Mobilisation of Heavy Metals from a Contaminated Calcareous Soil Using Organic Acids

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ABSTRACT

Ethylenediaminetetraacetic acid (EDTA) is an effective chelating agent in removing heavy metals from contaminated soils, although extraction efficiency depends on many factors. Moreover, extraction of heavy metals by low molecular weight organic acids (LMWOAs) of citrate, oxalate, and acetate is likely to be more representative of the available fraction to plants. This study examined the potential of these two chelating agents to decontaminate a calcareous soil (with a total heavy metal concentration of 80.6 mmol kg^{-1}) from the zinc-lead smelting plant area in Zanjan Province, Iran. This was carried via 12 successive washings of soils with 0.01 M concentration chelating agent. For EDTA and citric acid, the orders of extraction efficiency of heavy metals (in decreasing order) were found to be lead (Pb)>zinc (Zn)>cadmium (Cd), and Zn > Pb > Cd, respectively. Oxalic acid removed more Zn than Cd. Acetic acid removed more Cd than Zn. Neither showed any efficiency for Pb removal. Therefore, EDTA and citric acid were efficient extraction agents for Pb and Zn, respectively. However, both of these agents were unable to efficiently remove Cd from the soil, even at high concentrations. This study found that chelating agents showed different efficiencies in removing a variety of heavy metals from contaminated soils and more than one chelating agent may be necessary to optimise cleanup efforts.

Keywords: Citiric acid, oxalic acid, acetic acid, chelating agent, EDTA.

INTRODUCTION

Contamination of soils by heavy metals is one of the most important environmental issues throughout the world, and the cleanup of these soils is a difficult task. One possible decontamination technique is ex-situ soil washing using a variety of agents such as acids, surfactants, electrolytes and chelating agents. Chelating agents are the most popular extraction reagents for soil washing. Since chelating agents such as ethylene-diaminetetraacetic acid (EDTA), ethylenediamine-*N,N'*-disuccinic acid (EDDS), diethylene triaminepentaacetic acid (DTPA) and nitrilotriacetic acid (NTA) form stable complexes with most heavy metals over a broad pH range, they have proven to be the most efficient at heavy metal removal. Unfortunately, they also have disadvantages such as persisting in the environment (particularly EDTA), adversely affecting health (particularly NTA) and being expensive (particularly EDDS), which have excluded their

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use in remediation of metal contaminated sites (Tandy *et al.*, 2004). There are advantages and disadvantages associated with the use of EDTA. EDTA is able to form stable complexes with a wide variety of metals (non-selective nature). The extraction is pH-independent and takes place quickly. Moreover, EDTA has been recognised to improve phytoextraction. Additionally, EDTA solution offers good possibilities for recovery and recycling. Among the disadvantages are the high cost, non-selective nature and low degree of biodegradability which have limited its use. Moreover, the washing efficiency of EDTA is dependent on the source of metal contamination in the soil and on metal distribution among the soil fractions (Barona *et al.*, 2001).

Low molecular weight organic acids (LMWOAs) are alternative agents for the extraction of heavy metals from the soils. In contrast to strong acids, LMWOAs cause less damage to the soil's crystalline structure over extended contact times (Yu and Klarup, 1994). Natural LMWOAs include oxalic, citric, acetic, lactic and malic acids which are natural products of root exudates, microbial secretions, and plant and animal residue decomposition in soils (Naidu and Harter, 1998). Thus, metal dissolution by organic acids is likely to be more representative of a mobile metal fraction that is available to plants (Labanowski *et al*., 2008). Metals extracted by a mixture of organic acids are well-correlated with the mobile metal fraction in the soil solution (Naidu and Harter, 1998). The chelating LMWOAs are able to dislodge the exchangeable, carbonate, and reducible fractions of heavy metals via washing procedures (Peters, 1999). Citrate has been reported to be one of the LMWOAs in soil solution. Among the LMWOAs used to simulate metal mobilisation, citric acid presents a high metal complexation strength (Labanowski *et al*., 2008; Huang *et al*.,2008).

