

Removal of heavy metals from a contaminated calcareous soil using oxalic and acetic acids as chelating agents

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Abstract— Extraction of heavy metals by organic acids is likely to be representative of a available fraction to plants. Oxalic and acetic acids commonly are known as moderate and weak chelating agents, respectively. In this research the potential of these two organic acids 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 was investigated. This was carried out via 12 times successive washing experiments with concentration of 0.01 M. Results showed that oxalic acid extracted greater Zn than Cd and the reverse occurred for acetic acid. This may be due to the formation of calcium oxalate which removed oxalate from the solution and decreased its extraction power. The results of our study indicate that no general efficiency order for chelating agents could be distinguished

Keywords -extraction, organic acids, zinc, cadmium

I. INTRODUCTION

Contamination of soils by heavy metals is one of the most important environmental issues throughout the world and the clean up of these soils is a difficult task. One possible decontamination technique is ex-situ soil washing using acids, surfactants, electrolytes and chelating agents. Chelating agents are the most popular extracting reagents for soil washing. Since chelating agents such as EDTA, EDDS, DTPA, NTA and ..., form stable complexes with most heavy metals over a broad pH range, they have proved to be the most efficient ones. Unfortunately, these also have disadvantages including persistent in the environment (particularly EDTA), adverse health effects (particularly NTA) and expensive cost (particularly EDDS) which has precluded their use in remediation of metal contaminated sites [1]. On the other hand, strong acids attack and degrade the soil crystalline structure at extended contact times. For less damaging washes, organic acids are often suggested as alternatives to straight mineral acid use [2]. Natural, low-molecular-weight organic acids including oxalic, citric, acetic, lactic and malic acids are natural products of root exudates, microbial secretions and plant and animal residue decomposition in soils [3]. Thus, metal dissolution by organic acids is likely to be more representative of a mobile metal fraction that is available to plants [4]. Metals extracted by a mixture of organic acids are well-correlated with the mobile metal fraction in the soil solution [3]. The chelating organic

acids are able to dislodge the exchangeable, carbonate and reducible fractions of heavy metals by washing procedures [5]. Oxalate has been reported to be one of the organic acids in soil solution. Among the low-molecular-weight organic acids used to simulate metal mobilization, oxalic acid presents a moderate metal complexation strength compared to other similar chelating agents. On the other hand, acetic acid is known as a weak chelating agent for removal of soil heavy metals [6].

Many researchers have studied various natural and synthetic chelating agents for their ability to remediate heavy metal contaminated soils. Determining the effectiveness of a chelating agent for washing heavy metal contaminated soils has commonly been accomplished in one-step batch extractions at the laboratory-scale [7]. Such extractions often encounter with some limitations or problems. As an 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 the present study was to assess the potential of two natural, low molecular weight organic acids, oxalic acid (OA) and acetic acid (AA) to decontaminate a highly contaminated calcareous soil via soil successive washing experiments.

II. MATERIALS AND METHODS

The Zn, Pb and 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 homogenized and stored until analysis. Soil pH was determined in 1:1 soil-water suspensions [8]. Electrical conductivity was measured in saturation extract [9]. Particle size analysis was performed using an ASTM 152-H type hydrometer [10]. Calcium carbonate equivalent (CCE) content was determined by titration method [11]. The content of organic carbon was determined by Nelson and Sommers method [12]. Cation exchange capacity (CEC) was measured using Bower method [9]. The total contents of Zn, Pb and Cd in the soil were determined by acid digestion with 4 M HNO₃ [13].

Two organic acids were chosen: 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 oxalic acid (or acetic acid) were agitated using an end-over-end shaker at a speed of 140 rpm at room temperature for 25 minutes. The suspensions were centrifuged at 3000 rpm for 5 min and the supernatants were then filtered through a Watman-42 filter paper for heavy metal analysis. Then new extracting solution was added to the treated soil sample and the tubes returned to the shaker. Twelve series of consecutive 25 minutes extractions were carried out. The concentrations of Zn, Pb and Cd were measured by a Shimadzu model 6300 flame atomic absorption spectrometry (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 two 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. The percent of each metal removed were calculated using an equation similar to the one earlier reported [14] as:

$$\text{Percent metal removed}(\%) = (C_i V_1 / C_s m_s) \times 100$$

Where C_i and C_s are the metal concentrations in supernatant (mmol L^{-1}) and soil (mmol kg^{-1}), respectively; V_1 is the volume of supernatant (L) and m_s is the dry mass of the soil (kg).

III. RESULTS AND DISCUSSION

Selected properties of the studied soil is presented in table 1. It was moderately fine textured, slightly alkaline (calcareous) with a low level of organic matter. The major heavy metals of concern in this soil were lead (Pb), cadmium (Cd) and especially zinc (Zn) whose concentration was very high.

Table 1. Characteristics of the studied soil.

| Soil properties | Value |
|---|-------|
| Texture | SCL |
| pH | 7.6 |
| EC (mS cm^{-1}) | 5.0 |
| CEC ($\text{cmol}_c \text{ kg}^{-1}$) | 15 |
| 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 |

As according to the materials and methods, the amount of chelating agents added ($1200 \text{ mmol kg}^{-1}$) was much higher than the total amount of heavy metals in the soil ($80.6 \text{ mmol kg}^{-1}$). Percentages of Zn and Cd removed from the soil using successive soil washing with 0.01 M solutions of OA and AA are presented in Figures 1 and 2, respectively. Both of chelating agents (OA and AA) were ineffective in removing Pb from the soil as previously reported [15]. Figures 1 and 2 indicate that renewing the extracting solutions greatly increased the removal of metals, but not by the same extent.

