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Experimental study for heavy metals mitigation in polluted soil

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Abstract

This work describes the removals of heavy metals from contaminated sandy loam soil using various extractants. The following extracting solutions were investigated for the removal of heavy metals from the soils using de-ionized water and organic acids (citric, gallic, DL - malic, oxalic, succinic and tartaric acids) suspended in calcium chloride. Overall, this study showed that complete removal of Cd^{2+}, Cu^{2+}, Ni^{2+}, Mn^{2+}, Pb^{2+} and Zn^{2+} from sandy loam soil is difficult to be achieved using the soil washing process, and also the use of one extractant may not be effective in removing all metals. A sequential extraction using different extractants may be needed for the removal of multiple metal contaminants from sandy loam soil.

Keywords: Soil washing; Citric; Gallic; DL - malic; Oxalic; Succinic; Tartaric.

INTRODUCTION

Recently, the environment contamination has become especially serious problem, as it is being transformed from the local level into regional and is gradually becoming a global issue (Juknys, 1994; Kuiters, 1996; Medvedev, 1999; Lopez Alonso *et al.*, 2000). Anthropogenic factors (industrial activity, mining, sewage disposal, traffic, etc.) are mainly responsible for increasing trace element concentrations in soil. The access of an element to plants is determined primarily by its origin, which influences its chemical forms, and by its association with soil components (Kabata-Pendias, 1995). Heavy metals are long-term contaminants with the ability to accumulate in soil and plants, and there is no natural way to remove those (White *et al.*, 2002).

Organic substances released by roots play a key role in these interactions. Indirect effects include the solubility, sorption, and transport of both: nutrients and pollutants. Direct influences involve acidification, chelation, precipitation, and oxidation reduction reactions (Awad *et al.*, 988; Dinkelaker *et al.*, 1989; Mench *et al.*, 1988;

Merbach *et al.*, 1999; Morel *et al.*, 1986; Schilling et al., 1998; Uren and Reisenauer, 1988; Zhang *et al.*, 1991). Natural, low molecular weight organic acids including oxalic, citric, formic, acetic, malic, succinic, malonic, maleic, lactic, aconitic and fumaric acids are natural products of root exudates, microbial secretions, plant and animal residue decomposition in soils (Naidu and Harter 1998; Yan *et al.*, 2012; Badri *et al.*, 2013; Huang *et al.*, 2014). The quantities and types of organic anions released vary considerably between plant species and on the environmental conditions, and their effects operate through multiple mechanisms (Jones, 1998). Thus metal dissolution by organic acids is likely to be more representative of a mobile metal fraction that is available to biota (Labanowski *et al.*, 2008). Because the dissociation constant of most organic acids is low compared with the neutral pH of plant cell contents, they are dissociated within the cell and released as organic anions rather than as acids (Hinsinger, 2001). The release of organic anions may contribute to acidification of the
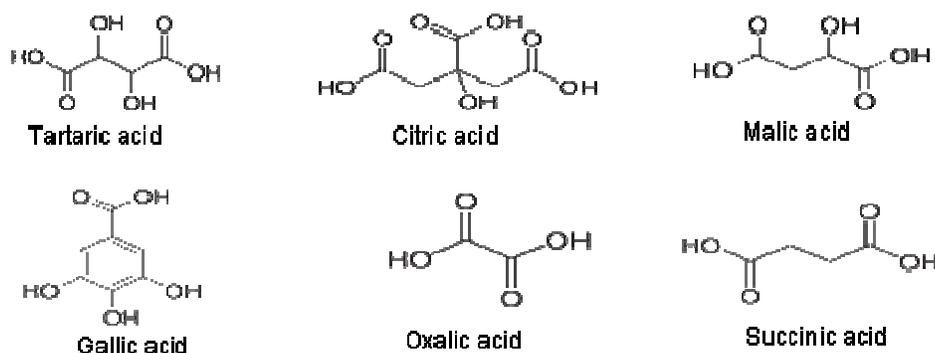
Figure1. Chemical structure of organic acid used in this work

rhizosphere via compensation for the release of net negative charge that they represent (i.e. organic anion efflux should be counterbalanced by an equivalent influx of OH^- or efflux of H^+) but, in general their effect on pH is small relative to the effect of the inorganic cation/anion balance of the plant (Kirk, 1999; Hinsinger *et al.*, 2003).