Many researchers have studied various natural and synthetic chelating agents for their ability to remediate soils contaminated by heavy metals. Determining the effectiveness of a chelating agent for washing soils contaminated by heavy metals has commonly been accomplished in one-step batch extractions at the laboratory-scale (Andrade *et al.*, 2007). Such extractions often encounter some limitations or problems. For example, reverse reactions and precipitation of the released species must be taken into account in the data analysis. For these reasons multi-step (successive) extractions are preferred. The objective of this study was to assess the potential of four organic acids to decontaminate a highly contaminated, calcareous soil via successive washings.

MATERIALS AND METHODS

The zinc (Zn), lead (Pb) and cadmium (Cd) contaminated soil used in this research was sampled from an orchard located near a local zinc-lead smelting plant in Zanjan Province, Iran. The soil sample was air dried and ground to pass through a 2-mm sieve, then homogenised and stored for further analyses. Soil pH was determined in a suspension with a soil to water ratio of 1:1 (McLean, 1982). Electrical conductivity was measured in a saturation extract (Richards, 1954). Particle size analysis was performed using an ASTM 152-H type hydrometer (Gee

and Or, 2002). Calcium carbonate equivalent (CCE) content was determined by the titration method (Jackson, 1958). Organic carbon content was determined using the method by Nelson and Sommers (1982). Cation exchange capacity (CEC) was measured using the Bower method (Chapman, 1965). The total contents of Zn, Pb and Cd in the soil were determined by acid digestion with 4 M HNO_3 (Sposito *et al.*, 1982). The heavy metal fractionation in the contaminated soil sample was determined by a sequential extraction procedure (Sposito *et al*., 1982) in five fractions, namely, exchangeable (0.5M KNO_3 for 16h), sorbed (distilled H_2O for 2h, repeated three times), organic-bound (0.5M NaOH for 16h), carbonate-bound (0.05 M Na_2-EDTA for 6h), and residual (4M HNO_3 at 80°C for 16h).

Four organic acids were chosen, namely, Na_2H_2EDTA (or EDTA), citric acid, oxalic acid, and acetic acid. Batch extractions of heavy metal contaminants using a common extractant concentration of 0.01M were conducted. The extraction tests were conducted in 50 mL polyethylene tubes. The tubes containing 1.00 g soil sample and 20 ml of 0.01 M EDTA (or citric acid) were agitated using an end-over-end shaker at a speed of 140 revolutions per minute (RPM) at room temperature for 25 min. The suspensions were centrifuged at 3000 RPM for 5 min and the supernatants were then filtered through a Whatman-42 filter paper for heavy metal analysis. Then new extracting solution was added to the treated soil sample and the tubes were returned to the shaker. Twelve consecutive series of 25 min long extractions were carried out. The concentrations of Zn, Pb and Cd were measured by a Shimadzu model 6300 flame atomic absorption spectrometer (FAAS). The pH of the solutions after washing was measured using a pH meter. Additionally, the effect of different concentrations (0.001, 0.005, 0.01, 0.05 and 0.1 M) of organic acids on the removal efficiency of heavy metals was investigated. All tests were performed in duplicates and the results were presented as averages of the duplicate extracts. Percent of each metal removed was calculated using an equation similar to the one used by Reddy and Chinthamereddy (2000) and is shown below:

$$\text{Percent metal removed (\%)} = (C_l V_l / C_S m_S) \times 100$$

where C_l and C_S are the metal concentrations in supernatant (mmol L^{-1}) and soil (mmol kg^{-1}), respectively; V_l is the volume of supernatant (L) and m_S is the dry mass of the soil (kg).

RESULTS AND DISCUSSION

Selected properties of the soil used in this study are presented in Table 1. The soil was moderately fine textured, slightly alkaline (calcareous),and had a low level of organic matter. The major heavy metals of concern in this soil were Pb, Cd and especially Zn, which had a very high concentration.

