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# Comparison of Heavy Metals Extraction Efficiency in Contaminated Soils by Various Concentrations of EDTA

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**Abstract:** This study aimed to establish an optimized concentration and application of $Na_2$-EDTA in heavy metals removal from contaminated soils. Laboratory experiments were conducted to evaluate the interaction of metals (Cd, Zn and Pb) in soil. Thus, the feasibility of soil washing for the decontaminated silt, clay and loam with single and several metals were evaluated in laboratory-scale batch experiments. Extraction of Cd, Zn and Pb in experimental soils was determined by several different concentrations of extraction solutions. Batch washing of the contaminated soil with deionised water was used as a control. Of the washing reagent test, $Na_2$-EDTA 0.1 M solutions were generally more effective for removing heavy metals from soils. $Na_2$-EDTA 0.1M preferentially extracted lead over Cd and Zn. However, $Na_2$-EDTA 0.005 M solution indicated higher removal efficiency for Cd and Zn.

**Key words:** Heavy metal, contaminated soil, EDTA

## INTRODUCTION

Metal pollution of soil is widespread across the globe and the clean up of these soils is a difficult task[1]. Heavy metals contamination in the natural environment is a major problem for human and environmental quality[2-5]. Geochemical forms of heavy metals existing in the soils affect their solubility, which may directly influence their phytoavailability[6]. Most of heavy metals are persistent in the soil because of their immobile nature. Cadmium is known as more mobile and soluble than many other metals in soil, but Pb is well known to be relatively immobile and unavailable for plant uptake. Soil is a concern for human health when deposit on plant surfaces[2]. Soil washing is a variable treatment alternative for metal contaminated sites. Chemical extractions are some times introduced in the washing fluid to enhance the efficiency of heavy metal extraction. These extractions include acids, bases, chelating agents, electrolytes and redox reagents. Process parameters in soil washing include the mode of extraction (e.g., batch or column), extractant type and concentration, pH, electrolyte concentration, Liquid -to- Solid ratio (L/S) and retention time. The soil related parameters are pH, particle size distribution and mineral type of metal to be extracted and their concentration, distribution and physicochemical forms in the soils. The kinetics of metal desorption/dissolution is also a crucial parameter as it can affect the treatment duration and cost[1,7,8].

In the past, soil washing/flushing has been limited to small scale applications due to lack of knowledge on the chemistry of metal specification in soil, interparticle extraction dynamics, extraction fluid transport mechanism within the aquifer and spent extractant recycling, techniques[9]. The advantages of using chelating agents in the soil washing is high efficiency of metal extraction, high thermodynamic stabilities of the metal complexes formed, good solubility of metal complexes and normally low adsorption of the chelating agents and their metals complexes on soils[10-12].

The objective of this study was to asses the suitability of using various widely used chelating agents such as EDTA to clean up a heavy metal contaminated soil at different pH.

## MATERIALS AND METHODS

The Silt-clay-loam which has been sampled from agricultural lands of Gilan province in Iran was selected for this study. This research was conducted for 9 months in the Department of Environmental Health engineering and department of Chemistry of Tehran University in 2004.

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Table 1: Selected properties and concentration of the Cd, Zn and Pb in unpolluted field soil

| | | | Particle size analysis (%) | | | | Total content (mg kg$^{-1}$ soils) | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Soil texture | pH $H_2O$ | OC (%) | Sand | Silt | Clay | CEC Meq/100 g | Cd | Zn | Pb | Ca | Mg |
| Si-C-L | 6.8 | 1.61 | 13 | 49 | 38 | 33.2 | 2.12 | 76.8 | 21.42 | 5938 | 338 |

Si-C-L: Silt-Clay-Loan

Table 2: Remediation efficiency (%) vs. Reaction time of contaminated soil (Si-C-L) with conc. 500 mg kg$^{-1}$ using 0.1 M EDTA

| | Time (h) | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| Heavy metal | 0.5 | 1 | 2 | 3 | 4 | 6 | 12 | 24 | 36 | 48 |
| Pb | 97.1 | 96.8 | 96.8 | 97.5 | 98.1 | 97.6 | 98.9 | 99.2 | 99.2 | 99.9 |
| Zn | 78.1 | 78 | 77.3 | 76.8 | 77.7 | 79.5 | 79.6 | 79.8 | 79.7 | 79.8 |
| Cd | 73.6 | 73.2 | 74.4 | 74.2 | 75.8 | 75.4 | 75.2 | 75.7 | 75.6 | 75.6 |

The surface soils (0-20 cm) of sites were sampled, air dried, ground a 2 mm sieve and stored in plastic bags prior to laboratory analysis and use in bath experiments. Soil pH values were determined using glass electrodes in a soil: water ratio of 1:1 and the particle size distribution of two soils were analyzed by the Pipete method[12]. Organic carbon was determined by the Walkley-Black wet combustion method[13]. Exchangeable cations and Cation Exchange Capacity (CEC) were determined using ammonium acetate pH 7[13].