Chelating agents increase metals diffusion in the soil solution and keep them in plant available forms by forming large, less reactive ions, by increasing the concentration of these larger chelated ions in solution, and by decreasing the ability of the free ions to react with the soil. The chelating organic acids are able to dislodge the exchangeable, carbonate and reducible fractions of heavy metals by washing procedures (Peters, 1999). Although many chelating compounds including citric acid (Naidu and Harter, 1998), tartaric acid (Ke *et al.*, 2006) and EDTA (Tejowulan and Hendershot, 1998; Peters, 1999; Sun *et al.*, 2001) for mobilizing heavy metals have been evaluated, there remain uncertainties as to the optimal choice for full-scale application.

The objective of this is work to evaluate the appropriate procedure to extract heavy metals using organic acids (gallic acid, tartaric acid, citric acid, DL - malic acid, oxalic acid and succinic acid) to decontaminate a soil via soil washing experiment. Figure 1 above.

MATERIALS AND METHODS

Chemicals, reagents and apparatus

All reagents used were of analytical grade. Deionized water was used for all the prepared reagent solutions. Stock standard solutions of cadmium (Cd), copper (Cu), lead (Pb), nickel (Ni), manganese (Mn) and zinc (Zn), were obtained from Merck in concentrations of 1000 mg/L (Merck, Darmstadt, Germany). Citric and oxalic acids were Loba Chemie Pvt. Ltd. product, while DL-malic, L(+) tartaric, succinic and gallic acids were Oxford laboratory

products.

Normal laboratory glassware (borosilicate), polyethylene vessels, a pH meter, shaker (Model TT 12F, Techmel and Techmel, US) and a digitally operated high speed centrifuge (Model TGL- 16G) were used.

Soil sampling, saturation extract and characterization

Sampling: Surface triplicate soil samples (0-15 cm) were collected from an agricultural lands using auger from El-Giza government. The soil samples were air-dried, ground and sieved to give < 2 mm particle size, bulked up to get a composite sample.

Mechanical analysis was conducted in two stages: 1) sieve analysis (Nawy, 1997) for coarse fractions (gravel and sand) and 2) pipette methods (Gee and Bauder, 1986) for fine fractions (silt and clay). Soil organic matter (OM) was digested with H_2SO_4 + $K_2Cr_2O_7$ and determined with phenanthroline titration. Digestion sample; A representative sample of 0.25 g was ashed at 450°C for 4 h prior to digestion in 9 mL concentrated HNO_3 and 3 mL concentrated HCl (US EPA, 1998).

Saturation extract: Soil saturation extracts were prepared by mixing 200 g of soil with deionized water (DI) and, then, the watery soil (sealed with a plastic cover; parafilm) was equilibrated for 24 h (Rhoades, 1996). Three replications were performed for each soil sample. The watery soil solutions were extracted by vacuum and the solution extracts were spilt in 2 portions for the following analysis. Then the one of the extract samples was acidified with 1% of concentrated HNO_3 for heavy metal determination by ICP-MS. The other portion was used for determination of pH and EC parameters using pH and EC were measured at 25°C using Info Lab meters.

Natural aliphatic acids (citric, oxalic, DL-malic, succinic acid and tartaric acid) and natural aromatic acid (gallic acids) were selected in this work. The soil samples (3 g) were added to different concentration (0, 1, 5, 10, 15, 20

Table 1. Physicochemical properties and studied heavy metals (mg/kg) of soil samples

Parameter	Concentration	Parameter	Concentration
Sand (%)	78.48±1.10	Organic carbon (%)	15.36±0.1
Silt (%)	8.01±1.70	Cadmium (mg/kg)	3.79±0.03
Clay (%)	13.51±1.25	Copper (mg/kg)	419.61±1.85
Soil texture	Sandy loam	Lead (mg/kg)	463.25±1.21
pH	7.85±0.01	Manganese (mg/kg)	2099.21±0.17
EC (µS/cm)	775.54±1.21	Nickel (mg/kg)	164.9±0.52
Calcium carbonate (%)	0.79±0.005	Zinc(mg/kg)	1785.64±7.52

Table 2. Heavy metals studied in extracted water soluble solutions from soil samples.