According to the fractionation analysis (*Figure 1*), Zn was present mainly in the residual and carbonate-bound fractions. Lead and Cd were mainly accumulated in the carbonate-bound fraction. There was a clear trend of migrating heavy metals

TABLE 1

Characteristics of the studied soil

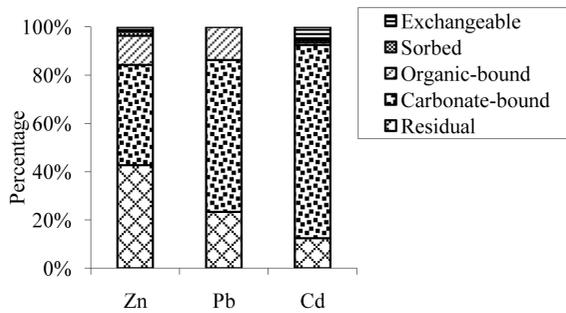| Soil properties	Value
Texture	SCL
pH	7.6
EC (mS cm^{-1})	5.0
CEC (cmolc kg^{-1})	15.0
CCE (g kg^{-1})	109
Clay(g kg^{-1})	230
OC(g kg^{-1})	3.0
Zn (mmol kg^{-1})	74.3
Pb (mmol kg^{-1})	5.21
Cd (mmol kg^{-1})	1.14

Figure 1: Fractionation of heavy metals in the studied soil

from the carbonate-bound fraction to the residual fraction. The order of migration was Zn >Pb > Cd. Only traces of all the three investigated metals were detected in the exchangeable fraction in the order of Cd > Zn >Pb. This was consistent with the pH of the soil, since other studies have already reported that when soil pH is higher than 5.6, the exchangeable amount of metals becomes negligible (Kim *et al*., 2003).

According to materials and methods, the amount of chelating agents added (1200 mmol kg^{-1}) was much higher than the total amount of heavy metals in the soil (80.6 mmol kg^{-1}). Kim *et al.* (2003) showed that if a sufficiently large amount of EDTA was applied (EDTA:Pb stoichiometric ratio greater than 10), most of the Pb was extracted for all soils tested, except for soil from a Superfund site from a Pb mining area. Percentages of Zn, Pb and Cd removed from the soil using successive soil washings with 0.01 M solutions of EDTA, citric acid, oxalic acid, and acetic acid are presented in *Figures 2, 3, 4 and 5*, respectively.

EDTA and citric acid were able to remove all three heavy metals (Zn, Pb and Cd) from the soil, while oxalic and acetic acids did not extract Pb from the soil.
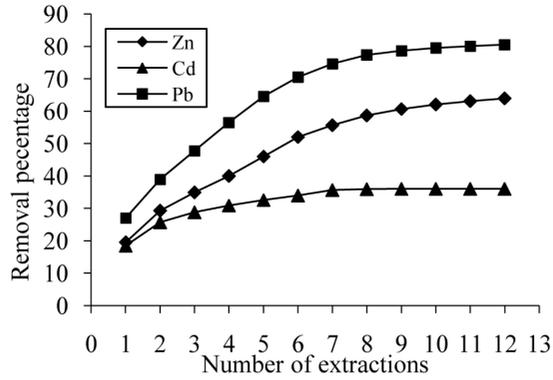
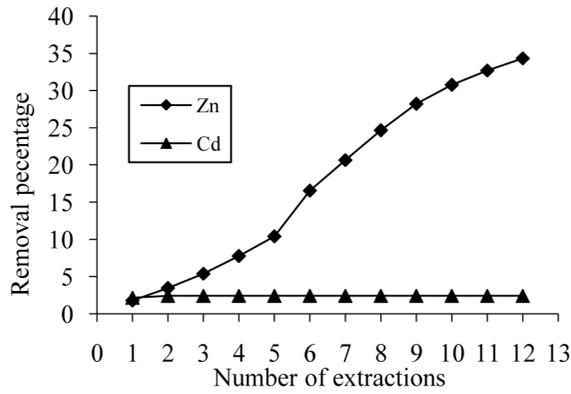*Figure 2: Removal percentage of heavy metals vs. number of extractions by EDTA*