**Soil preparation:** As far as the concentration of heavy metals in soil samples is usually less than 100 mg kg$^{-1}$ hence the soil samples have been contaminated artificially (Table 1).

Several solutions containing Zn, Cd and Pb were prepared by using acetate of these metals. These solutions were added to a portion of the mentioned soil sample at a rate of 100 mL/10 g (solution/solid) in centrifuge tubes. Therefore, the soil sample received 500 or 1000 mg kg$^{-1}$ heavy metals. The suspension samples were then placed on a shaker table (mechanical shaker) operated at 180 rpm and at a room temperature (25-27°C) for 48 h.

The wet-aging stage was essential to ensure complete and even exposure of every soil particle to contamination. At the end of the 48 h wet-aging period, the suspension was centrifuged to separate the solid phase from solution. The supernatant liquid phase from the centrifuge tubes was filtered and the equilibrium concentration of heavy metals in the liquid was measured using AAS. The pH of the solution was measured and all the contaminated samples pH was about 7. The contaminated soil was then washed with Deionized water to remove the entrapped water in the soil.

So an artificially contaminated soil sample was used in this study. The advantage of deliberately contaminating the soil is that a rather homogeneous test sample, with consist heavy metal concentration and specification, soil composition, contamination process and contamination period can be obtained. This would minimize ambiguity in the extraction of potential results arising from sample heterogeneity[5].

**Batch extraction with EDTA:** Batch extraction experiments were conducted using an EDTA solution at various concentration and contact time to determine appropriate range of concentration and dosage of the washing solution to extract the heavy metal decontamination studies.

The extraction solution was prepared from reagent-grade disodium ethylenediaminetetraacetat ($Na_2$-EDTA). The EDTA concentration was 0.005, 0.01 and 0.1 M and the pH values of the three solutions were 4.7, 4.53 and 4.46, respectively. The contact time for metal extraction was two hours. All the experiments were performed at room temperature (25-27°C). A soil sample of 10 g was used with a 2.5:1 liquid/solid ratio was employed for all soil extraction experiments.10 gram of soil sample and 25 mL of EDTA solution were added to a polyethylene centrifuge tube. The tubes was sealed with a lid and then placed on a mechanical shaker operated at 180 rpm at room temperature for the desired contact period. Two hour reaction time was deemed sufficient based upon batch rate desorption tests conducted over 48 h period. After mixing, the samples were allowed to settle for about 15 min and then centrifuged and filtrated through a 0.45 μm member filter. The pH of the washing solution before contact with the soil and the pH of the filtrate were measured and recorded. Following filtration, the filtrate was acidified to a pH of < 2.0 with 1:1 $HNO_3$ for heavy metals analysis.

It was assumed that the metal concentration of the filtrate represents that released from the contaminated soil. Remediation efficiencies were determined by dividing the heavy metal release quantities the initial quantity in the soil. All heavy metal analysis performed using a Perkins-elmer Atomic Absorption Spectrometer (AAS).

DI water was performed to provide a baseline for the removal obtained by chemical washing.

## RESULTS AND DISCUSSION

The results shown in Table 2 a reaction time of 2 h was considered feasible since the curves illustrate that no appreciable amount of metal was extracted beyond this time. Table 2 represents the remediation efficiency of the contaminated soils in 0.5, 1, 2, 3, 4, 6, 12, 18, 24, 36 and 48 h time periods for these three types of metals Cd, Zn and Pb. The vacillation of remediation process results usually occurs in initial hours and then the efficiency will follow a constant rate, therefore the optimum time period, which is used as a bench mark for comparison is 2 h.