Parameter	Concentration	Parameter	Concentration
Cadmium (mg/kg)	0.01	Copper	0.90
Manganese (mg/kg)	6.41	Lead (mg/kg)	0.10
Nickel (mg/kg)	0.86	Zinc (mg/kg)	1.45

mmol/kg) of each organic acid and after that were suspended in 30 mL CaCl$_2$ (10 mmol/L) in 50 mL centrifuge tube. The samples were shaking for 24 h at 300 rpm, then the tubes were centrifuged at 3000 x g for 15 min, and the supernatant filtered. The filtrated samples were analyzed on ICP-MS to determine the concentration of cadmium (Cd), copper (Cu), lead (Pb), nickel (Ni), manganese (Mn) and Zinc (Zn).

All tests were performed in triplicates and the results were presented as averages of the triplicate extracts. The percent of each metal removed were calculated using the following equation:

$$Percent\ metal\ removed\ (\%) = [\frac{C_1 V_1}{C_S m_S}] \times 100$$

Where C_l and C_S are the metal concentrations in supernatant (mg/L) and soil (mg/kg), respectively; V_l is the volume of supernatant (L) and m_S is the dry mass of the soil (kg).

Statistical analysis

SPSS, ver. 17, 2008, statistical model was used to calculate mean values, standard deviation and correlation between parameters measured through this study.

RESULTS

Soil characteristic

Physicochemical properties of soil are presented in Table 1. The pH of soil is 7.85 within the range of agricultural soils and slightly alkaline. EC value is less the limit recommended for agriculture (2000 µS/cm). Textural analysis showed the preponderance of sand fraction (78.48%) followed by clay fraction (13.51), then silt fraction (8.01%), thus classifying the parent soil as sandy loam (Soil Survey staff, 1975). The soil sample contains 15.36% organic carbon and 0.79% calcium carbonate. Cd, Cu, Ni, Pb and Zn were higher than the recommended limit 1.4, 63, 50, 70 and 200 mg/kg (CCME, 1991/ 1996). There is no recommended level for Mn^{2+}.

The results of soil sample extracted by deionized water were depicted in Table 2. The water soluble fraction represents the most soluble fraction in which the metals are easily removable by deionized water. The mean values of deionized water extractable Cd, Cu, Mn, Ni, Pb and Zn in the soils (as percentage from total) are 0.3, 0.2, 0.3, 0.5, 0.02 and 0.08%, respectively.

Effect of changing concentrations of chelating agent and its corresponding pH on heavy metals

Extraction efficiency of Cd, Cu, Mn, Ni, Pb and Zn contaminated soil by the six chelating agents (citric, oxalic, malic, tartaric and vanillic acids) were determined at different concentrations of chelating agent and its corresponding pH. The amount of Cd, Cu, Mn, Ni, Pb and Zn (%) from the contaminated soil that was determined in the filtrate obtained in the extraction test, with respect to their initial content in the contaminated soil is given in Figure 2 to 7. The mean values of the three replicate tests are reported and the standard deviation calculated for the replicate tests was about 1% of the average value.