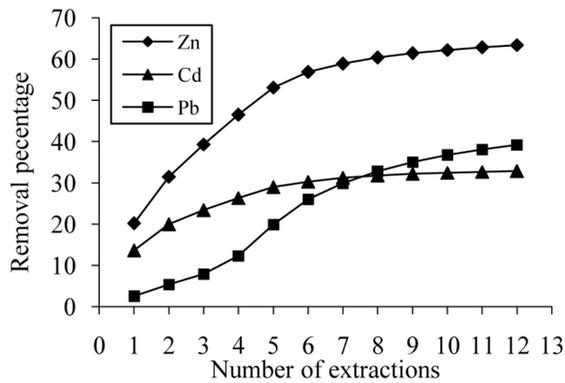*Figure 3: Removal percentage of heavy metals vs. number of extractions by oxalic acid*

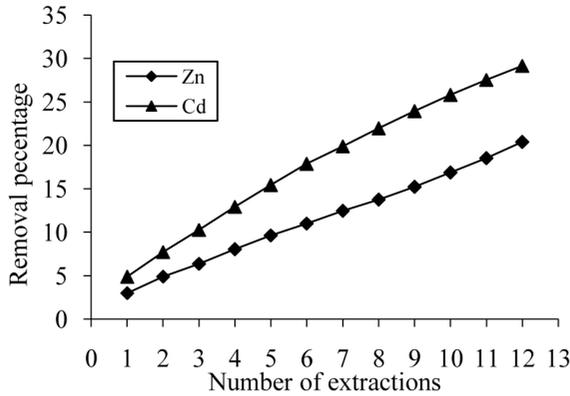*Figure 4:. Removal percentage of heavy metals vs. number of extractions by citric acid*

Figure 5: Removal percentage of heavy metals vs. number of extractions by acetic acid

Figures 2 and *3* indicate that renewing the extracting solutions greatly increased the removal of metals, but not to the same extent. The cumulative releases of Zn, Pb and Cd from the soil for EDTA and citric acid were 19.5%, 27% and 18.4%, and 20.2%, 2.5% and 13.6%, respectively, at the first cycle of extraction. The corresponding figures for Zn, Pb, and Cd extracted in the last (twelfth) cycle for EDTA and citric acid were 63.9%, 80.5%, and 36%, and 63.4%, 39.3%, and 32.9%, respectively. The cumulative releases of Zn and Cd from the soil for oxalic acid and acetic acid were only 1.8% and 2.4%, and 3% and 4.9%, respectively. The corresponding figures for Zn, Cd extracted in the last (twelfth) cycle for oxalic acid and acetic acid were 34.3% and 2.4%, and 20.4% and 29.1%, respectively. The trends in removal of the heavy metals with successive washings are expressed by the equations listed in Table 2.

It can be seen that all of the extraction curves, except those of the acetic acid, are mostly described properly by second order polynomial equations. The extraction of Pb by citric acid is described well by a third order polynomial equation. The power equation has a proper fit to the extraction curves of acetic acid.

TABLE 2
The trends in removing of the heavy metals with successive washings

Heavy metals		Equations	
EDTA	Zn	$y = -0.38x^2 + 8.8815x + 11.628$	$R^2 = 0.998$
	Pb	$y = -0.618x^2 + 12.696x + 15.592$	$R^2 = 0.998$
	Cd	$y = -0.239x^2 + 4.4149x + 16.398$	$R^2 = 0.966$
Citric acid	Zn	$y = -0.5293x^2 + 10.431x + 12.262$	$R^2 = 0.990$
	Pb	$y = -0.0428x^3 + 0.619x^2 + 1.9761x - 0.8369$	$R^2 = 0.991$
	Cd	$y = -0.2452x^2 + 4.6846x + 10.84$	$R^2 = 0.979$
			$R^2 = 0.998$
Oxalic acid	Zn	$y = -0.046x^3 + 0.903x^2 - 1.570x + 2.850$	
Acetic acid	Zn	$y = 2.864x^{0.765}$	$R^2 = 0.997$
			$R^2 = 0.999$
	Cd	$y = 4.743x^{0.733}$	