Apparently Pb, Zn and Cd release were very rapid that reached equilibrium with in 1-2 h of extraction time. Bermond and Ghestem[14] also reported a rapid initial release of Pb and Cd from the contaminated soil into the EDTA extracting solution. Extraction process has been done by Na 2EDTA with the different concentrations on soil with a ratio of 2.5:1 L/S. Table 3 and 4 represent the remediation efficiency by various rates of EDTA concentrations in pH original (about 7) on a Silt-clay-loam soil samples with the contamination rate of 500 mg $kg^{-1}$. The results represent the cardinal effect of EDTA on Pb; meanwhile the increase of the EDTA concentration in Zn and Cd has not a considerable effect on the remediation efficiency (Table 3 and 4).

According to the Table 3 the remediation efficiency for Pb with the concentration of 0.1 M EDTA was 96.2% and for the EDTA with the concentration of 0.005 M the efficiency was just 55.3%. Also the effect of EDTA concentration on remediation process of mixed soil (multimetal-soil) was investigated and the results represents that the maximum and minimum efficiencies for the Pb are with EDTA 0.1 and 0.005 M, respectively (Table 4).

It means that EDTA in single-metal contaminated soils is more efficient than in a multi-metal contaminated soil which this is possibly because of the greater ratio of the EDTA to the metal.

The excess dosage would ensure that there were always sufficient molecules of chelating agents available to these heavy metals, even though some molecules of the chelating agent might be precipitated, adsorbed by the soil, or might form complexes with other cations (Ca, Mg, Fe, Al and other trace heavy metals) originally present in the soil. It shows that Pb, Cd and Zn could be easily extracted by 0.1 M EDTA. It was believed that the high Pb, Cd and Zn extraction efficiencies demonstrated by the chelating agent could be attributed to the formation of strong and stable metal complexes which could overcome the adsorption interaction between the heavy metals and soil solids[7].

Table 3: Remediation efficiency (%) of single metal contaminated soil (Si-C-L) with conc. 500 mg $kg^{-1}$ using various M EDTA

| EDTA | Pb | Cd | Zn | pH |
|---|---|---|---|---|
| 0.1 | 96.2 | 73.8 | 78.6 | 7 |
| 0.01 | 85.6 | 68.3 | 75.2 | 7 |
| 0.005 | 55.3 | 62.1 | 67.8 | 7 |

Table 4: Remediation efficiency (%) of multi metal contaminated soil (Si-C-L) with conc. 500 mg $kg^{-1}$ using various M EDTA

| EDTA | Pb | Cd | Zn | pH |
|---|---|---|---|---|
| 0.1 | 92.7 | 71.5 | 75.2 | 7 |
| 0.01 | 80.2 | 66.7 | 71.9 | 7 |
| 0.005 | 50.1 | 59.3 | 61.2 | 7 |

Table 5: Remediation efficiency (%) of single meta contaminated soil (Si-C-L) with conc. 500 mg $kg^{-1}$ using 0.1 M EDTA

| EDTA | Pb | Cd | Zn | pH |
|---|---|---|---|---|
| 0.1 | 96.4 | 72.5 | 73.5 | 3 |
| 0.1 | 93.7 | 71.8 | 75.3 | 5 |
| 0.1 | 89.4 | 71.2 | 76.3 | 7 |
| 0.1 | 86.5 | 70.2 | 77.4 | 9 |

In the next stage of this study the effect of pH on remediation soil was investigated. The remediation was not considerably affected by pH. The remediation efficiency in pH 3 for the Pb was approximately 10% more than in pH 9. This increase of efficiency for the Cd was smaller and was about 2% (Table 5). Recovery or desorption of Pb was generally greatest under acidic condition and decreased modestly as the pH became alkaline (Table 5). For Zn, a decrease of 4% in efficiency at pH 3 was observed that it may be due to the distribution of metals in the different solid phase of the contaminated soil. This finding is supported by Ottoser *et al.*[15] who found that Zn is desorbed at a higher pH than Cu which again it desorbed at higher pH than Pb. An important observation from recent soil washing research is that removal efficiencies of metals from soils artificially contaminated via metal adsorption were significantly grater than those for soils from actual waste sites. As observed, the initial Zn contaminated soil is higher than Pb and Cd and as a result the removal efficiency of Zn is lower than those of Pb and Cd (Table 1). Tuin and Tels[16] found that metal removals from actual waste-site soils were not as high as from an artificially contaminated soil when both soils were washed under similar conditions.

With progressively alkaline conditions, the ability of chelats to enhance solubility of oxides and other solid phase decreases because hydrolysis (the attachment of -OH as ligand ) is favoured over completion by EDTA NTA[11].