The cumulative releases of Zn and Cd from the soil were, respectively, 1.8 and 2.2% for OA, 3.0 and 4.9% for AA at the 1st cycle of extraction. The corresponding figures for the last (12th) cycle of extraction were 34.3 and 2.4% for OA, 20.4 and 29.1% for AA. The trends in removing of the two metals with successive washings could be expressed by the following equations:

Oxalic acid :

$$\text{Zn : } y = -0.046x^3 + 0.903x^2 - 1.570x + 2.850$$

$$R^2 = 0.998$$

Acetic acid :

$$\text{Zn: } y = 2.864x^{0.765}$$

$$R^2 = 0.997$$

$$\text{Cd: } y = 4.743x^{0.733}$$

$$R^2 = 0.999$$

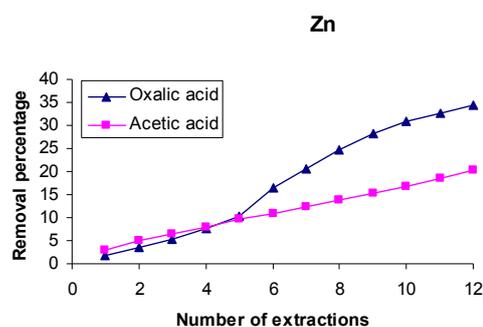


Fig. 1- Removal percentage of Zn vs. number of extractions by OA and AA.

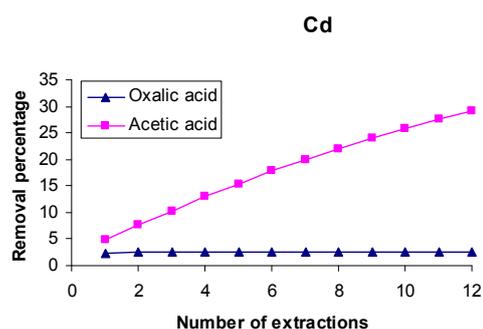


Fig. 2- Removal percentage of Cd vs. number of extractions by OA and AA.

Oxalic acid extracted more Zn than Cd. Surprisingly, the reverse occurred for acetic acid. This was not expected, because of theoretically higher extraction strength of oxalic acid compared to acetic acid. Changes in pH during the successive extraction steps are presented in Fig. 3. As it can be seen, the pH of oxalic acid treated soil was decreased

abruptly (6 units) at extraction steps between 5 and 7. Meanwhile, the removal of Zn was increased abruptly at extraction step 5. This indicates that the extraction strength of oxalic acid for Zn was increased with decreasing pH. It seems that a considerable amount of Zn in the studied soil is present in exchangeable or carbonate fractions as previously reported [16]. Furthermore, pH as a main factor has a dominant role in the removal of Zn. On the other hand, a slight decrease in pH values was observed for acetic acid which is in agreement with a slight increase in extraction of both Zn and Cd. Nevertheless, a higher removal efficiency of Cd than that of Zn for OA has been reported previously [5]. This may be due to the presence of carbonate materials in the studied soil. Figures 4 and 5 show the effect of concentration of organic acids (OA and AA) on the removal efficiency of Cd and Zn in the studied soil, respectively. As can be seen, increasing concentration of OA was ineffective in Cd removal from the soil. Furthermore, raising the concentration of OA caused only 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. While, the reverse occurred for acetic acid, i.e. as the concentration of AA increased, the removal of Cd and Zn increased considerably. Figure 4 demonstrates that the removal of Cd was not easy. This may be due to the presence of Cd in less removable fractions (i.e. residual fraction) as reported by other workers [17]. Surprisingly, raise in the concentration of organic acids had no effect on extraction efficiency of Pb. The results of our study indicate that no general efficiency order for chelating agents could be distinguished a need for fractionation studies to improve understanding of heavy metal mobilization and removal in soils.

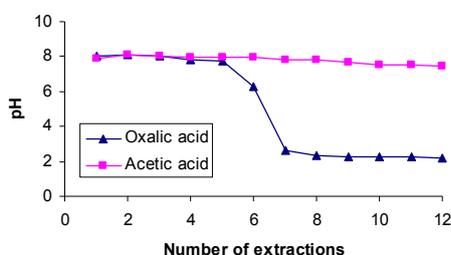


Fig 3- Changes in pH during the extractions.

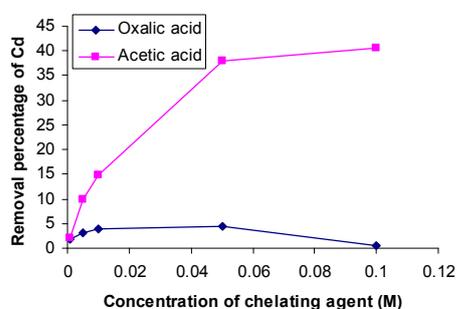


Fig. 4- Effect of organic acid concentration on removal percentage of Cd

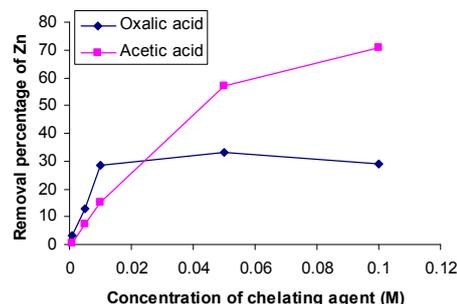


Fig. 5- Effect of organic acid concentration on removal percentage of Zn

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