For EDTA, the order of extractionwas Pb > Zn > Cd which agreed with the order of stability constant of EDTA complexes (Palma and Mecozzi, 2007):

$LogK_{Pb}$-EDTA (18.04) > $logK_{Zn}$-EDTA (16.5) >$logK_{Cd}$-EDTA (16.42)

However, the higher amount of Zn extracted could be due to higher amounts of Zn compared to Cd in the soil sample. Huong and Ohtsubo (2007) found a reverse order of extraction using EDTA (Cd > Zn >Pb). The findings of this study with respect to extraction order was similar to that observed by Peters (1999). Abumaizar and Smith (1999) found that EDTA preferentially extracts Pb over Zn and Cd. Moreover, Finzgar and Lestan (2007) found that EDTA extracts Pb more efficiently than Zn from three of the four soils they studied. Chang *et al*. (2007) also reported that EDTA does not show considerable preference for the chelation of any particular Zn species during extraction. Huong and Ohtsubo (2007) found a large proportion of Cd present in the residual fraction of the soils they studied. In contast, the Cd soil sample in this study was mainly accumulated in the carbonate-bound fraction. Others found the EDTA to be a strong extractant for Pb due to its high log K value (Tandy *et al.*, 2004).The results of this study found no general efficiency order for chelating agents.

The mobility of heavy metals when extracted by citric acid was Zn>Pb>Cd. Lobanowski *et al*. (2008) noted that that citric acid is better at extracting Zn than Pb. This study's results showed that EDTA extracted greater amounts of heavy metals from the soil than citric acid. In contrast to EDTA, citric acid extracted more Cd than Pb at early cycles of extraction. After the seventh cycle, the reverse occurred.

Oxalic and acetic acids were ineffective in extracting Pb from the soil as previously reported by Nascimento (2006). However, Reddy *et al.,* (2006) showed the effectiveness of acetic acid at high concentrations, up to 2M. The reason for the low removal of Pb by oxalic acid was presumably due to the formation of a low-solubility lead oxalate precipitate (Ksp=2.74×10^{-11}). Oxalic acid extracted Cd only at first extraction cycle. The solubilities of cadmium oxalate (Ksp=9.00×10^{-8}) as well as zinc oxalate (Ksp=1.35×10^{-9}) were sufficiently high compared to that of lead oxalate. It could be that oxalate ions in calcareous soils react with calcium (Ca) to form calcium oxalate. The occurrence of this precipitate hindered the removal of heavy metals from these soils. Oxalate could inhibit the dissolution of calcium carbonate through the coating of calcium oxalate. Such a coating around calcium carbonate may provide protection from releasing co-precipitated or occluded cadmium carbonate. Co-precipitation of Cd with calcium carbonate has been well demonstrated (Kumagai and Matsui, 1992).

Changes in pH during the successive extraction cycles are presented in *Figure 6*. The pH of soils treated with the two chelating agents decreased abruptly (about 4 units for EDTA and 6 units for citric acid) between the fifth and seventh extraction cycles. The removal of Pb increased abruptly at the fifth extraction cycle. This indicates that the extraction strength of citric acid for Pb increased
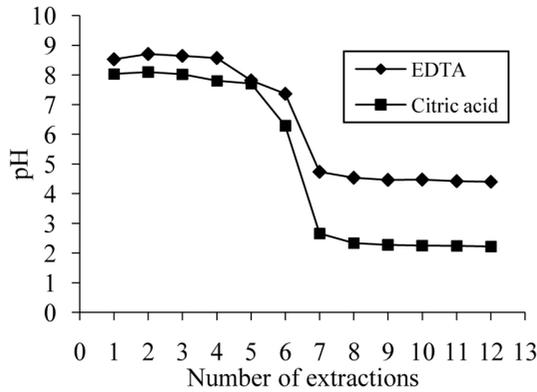
Figure 6: Changes in pH during the extractions using EDTA and citric acid

with decreasing pH. Since Pb was mostly bound to carbonates (*Figure.1*), and under alkaline conditions precipitation of $PbCO_3$ is favoured (Lo and Yang, 1999), the decrease in pH at fifth cycle played a dominant role in the extraction of Pb. The decrease in pH showed no effect on the extraction of Zn and Cd.