The data presented in Figure 2, clearly demonstrate the desorption percentage of extractable Cd varied considerably depending on the type of organic ligand. The Cd desorption percentage increased as the organic acid concentration increased, but the desorption characteristics differed between studied acids. Among the organic acids
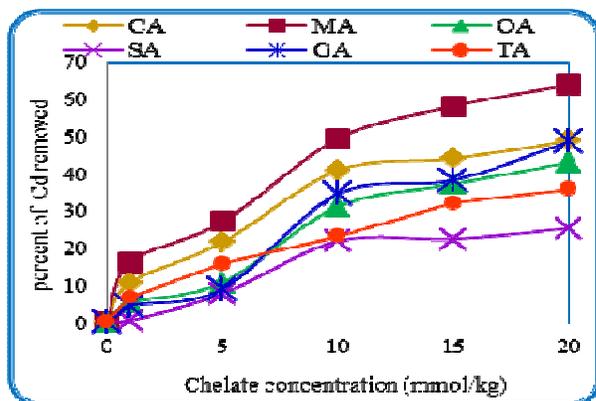
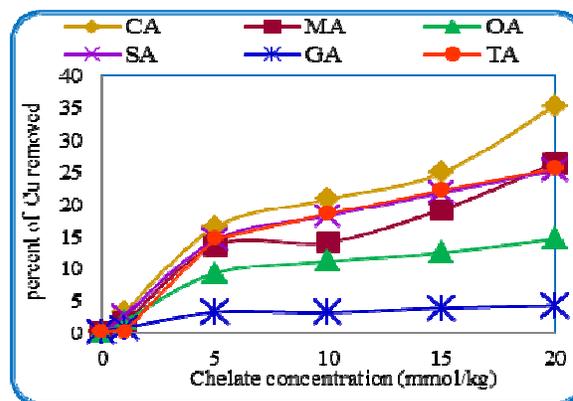**Figure 2.** Effect of chelating agents concentration on removal efficiency of cadmium from soil.

Figure 3. Effect of chelating agents concentration on removal efficiency of copper from soil.
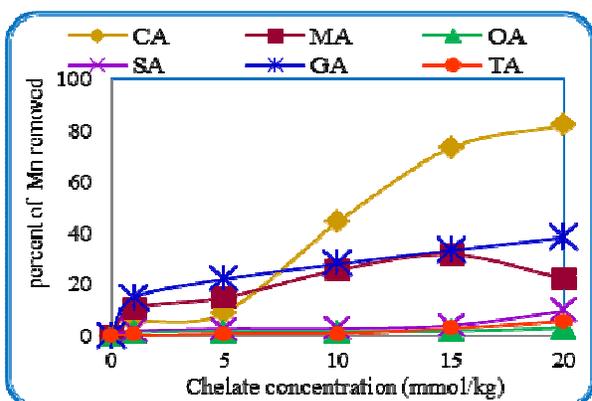

Figure 4. Effect of chelating agents concentration on removal efficiency of manganese from soil.
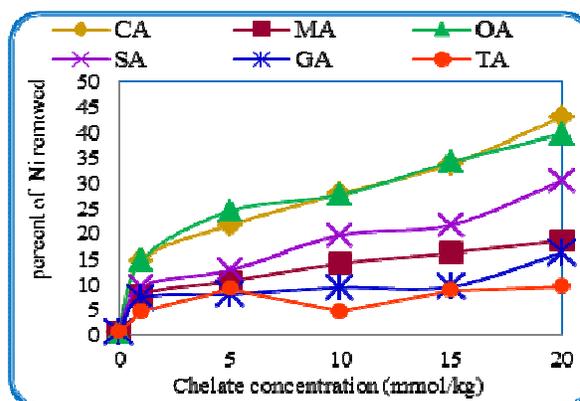

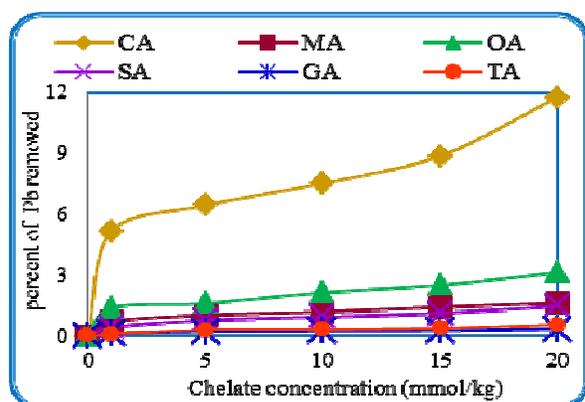**Figure 5.** Effect of chelating agents concentration on removal efficiency of nickel from soil.

