil and suggest that it might be amendable to remediation by soil washing (Ehsan *et al.*, 2006; Atafar *et al.*, 2010).

Contaminated soil was analyzed to determine the initial metal content of the soil (see Fig. 1). Based on our metal speciation calculations, the distribution of free metal was 67% (Cu), 72% (Zn), and 84% (Pb), respectively (data not shown). The lead content was greatest due to its high adsorption to soil and the presence of more free cations in solution. Fig. 1 also shows the amounts of Cu, Pb, and Zn that were extracted by pH-adjusted distilled water (pH = 3.5), representing the amounts of water-soluble metals.

3.2 Metal Mobilization using Oxalic Acid

Appropriate amounts of potassium oxalate ($K_2C_2O_4$) and oxalic acid ($H_2C_2O_4$) at the same concentrations were mixed to prepare the buffered solution at the desired pHs. The pH of each mixture, which represents a fixed ratio of [potassium oxalate]/[oxalic acid] at the same concentrations, is shown for oxalate concentrations of 1, 10, and 100 mM in Fig. 2. Because the addition of HCI to an oxalate sample is not necessary to adjust its pH, Fig. 2 shows results that can be used to prepare oxalate solution samples at a

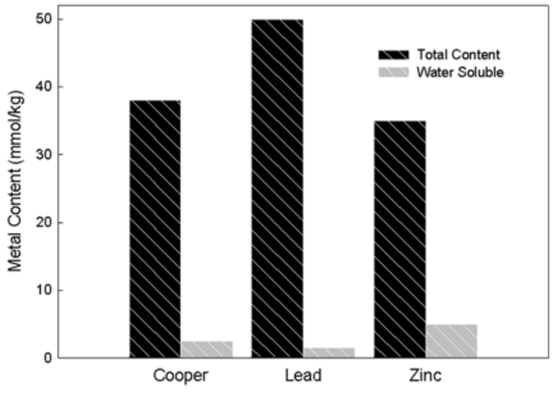

Fig. 1. Initial Metal Content and Water-soluble Amounts in Contaminated Soils

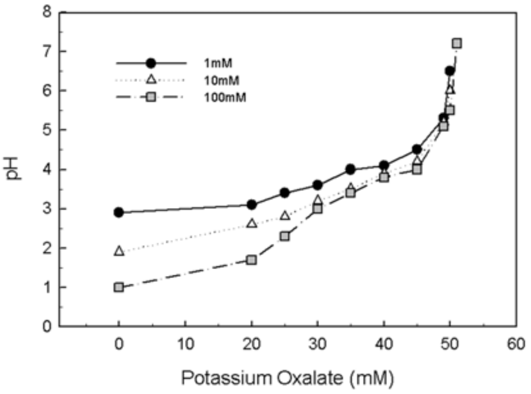

Fig. 2. pH of the Solution of a Mixture of Potassium Oxalate and Oxalic Acid

desired pH. The pH of 1, 10, and 100 mM oxalic acid is 1.0, 1.9, and 2.9, respectively.

The prepared potassium oxalate solution, however, had a neutral pH, regardless of the concentration. For example, 25 mL of 1 mM potassium oxalate and 25 mL of 1 mM oxalic were mixed to obtain a 1 mM oxalate sample at pH 3.5 for desorption experiments, based on the results of Fig. 2.

The effects of various levels of oxalic acid on the mobilization of Cu and Zn from contaminated soil are shown in Figs. 3(a) and 3(b), respectively. In general, high oxalic acid concentrations enhanced the mobilization of heavy metals from contaminated soil. We expected this result, because oxalic acid forms relatively strong water-soluble complexes with Cu and Zn. At 100 mM oxalic acid, over 90% of the copper was removed, regardless of its initial pH. Higher concentrations of organic acid were more effective to immobilize metals, highlighting that the importance of surface complexation reactions as a possible mechanism of metal release and metal complexation into solution.

For zinc, we observed competition between protons (log K = 3.82) and zinc (log K=3.88) for oxalic acid binding, which might explain the decrease in the zinc that was leached at a lower pH and concentration of ligand (K is a stability constant). As pH increases –i.e., as the amount of protons (H^+) decreases– the uncomplexed free oxalate ($C_2O_4^{2-}$) in solution can complex with more zinc in solution. This mechanism governs all three metals at lower organic ligand concentrations or higher pHs, because a proportion of the metals that have been leached can not complex with the organic ligand. The higher pH of the oxalic acid solution on removal is more effective because oxalate competes with protons and zinc at lower pHs. The differential behaviors of Cu and Zn during leaching can be attributed to variations in their coordination chemistry within the contaminated soil.