The percentage of Pb removed at each extraction cycle is shown in *Figure 7*. For EDTA, after a quick decrease in heavy metal extraction, a plateau was reached at about the fourth extraction cycle, which was followed by a second decrease and a plateau at the tenth extraction cycle. The second decrease in the extraction of Pb may be due to the decrease in pH creating competition between Pb and iron (Fe).
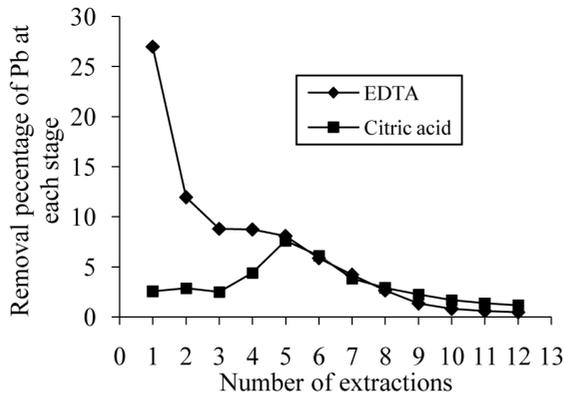

Figure 7: Removal percentage of Pb at each successive cycle of extraction

Trivalent Fe forms very stable complexes with EDTA (log K EDTA-Fe = 25.1). For citric acid an increase in extraction was followed by a decrease. The early low efficiency of citric acid is attributed to co-dissolution of soil calcium carbonates and release of huge amounts of Ca which forms calcium citrate precipitate. After a few cycles of extraction, sufficient amounts of citrate ions are available to remove Pb from the soil. The late decrease in the extraction may be due to a decrease in pH

and a release of huge amounts of Fe, which in turn formed stable complexes with citrate and reduced Pb extraction efficiency. Palma and Mecozzi (2007) observed Fe dissolution up to about the 39% of the total Fe content in the sediment under citric acid treatment. It seems that the removal heavy metals from the soils should increase with decreasing pH, but this is offset by an increase in the extraction of Fe and Ca (Tandy *et al*., 2004).

Oxalic acid extracted more Zn than Cd and the reverse occurred for acetic acid. This was not expected, because of the theoretically higher extraction strength of oxalic acid compared to acetic acid. A higher removal efficiency of Cd than that of Zn by oxalic acid has been reported previously (Peters, 1999).

Changes in pH during the successive extraction cycles are presented in *Figure 8*. As can be seen, the pH of soil treated with oxalic acid decreased abruptly (6 units) between the fifth and seventh extraction cycles. Meanwhile, the removal of Zn increased abruptly at the fifth extraction cycle. This indicated that the extraction strength of oxalic acid for Zn increased with decreasing pH. This decrease in pH was not effective at all for the removal of Cd from the soil. As shown earlier (*Figure 1*), Zn and Cd in the studied soil were mainly bound to residual and carbonate fractions, respectively, which is in agreement with the literature (Ramos *et al*., 1994: Khanmirzaei *et al*., 2013).
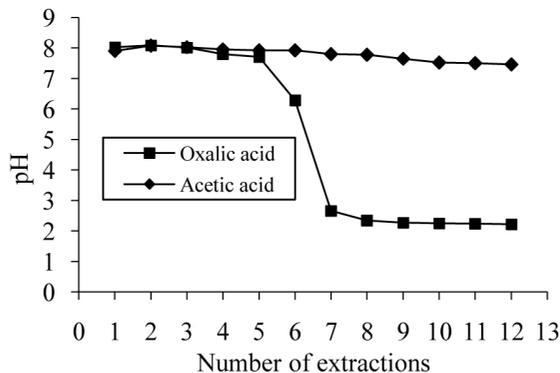