Such metal ions can be immobilized in the soil by the formation of insoluble precipitates, incorporation into the crystalline structure of clay particles and metal oxides and/or by physical entrapment in the immobile water surrounding the micro and macropores of soils[9].

Moreover the effect of initial metal concentration in soil for the remediation rate has been investigated by $Na_2$ EDTA. When the initial metal concentration was increased two times (1000 mg $kg^{-1}$) remediation efficiency by 0.1 M EDTA decreased, approximately 16% for Pb and 10% for Cd and 8% for Zn, but when the contamination rate was twice and the 0.005 M EDTA was used, a 50% decrease has been observed for lead remediation efficiency which is completely considerable, whereas this decrease for Cd and Zn are lower than 18% (Table 6). As another part of the study the remediation process has been done on some samples with the contamination rate of 500 mg $kg^{-1}$ by DI. The results represent the poor remediation efficiency especially for the lead contaminated soil. An insignificant amount of metals removal by this method resulted in a poor removal efficiency that was less than 12% for Zn, 9% for Cd and 4% for Pb, indicating that the adsorbed HMs could not be readily removed by rising along even though the soil were artificially contaminated in the laboratory. Table 7 represents the removal efficiency with DI water in contaminated soil.

The washing efficiency with EDTA has been reported to be strongly dependent on the source of metal contamination in the soil[17] and on metal distribution among the soil fraction[18]. However, not only must the extraction be taken into account, as the condition and future use of the treated soil are also decisive.

By comparing the results of the study, It is also concluded that the remediation efficiency is dependent to the type of soils too. As observed, efficiency is different in the mentioned soil with the different concentration of EDTA even for all of these three metals and the remediation efficiency is maximum for lead. Table 5 provides the remediation efficiency at various pH values that it is nearly independent to pH.

Ya and Klarup[19] studied the influence of pH and concentration of EDTA on the solubilisation of certain metals in contaminated sediments and found that, in all cases, the lower the pH and the higher the EDTA concentration the greater the extraction recovery.

The vacillation of remediation process results usually occurs in initial hours. A rapid uptake of lead from contaminated soil by $Na_2$-EDTA was observed by Fisher *et al.*[20]. The possible disadvantages of chelating agent include: 1-EDTA is not easily biodegradable and pose a potential environmental hazard if they remain in the treated soil and 2- chelating agents are relatively expensive chemical compound.

Table 6: Remediation efficiency (%) of single metal contaminated soil (Si-C-L) with conc. 1000 mg $kg^{-1}$ using various M EDTA

| EDTA | Pb | Zn | Cd | pH |
|---|---|---|---|---|
| 0.1 | 80.3 | 63.5 | 70.4 | 7 |
| 0.01 | 71.6 | 60.9 | 68.2 | 7 |
| 0.005 | 48.9 | 56.7 | 60.3 | 7 |

Table 7: Remediation efficiency (%) of single metal contaminated soil (Si-C-L) with conc. 500 mg $kg^{-1}$ using DI water

| Heavy metals | Pb | Cd | Zn | pH |
|---|---|---|---|---|
| DI water | 3.85 | 8.67 | 11.46 | 7 |

The results of batch washing experiments completed in this study indicate that Pb, Cd and Zn can be extracted from artificially contaminated soil using a chelating agent solution. There are significant decrease in the extraction of Pb with low concentration of EDTA (0.005 M).By using a washing solution at a concentration of 0.1 M of EDTA, extraction yields of 96.25% for Pb, 78.6% for Zn and 73.8% for Cd were obtained.

Metal extraction kinetic was found to be fast, a reaction time of 2 h was deemed sufficient contact time between the contaminated soil and the washing solution based upon batch desorption tests conducted over a 48 h period.

Ghestem and Bermond[21] recorded the effect of 0.0001-0.05 M EDTA and pH 2-8 on the mobilisation of Cd, Pb, Zn and Cu from three contaminated soils. For excess EDTA, the concentration of extracted cations were ph-independent but for limited EDTA concentrations, the quantities of extracted cation displayed a complex behaviour versus pH, that varied with the type of cation and with the level of soil contamination.

Result of Table 5 agreed with Lim *et al.*[7] who found at the pH 4.7, the amounts of Pb and Cd extracted were slightly higher than those achieved at higher pH values, which were believed to be partly due to dissolution of soil minerals that caused simultaneous release of the adsorbed metals.

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