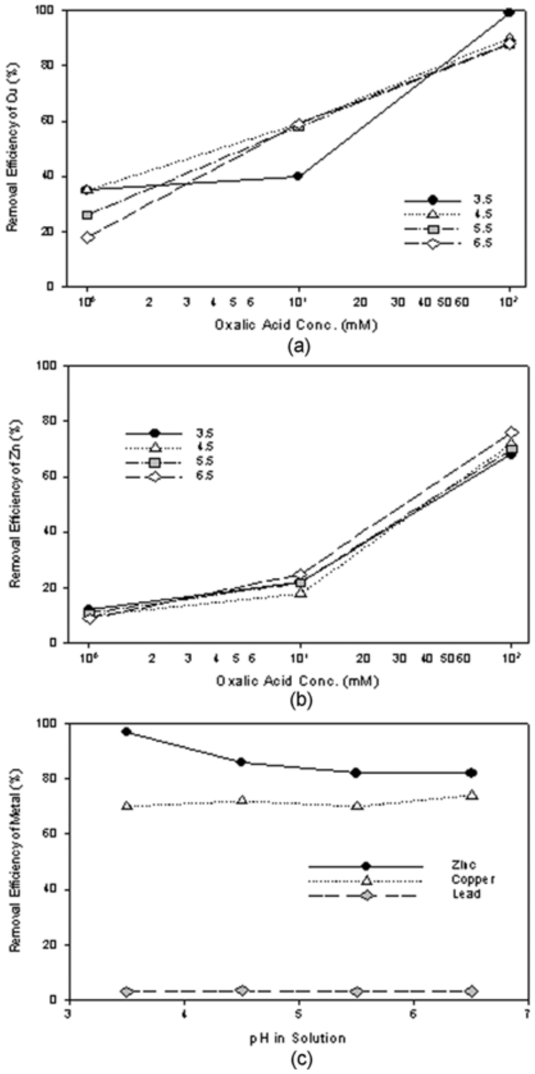

Fig. 3. Copper (a) and Zinc, (b) Removal with different Concentration of Oxalic Acid and Comparison of Metal Removal with Different pHs (c) from Contaminated Soil under the Addition of 100 mM Oxalic Acid

Figure 3(c) shows the removal of Cu, Zn, and Pb from contaminated soil as a function of initial pH at a fixed initial concentration of oxalic acid of 100 mM. This result indicates that oxalic acid is ineffective in removing lead from contaminated soil. The stability constants of Cu, Zn, and Pb with oxalic acid at 25°C and an ionic strength of 0.1 M were 4.8, 3.9, and 4.0, respectively. Based on these constants, oxalic acid can be a useful tool to remediate Cu- and Zn-contaminated soil. Since the solubility of the lead-oxalate complex is very low in water (0.00015 wt%), less than 5% of the total lead was removed from the contaminated soil. Based on modeling results, the extracted lead was precipitated as insoluble lead-oxalate complexes, which can not be separated from soil.

3.3 Metal Mobilization using Succinic Acid

The total amounts of Cu, Zn and Pb that were mobilized into the solution at various concentrations of succinic acid are shown in Fig. 4. The extent of metal removal was, in descending order, Zn>Cu>Pb, which was the opposite of our expectation, based on the stability constant (log K) values (see Table 1).

In general, organic ligands influence the dissolution of metals in soil by forming stable water-soluble complexes with them in soil solutions and thus depend on the log K of the ligand. Metal