Figure 6. Effect of chelating agents concentration on removal efficiency of lead from soil.
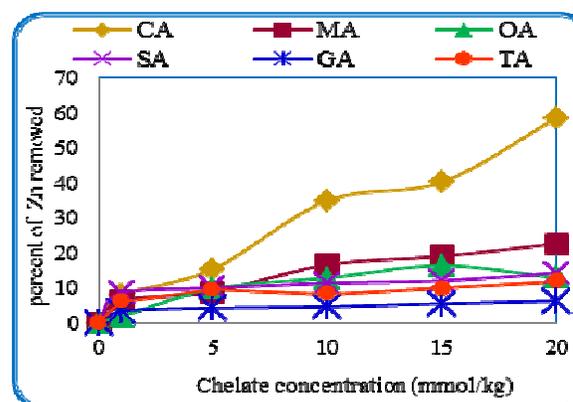

Figure 7. Effect of chelating agents concentration on removal efficiency of zinc from soil.

in this study, malic acid increased Cd desorption most, whereas succinic acid had the least effect. Figure 3 showed the influence of chelating organic acid on copper in soil; the removal efficiency of copper followed the order citric acid > succinic acid ≈ tartaric acid > malic acid >

oxalic acid > gallic acid. Figure 4 showed that citric acid was the most effective acid salt to remove manganese and the removal efficiency of different acids are arranged as the following; citric >> gallic > malic > succinic > tartaric > oxalic. Figure 5 showed the ranking order for nickel
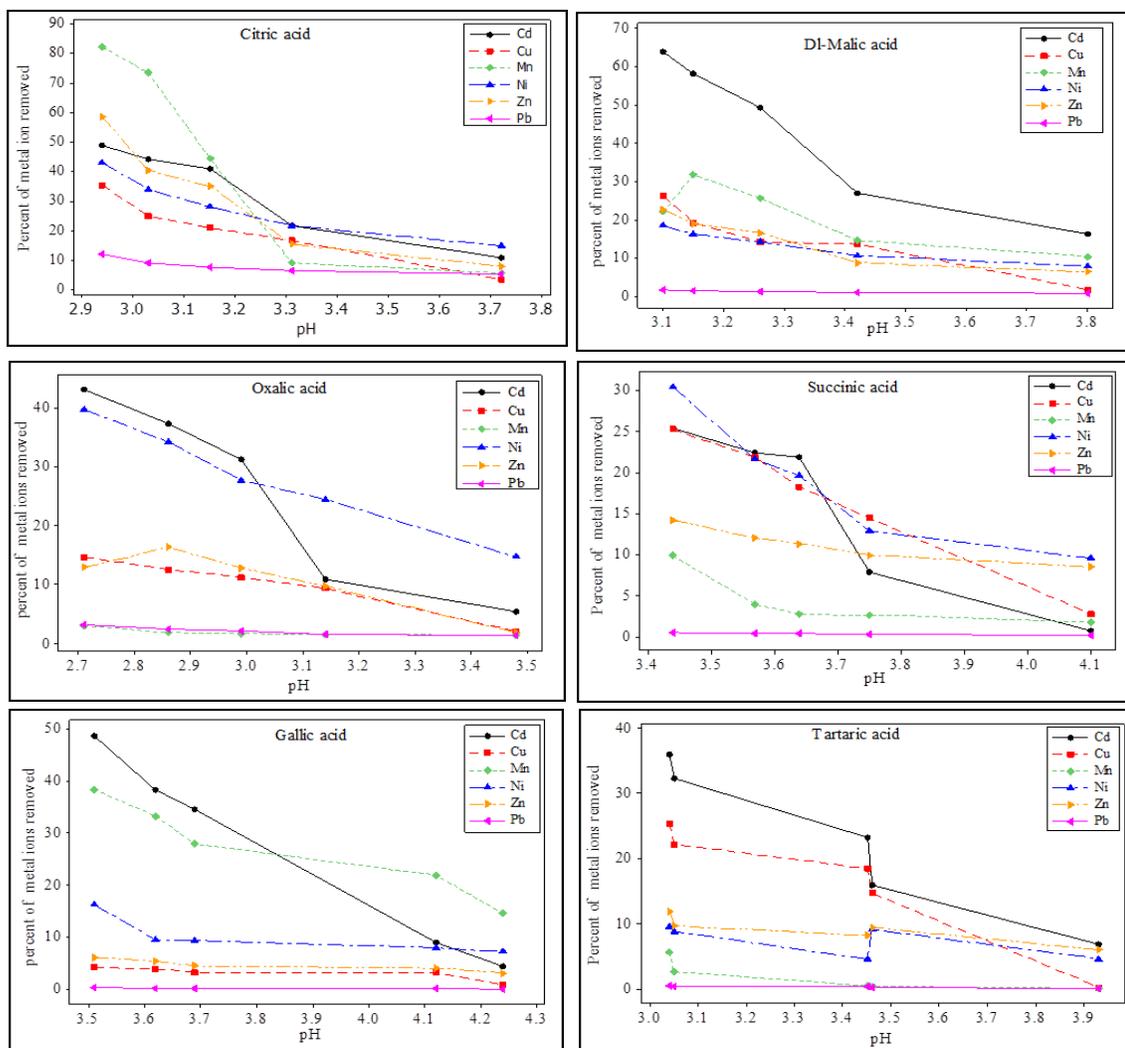
Figure 8. Effect of changing pH of organic acids suspended in $CaCl_2$ applied on metal ions desorption from soil.