Figure 8: Changes in pH during the extractions using oxalic and acetic acids

The sequential extraction procedure by Sposito *et al*. (1982) failed to separate the Fe and manganese (Mn) oxides bound fractions which were found within the residual fraction. Han and Banin (1995) found that in eight calcareous soils from arid and semi-arid regions of China, Zn bound to the Fe oxides accounted for 20% to 30% of total Zn, which was higher than Zn bound to carbonates (< 5%). It might be possible to consider the decrease in soil pH values as favouring solubilisation of co-precipitated Zn from Fe and Mn oxides. Another explanation for the higher removal of Zn compared to Cd in oxalic acid extraction could be due to the higher complex stability of Zn (log K=3.4) compared to Cd (log K=2.73). According to this explanation, as pH decreases, the amount of both Zn and Cd released

increases with increasing calcium carbonate dissolution. Therefore, because of the higher complex stability, the removal of Zn is favoured.

For the removal of heavy metals with acetic acid (*Figure 5*), similar trends of removal for Zn and Cd were observed. A slight decrease in pH coincided with a slight increase in the extraction of both Zn and Cd.

The effect of concentration of chelating agents (EDTA and citric acid) on the removal efficiency of heavy metals in the studied soil is shown in *Figures 9* and *10*. Increasing the concentration of both chelating agents considerably favoured the extraction of Pb from the soil. Kim *et al*., (2003) state that the extraction of Pb from the Pb-contaminated soils was dependent on the quantity of the EDTA present. Nevertheless, increasing the concentrations of both chelating agents over 0.01M showed no further effect on the extraction level.
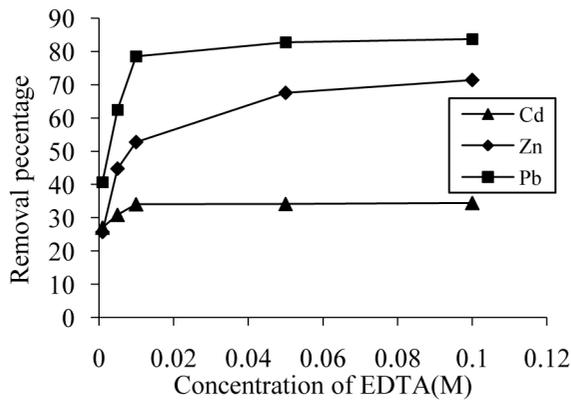

Figure 9: Effect of EDTA concentration on the percentage of heavy metals removed
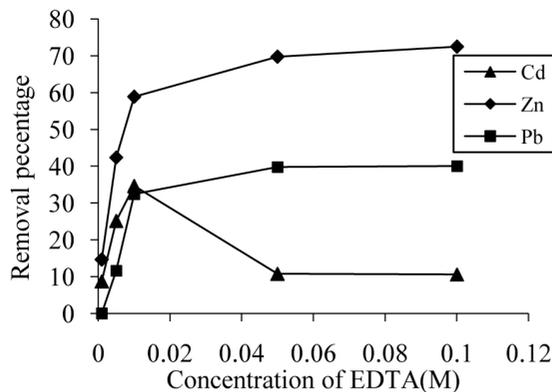

Figure 10: Effect of citric acid concentration on the percentage of heavy metals removed

Other workers reported that a 0.01M EDTA solution was less effective than a 0.05M or a 0.1M EDTA solution at extracting heavy metals (Lo and Yang, 1999). However, Zhang *et al.,* (2010) recommended a very dilute 0.0005 M EDTA solution. A more concentrated citric acid solution was ineffective in removing Cd from the soil. Extraction of Cd decreased for concentrations over 0.01M of this chelating agent. This may be the result of calcium citrate formation in the soil which removes citrate ions from the solution. Furthermore, raising the concentration of EDTA caused only a slight increase in the removal efficiency of Cd. This indicates that the effectiveness of supplying more concentrated solutions of chelating agents for removal of heavy metals depends on the stability constant of their complexes.