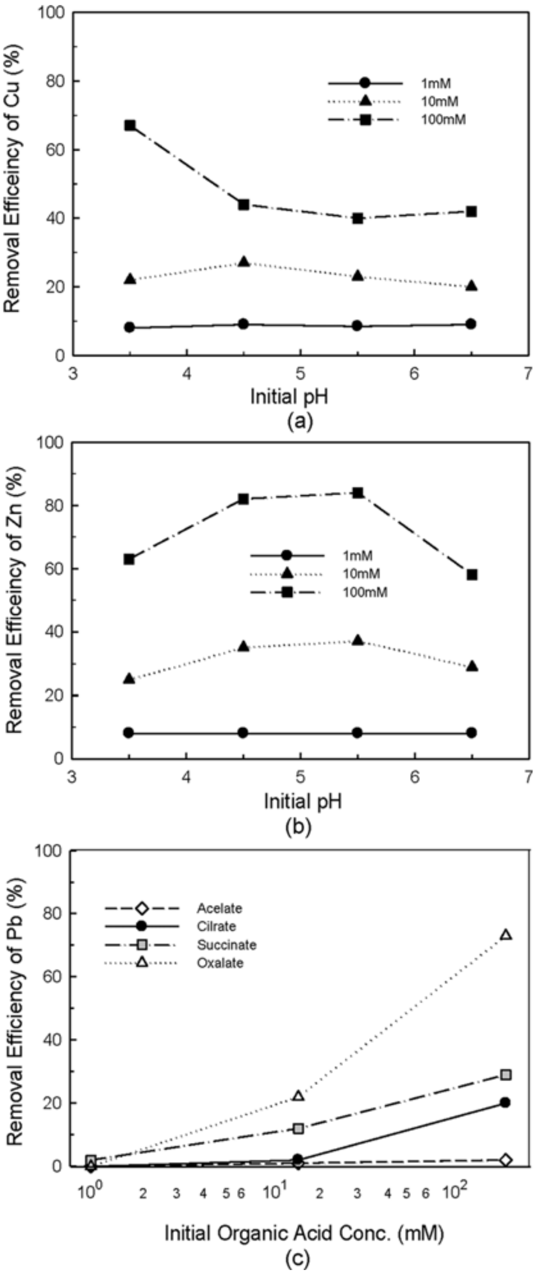

Fig. 4. Copper (a) and Zinc (b) Removal with different pHs and Concentration of Succinic acid and Lean Removal (c) with different Organic Acids

mobilization from soil also depends on its mode of retention in soil. Metal that is retained as inner sphere complexes is released through surface complexation reactions. In this case, there is a strong relationship between the released metal and the log K of the ligand. Although zinc had the lowest K value, it leached the maximum amount. Approximately 82%, 64%, and 41% of the total Zn, Cu, and Pb, respectively, in the soil leached out at 100 mM succinic acid and pH 3.5.

As shown in Figs. 4(a) and 4(b), lower pH values and higher concentrations of succinic acid are more effective in mobilizing metal from soil. At 100 mM succinic acid, copper removal from the contaminated soil decreased significantly with rises in initial pH. Further increases in pH promoted metal hydrolysis, which was accompanied by re-adsorption onto the soil surface or formation of copper hydroxide as a precipitate at approximately pH 4.5.

Table 1. Stability Constants of 4 Organic Acids with Cations at 25°C and an Ionic Strength of 0.1 M

Organic acids	H^+	Cu^{2+}	Zn^{2+}	Pb^{2+}
Acetic	4.56	1.89	1.10	2.15
Succinic	5.20	2.60	1.78	2.80
Oxalic	3.82	4.84	3.88	4.00
Citric	5.69	5.90	4.98	4.08

For zinc, the amount of zinc that was removed from the contaminated soil decreased in a specific pH range (pH>5.5 or pH<4.5) due to the competition of zinc and protons for binding succinate ions at lower pHs and the formation of zinc hydroxide at higher pHs. Because lead and copper have higher log K values with succinic acid, proton competition for these metals is not significant, and an increase in pH resulted in a decrease in metal concentrations in solution.

3.4 Comparison of Lead Removal Efficiencies using Organic Acids

Four organic acids – acetic, citric, oxalic and succinic acid– were compared with regard to removing lead from the contaminated soil at pH 5.5 and various initial concentrations of organic acids (see Fig. 4(c)). The total lead that was removed from the contaminated soil increased as organic acid concentrations rose. Approximately 80% of the initial lead content was removed with 100 mM oxalate. The total amount of lead that was removed depended on its stability constant with organic acid, with the exception of oxalic acid.