desorption from soil by organic acid: citric ≈ oxalic > succinic ≈ malic > tartaric > gallic. The six chelants showed the least extraction yields for lead possibly due to its strong association with the residual soil fraction, Figure 6. The desorption order of lead was; citrate > oxalate > malate >> succinate > valinate > gallate. Figure 7 summarized the ranking order for Zn removal by organic acid was: citrate > malate > oxalate > succinate > tartrate > gallate.

Figure 8 depicted the increase of mobility of Cd^{2+}, Cu^{2+}, Mn^{2+}, Ni^{2+}, Pb^{2+} and Zn^{2+} is directly related to an increase of the solution acidification, caused by the application of organic acids used.

Figure 2 to 8 demonstrated that the removal efficiency increased as the concentration of organic acids increased, while the efficiency decreased with increased pH of extract solution.

DISCUSSION

Preliminary visual inspection showed that the soil was dark brown in color indicating high amount of humus. The sandy loam soil has a poor retention capacity for both water and metals. The relatively low levels of silt and clay indicate the high permeability, hence leachability of heavy metals in the soil and suggest that it might be amenable to remediation by soil washing (Ehsan *et al.*, 2006; Atfar *et al.*, 2010). The soil sample has low proportion of calcium carbonate, and high proportion of organic carbon. This may be due to the usage of industrial wastewater and sewage water for irrigation, in addition to compost and agriculture activity and mainly attributed to the fact that sewage water contains appreciable amounts of suspended matter, which deposit in the soil by irrigation causing high organic matter.

From the combined effect of chelating agent and pH on

heavy metals; it was observed that increasing the concentration of chelating agents favored more removal of the heavy metals from the contaminated soil. Desorption studies of trace or heavy metals have shown biphasic reaction processes, a fast reaction followed by a slow reaction (Sparks, 1990). The desorption of heavy metals from soil will be affected by factors such as, competition with Ca^{2+} ions in the liquid phase, the solid/liquid ratio, and the strength of the chelation between the organic ligands and heavy metals. When the organic acid concentration is low, the solid/liquid ratio is high, and the adsorption of organic ligands by soil solids is favored, then the organic ligands bound with heavy metals. On the other hand, organic acids in the liquid do combine with some Ca^{2+} ions, thus weakening the substitution ability of Ca^{2+}. The results showed that low concentrations of organic acids suppressed heavy metals desorption. As organic acid concentrations increased, the S/L ratio declined, and the amount of organic acid in the liquid increased. This means that the organic ligands bond easily with heavy metals in the liquid phase. Therefore the desorption ability of organic ligands enhanced and desorption rate increased.