The high stability constant is consistent with more effectiveness. Both the chelating agents were unable to efficiently remove Cd from the soil, even at high concentrations. Considering the presence of Cd in the carbonate-bound fraction (easily soluble under acid attack), this could be due to competition from other major (Ca and Fe) or trace (Pb and Zn) metals. Potential benefits of increased concentration of chelating agents in removing Zn were more than that of Cd and less than that of Pb.

Figures 11 and *12* show the effect of concentration of oxalic and acetic acids on the removal efficiency of Cd and Zn in the studied soil, respectively. As can be seen, increasing the concentration of oxalic acid was ineffective in Cd removal from the soil. Furthermore, raising the concentration of oxalic acid caused only a slight increase in the removal efficiency of Zn. This may be the result of calcium oxalate formation in the soil which removes oxalate ions from the solution.In contrast, as the concentration of acetic acid increased, the removal of Cd and Zn increased considerably.

As can be seen in *Figures 11* and *12*, the removal of Cd was not easy. This may have been due to the presence of Cd in less removable fractions (i.e., residual fraction) as reported by other workers (Chen *et al*., 2008). Surprisingly, an increase in the concentration of organic acids had no effect on the extraction efficiency of Pb.
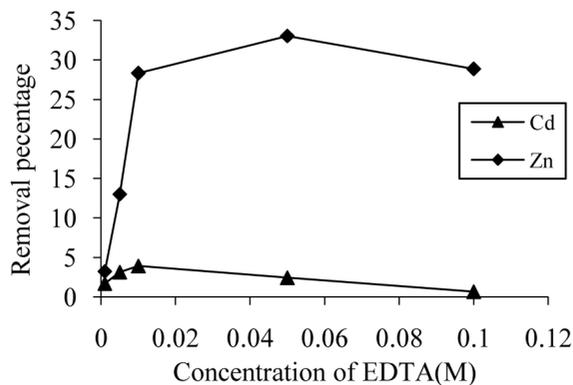

Figure 11: Effect of oxalic acid concentration on the percentage of heavy metals removed
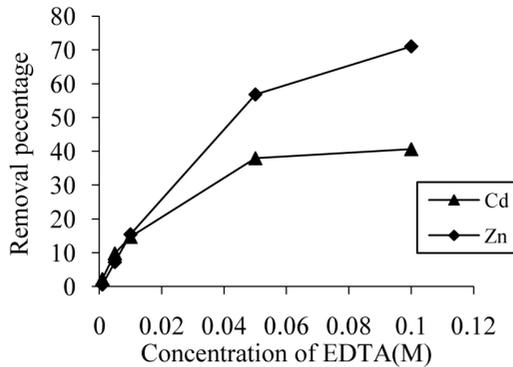
Figure 12: Effect of acetic acid concentration on the percentage of heavy metals removed

The results of our study indicate that no general efficiency order for organic acids could be distinguished and there is a need for further fractionation studies to improve understanding of heavy metal mobilisation in and removal from soils. It should be noted that heavy metals behave differently after the ageing of treated soils. For example, it has been observed that the mobility of Pb, Cd and Zn, increased, decreased, and did not change, respectively, after ageing (Udovic and Lestan, 2009).

CONCLUSION

EDTA and citric acid showed high but different efficiencies for removing Pb and Zn from a contaminated soil. Moreover, both the two chelating agents were ineffective in removing Cd from the soil. Oxalic acid and acetic acid were mild extractants, but effective for removing Zn and Cd, respectively. The complexity of soils and the presence of multiple heavy metals make soil remediation efforts difficult. Furthermore, heavy metals behave differently after the ageing of treated soils. For this reason, the fate of soil fractions after remediation should be investigated more thoroughly.

ACKNOWLEDGMENT

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