The stability constant of lead with oxalic acid was 3.32, which exceeded those of acetic and succinic acid. Yet, the lead ion that leached out from the contaminated soil precipitated as an insoluble lead-oxalate solid, a highly undesirable result. The order of solubilization of lead from the contaminated soil by organic acids suggests that the properties of organic ligands in solution, such as the stability constant and the solubility of the metal-ligand complex, are dominant factors. These observed sequences might be attributed to lead-organic ligand exchange and the solubilities of the complexes. The stability constants and solubilities of lead-organic complexes in water are summarized in Table 2.

3.5 Calculation of Metal Speciation

Speciation of the extracted heavy metals (Cu, Zn, and Pb) from contaminated soil in the presence of oxalate solution was calculated with a geochemical computer program, GEOCHEM-PC (Parker *et al.*, 1993). The calculations estimate the fate of each metal, oxalate, and inorganic ligand in the leachate at fixed conditions and inform us about the possible compounds in solution and their amounts with limited information, such as the given total concentration of metals and ligands. The results were

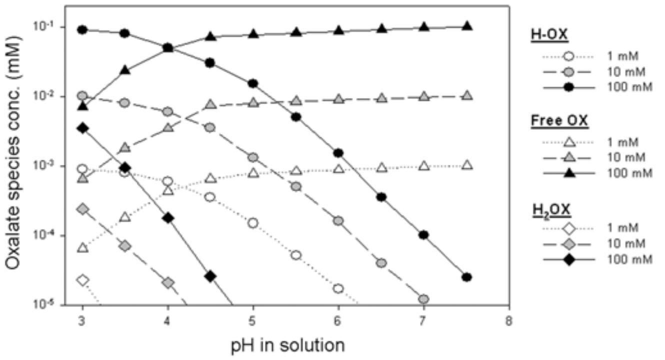

Fig. 5. Distribution of Oxalate Species in Solution as a Function of pH

determined by the geochemical modeling under the assumption that the association of metals and inorganic ligands (i.e., Cl^-, K^+, SO_4^{2-}, and OH^-) was negligible because the interference of the target metal-ligands complex can be resulted from various competition of metal and ligands existed in soil.

Oxalate (OX) exists primarily in three fractions –the undissociated form (H_2OX), partially dissociated form (HOX^-), and completely dissociated form (free oxalate ion, OX^{2-})– over an ordinary range of pH 3~7 (see Fig. 5).

Figure 6 shows the speciation of copper in solution at equilibrium as a function of initial pH at initial oxalate concentrations of 1 (Fig. 6(a)), 10 (Fig. 6(b)), and 100 mM (Fig. 6(c)). The major species of copper in the leachate solution consisted primarily of the free ionic form (Cu^{2+}) and complexed forms with mono- or dioxalate ions (i.e., Cu-mono-oxalate, Cu-di-oxalate).

At an initial oxalate concentration of 1 mM, the principal copper species were free ionic copper, Cu (OX), and Cu $(OX)_2$, in this order, over a range of pH 3 to 5. Above pH 5, the amounts of copper mono-oxalate and free ionic copper decreased, but the amount of copper di-oxalate rose with pH. The chief species of lead became lead di-oxalate as oxalate concentrations increased (see Figs. 6(b) and 6(c)). Higher pHs and oxalate concentrations favored the formation of copper that was complexed with dioxalate over free ionic copper and copper mono-oxalate.

The zinc species in the leachate were primarily complexed forms with oxalate (Zn(OX) or $Zn(OX)_2$) under the experimental