Cadmium

Desorption of Cd from soil will be affected by factors such as, competition with Na^+ or Ca^{2+} ions in the liquid phase, and the strength of the chelation between the organic acids and Cd. In summary, high concentrations of organic acids promoted Cd desorption, but low concentrations of organic acids suppressed Cd desorption. Gallate and citrate desorbed the same percentage from Cd which is equal at 20 mmol/kg, respectively. Also Do Nascimento *et al.* (2006**)** demonstrated that gallic and citric acids were able to induce removal of Cd from soil without increasing the leaching risk.

Figure 2 showed the effectiveness of various chelants on Cd desorbed from soil followed an order maleate >> citrate ≈ gallate > oxalate > tartrate > succinate. Similarly, Wu *et al.* (2003) found that the ranking order for Cd extracted by organic acids, malic acid >> citric acid. In addition to Krishnamurti *et al.*, (1997); Naidu and Harter, (1998) demonstrated that malate, fumarate, and succinate being the most effective to be desorb Cd from soils.

The result of the present study also, Figure 8, indicated that as pH of extracted solution increased, the amount of extracted metal reduced. Similarly Naidu and Harter (1996), studied the effect of pH and different organic ligands on sorption and extractability of Cd by soils varying widely in chemical characteristics. For all soils, the amount of Cd extracted decreased with increasing pH, irrespective of the nature of the organic ligand. The ability of ligand ions to desorb Cd followed the sequence maleate > citrate > fumarate> succinate = tartrate > malonate > oxalate > salicylate > acetate. Later Naidu and

Harter (1998) reported that, the role of organic acids in Cd mobilization. Complexation of metals by organic ligands plays an important role in controlling metal solubility. Metal – ligand complex stability generally decreases with a reduction in pH, reflecting the role of R COO⁻ in metal complexation. The ligands include low molecular weight organic acids including oxalic, citric, formic, acetic, malic, succinic, malonic, maleic, lactic, aconitic, and fumeric acids have been identified in soil system. Highest amount of Cd was released by malate and the least by acetate.

Copper

The higher removal of Cu was achieved by citrate, while the least removal of cu achieved by low molecular weight aromatic organic acid (gallic acid), Figure 3. This can be attributed due to citric acid can be effective in mobilizing heavy metals only when its application rate exceeded the buffering capacity of soil (Lesage *et al.*, 2005). Citric acid applied in the range of 3–20 mmol/kg was not phytotoxic (Huang *et al.*, 1998; Shahandeh and Hossner, 2002; Wu *et al.*, 2003; Quartacci *et al.*, 2005). The aromatic gallic acid was the least effective in desorbing the metals from soil. This result can be attributed to the low water solubility of this acid compared with the other studied chelates. Due to the phenolic hydrogen on the gallic acid molecule appears not be active as source of protons until the pH has increased considerably beyond 6.2, but phenolic hydrogens probably become available at about pH 8 and this pH do not available here as shown in Figure 8.

Manganese

Citric acid was the most effective acid salt to remove manganese, Figure 4, due to citric acid appeared to remove most of the metals associated with exchangeable and reducible fractions, and to a lesser extent, part of metal associated to the soil organic matter (Wuana *et al.*, 2010). The high solubility of manganese by gallic acid is due to gallic acid was an effective reducing agent reacting with ions of manganese to yield Mn^{2+} from soil. The low solubility of manganese by oxalate, tartrate and succinate may be explained due to theses salts removes the water soluble and exchangeable fractions.
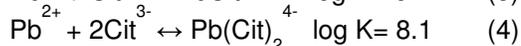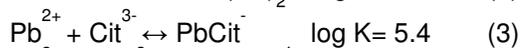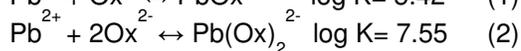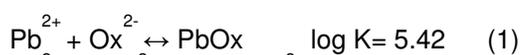
Nickel