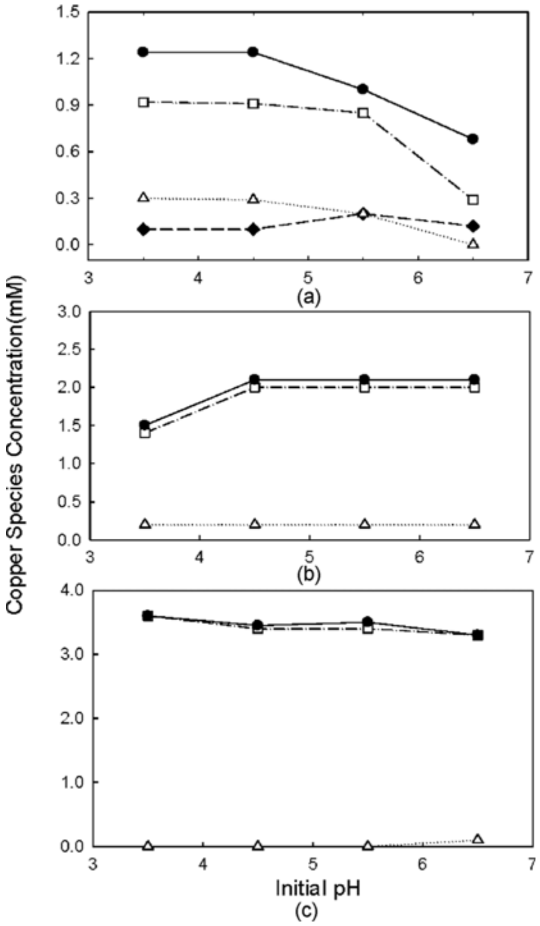

Fig. 6. Speciation Calculation of Copper that has been Mobilized from Contaminated Soil using: (a) 1 mM, (b) 10 mM, and (c) 100 mM, Respectively (●: total Cu, □: Cu-OX, ◆: $Cu(OX)_2$, △: Free Cu)

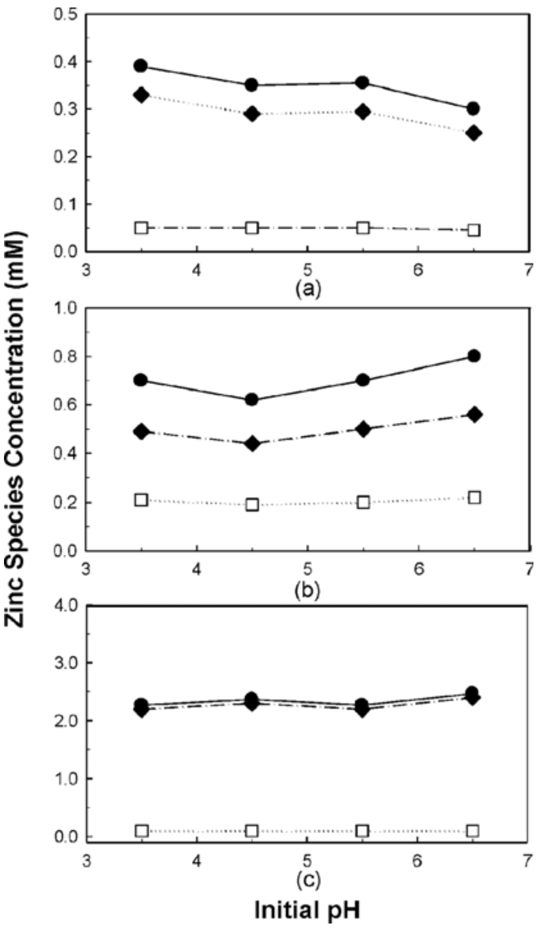

Fig. 7. Speciation Calculation of Zinc that has been Mobilized from Contaminated Soil using: (a) 1 mM, (b) 10 mM, and (c) 100 mM, Respectively (●: total Zn, □: Zn-OX, ◆: $Zn(OX)_2$)

conditions (see Fig. 7). The amount of zinc di-oxalate complex increased with rises in oxalic acid concentration, because more oxalate ions became available to complex with zinc in solution.

4. Conclusions

The effectiveness of organic acids in mobilizing heavy metals (Cu, Pb, Zn) from contaminated soils were investigated. Significant amounts of copper and zinc are removed from contaminated soil by oxalic acid and succinic acid. But, oxalic acid fails to remove lead due to the precipitation of lead-oxalate complexes out of solution. Of the four organic acids, citric acid is the most effective extracting agent in removing lead. Generally, the effectiveness of mobilizing and complexing heavy metals from contaminated soil increases with higher concentrations of organic ligand. Although the metal complexing abilities of organic acids are pH-dependent, the overall extent of heavy metal removal is insensitive to system pH, at higher ligand/metal concentration ratios. Chelating agents, such as low-molecular-weight organic acids, that convert soil-bound heavy metals through various mechanisms into soluble and stable complexes can be used in situ or ex situ soil washing/flushing technologies for cleanup of contaminated soils at actual polluted sites. Speciation calculations by GEOCHEM-PC predict that heavy metals exist primarily in two forms in the presence of oxalate solution: (a) complexed with oxalate and (b) in free metal ionic form.

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