Citrate and oxalate have approximately the same effect on Ni^{2+} desorption but the effect was differed at 20 mmol/kg, this may be the result of calcium oxalate formation in the soil which removes oxalate ions from the solution. The calcium oxalate precipitates causes that oxalate become

less available for heavy metals leading to a lower extraction for metals compared to citric acid (Veeken and Hamelers, 1999). Also, oxalate can attack Al and Fe oxides through ligand-promoted oxide dissolution mechanisms. They can form inner-sphere, ring-type surface complexes with Fe, and the resulting shift of electron density toward the central Al/Fe ions weakens the link between Al/Fe and the solid lattice, thus promoting detachment of Al/Fe into solution (Elliott and Shastri 1999). Also succinate and tartrate have the same effect at different point of extracted concentrations due to tartaric acid removed the exchangeable metal pools from soil; and the acid of these salts have the same number of carbon atoms.

Lead

The higher solubility of lead by citric acid other than the studied chelates was explained by Puigdomenech, (2001); Stumm and Morgan, (1996) they suggested that citrate form somewhat stronger complexes with Pb than oxalate. Oxalic acid was supposed to have the lowest effect on the dissolution in terms of H^+ affinity. The tricarboxylate citrate^{3-} chelates more strongly than the dicarboxylates malate^{2-} and oxalate^{2-}. The acids can form several different complexes with lead. The dissolution is pH dependent as well, and is governed by the pK_a values of the acid. This intricate system of complexes makes it difficult to compare log K values of the organic acids directly. The following log K values for complexes with oxalate and citrate are available in the literature (Puigdomenech, 2001; Stumm and Morgan, 1996);

$$Pb^{2+} + Ox^{2-} \leftrightarrow PbOx \qquad \log K= 5.42 \qquad (1)$$
$$Pb^{2+} + 2Ox^{2-} \leftrightarrow Pb(Ox)_2^{2-} \quad \log K= 7.55 \qquad (2)$$
$$Pb^{2+} + Cit^{3-} \leftrightarrow PbCit^- \qquad \log K= 5.4 \qquad (3)$$
$$Pb^{2+} + 2Cit^{3-} \leftrightarrow Pb(Cit)_2^{4-} \quad \log K= 8.1 \qquad (4)$$

Zinc

Figure 7 summarized the effect of organic acids on removal of Zn from soil, referring to higher removal was achieved by citric acid, while gallic acid removed the lower percentage from soil. Higher removal efficiency was achieved by citrate 58.5%, malate 22.6%, succinate 14.2%, gallate 6.3% and tartrate 11.8% from Zn present in soil samples.

CONCLUSION

The study demonstrated that depending on the nature of

the chelants, washing of higher percentage of Cu^{2+}, Ni^{2+}, Mn^{2+}, Pb^{2+} and Zn^{2+} was achieve by citrate, while the higher desorption of Cd^{2+} was achieved by maleate. The percentage of removal of heavy metals increased as well as the concentration of citric acid added increased.

Recommendation

The mixing between citrate and maleate will be applied in other research to study the effect of different parameters, (e.g. acid concentration and pH) on washing of soil to obtain to the optimum condition. In addition, a sequential extraction scheme with different extractants may be needed for the removal of multiple metal contaminants from sandy loam soil. Organic acids used in this research are natural materials that undergo biodegradation by the natural bacteria already live in the soil into more simple products can share in the food chain of plants and it does not represent a threat to groundwater.

In the coming researches, author will try to find some natural plants characterized by high, natural metal-accumulating capacity, high biomass crops plants, and high root exudates contains organic acids like that used in this research and try to apply the cultivation of these plants using contaminated water to get rid of heavy metals.

Acknowledgment

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