Effect of Different Organic Acids for Heavy Metal Extraction from Pb, Zn and Cd Contaminated Soil

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Abstract. The aim of this work was to select organic aids with most obvious activation to Pb, Zn and Cd compound in contaminated soil in order to assist phytoremediation. Five kinds of low-molecular organic acid were used to leach the soils, and then heavy metal contents in the filtrate were measured. The effect of organic acids was evaluated in mobilization of heavy metals and their impacts on soil pH were discussed. With increasing concentrations of organic acids, the activation effect increased while soil pH had negative correlation. Citric acid had the most obvious activation compared with the other four organic acids. The maximum extraction rate of Cd, Zn of citric acid was shown at concentration of 50 mmol·kg\textsuperscript{-1}, and that of Pb was at 40 mmol·kg\textsuperscript{-1}. The extraction rates were 7.36%, 28.79%, 0.56%, respectively. The activation effects of heavy metals in soil were Zn>Cd>Pb.

Introduction

In response to the increasingly serious problem of the soil heavy metal pollution, a growing number of experts and scholars devoted to the research of the remediation of metal-contaminated soils in recent years. Currently, phytoremediation is considered to be the most ideal method because of its environmental friendliness and cost-effectiveness[1]. Phytoremediation is a biological technique, taking into account its visual advantages and extensive applicability. However, phytoremediation is restricted by a variety of factors, such as small plant biomass, slow growth of plants, phytotoxicity, bioavailability of heavy metals and so on[2]. Heavy metal mobility and solubility in the soil are key factors to their bioavailability[3]. Therefore, different types of chelating agents have been used to enhance the solubility of heavy metals in the soil. Traditional synthetic chelators such as DTPA and EDTA can significantly increase the solubility of heavy metals in the soil, but they have some potential questions involved in leaching risk and poor biodegradability[4]. Low molecular weight organic acids are more biodegradable and can reduce metal leaching hazards compared to synthetic chelants[5]. Many studies had shown that low molecular weight organic acids might increase solubility and mobility of heavy metals. Gao and Miao et al. suggested that in the presence of multiple metal contaminants (Cd and Pb), citric acid treatment had significantly enhanced the Cd (10-30%) and Pb (10-20%) accumulation in S. nigrum compared to non-citric acid-treated controls[6]. Freitas et al. applied citric acid at a dose of 40 mmol·kg\textsuperscript{-1} of soil, it showed that citric acid was efficient in the mobilization of Pb in soil and increased the removal of Pb from soil by all tested plants[7]. The objectives of this
study were aimed to filter out a better one from a variety of organic acids in order to apply it to the next pot experiment in phytoremediation, and further researched the possibility mechanism that organic acids activated the heavy metals and affected the soil pH.

**Material and Methods**

**Soil Preparation**

The topsoil samples (0-20 cm) were collected from an agricultural field in Baoding, Hebei Province, China. The sample was air-dried, crumbled and then milled (2 mm). The soil was artificially contaminated with aqueous solution of ZnSO$_4$$\cdot$7H$_2$O, CdCl$_2$$\cdot$2.5H$_2$O and Pb(NO$_3$)$_2$ to achieve concentrations of Zn 1200 mg·kg$^{-1}$, Pb 1000 mg·kg$^{-1}$ and Cd 30 mg·kg$^{-1}$ dry soil. The soil was equilibrated for one month. Soil moisture was maintained at 60 % of the water holding capacity by adding deionized sterile water. The finally metal concentrations in the soil were Zn 1124.83 mg·kg$^{-1}$, Cd 30.83 mg·kg$^{-1}$ and Pb 1055.5 mg·kg$^{-1}$ dry soil.

**Experimental Procedure**

Five kinds of organic acids (citric acid, succinic acid, oxalic acid, acetic acid and tartaric acid) were used to leach soil samples. 1g of soil sample was placed in a centrifuge tube, then added 5 mL solution of organic acids. 5 mL of sterilized saline solution was added to the control treatment. The treatment content of organic acids were 20, 30, 40 and 50 mmol·kg$^{-1}$. Following the addition of 25 mL of 0.01 mmol·L$^{-1}$ KNO$_3$, the mixture was shaken in a water bath oscillator ((28 ±2)°C) for 24 h and centrifuged for 10 min at 3,500 rpm at room temperature. After filtration, element contents of Pb, Zn and Cd in the filtrate were analyzed by A3 atomic absorption spectrophotometer (Beijing Purkinje General Instrument Co., Ltd., China).

2g of soil samples were taken in plastic centrifuge tubes. Then 10 mL of organic acid solution and 10 mL of distilled water were added to the tubes. The mixture of soil and solution was stirred for 10 min, then stayed for 30 min. The pH was measured by a pH meter (HACH, USA). The sample was measured again after 24 h.

**Statistical Analysis**

All determination results described in this work are the mean of three replicates. Analysis of variance (ANOVA) was done by using the SPSS 18.0 software package (SPSS Inc., Chicago, IL, USA). To detect the statistical significance of differences (P<0.05) between means, the Duncan and Dunnett’s tests were performed. Different letters of a, b and c indicate that data are significantly different at P<0.05.

**Results**

**Effect of Organic Acids on The Extraction of Zn**

As shown in Fig. 1, the results showed that the contents of Zn at different acid contents were significantly different. The contents of Zn increased with the increasing organic acids. Citric acid had the most obvious activation effect on the extraction of Zn at each content, while acetic acid had smallest effect. The three other kinds of organic acids played almost similar roles. The Zn content that citric acid leached the soil was increased from 63.16 to 323.8 mg·kg$^{-1}$. For acetic acid, the Zn content was increased from 7.82 to 24.64 mg·kg$^{-1}$. For
the other organic acids, the Zn content was increased from 12.54 to 57.37 mg·kg\(^{-1}\). The highest value was shown in oxalic acid of 50 mmol·kg\(^{-1}\), but it did not exceed the lowest value of citric acid. The order of Zn maximum extraction content in soil was: citric acid> oxalic acid> succinic acid> tartrate acid> acetate acid.

**Effect of Organic Acids on The Extraction of Cd**

The content of Cd leached from the soil with four different contents of five kinds of organic acids was shown in Fig. 2. The extraction of Cd in each treatment had obvious difference, and the Cd contents of all organic acid treatments were bigger than the control treatment (0.24 mg·kg\(^{-1}\)). Cd content after acetic acid, succinic acid and citric acid leached the soil was increased with the increase of organic acid content. The highest value of oxalic acid and tartaric acid appeared under 40 mmol·kg\(^{-1}\). Cd content that citric acid leached the soil was increased from 1.35 to 2.27 mg·kg\(^{-1}\). The Cd content with four other kinds of organic acids was increased from 0.31 to 1.24 mg·kg\(^{-1}\). The order of Cd maximum extraction content in soil was citric acid> oxalic acid> succinic acid> acetic acid> tartaric acid.

![Figure 1. Zn contents in the soil filtrates.](image1)

![Figure 2. Cd contents in the soil filtrates.](image2)

**Effect of Organic Acids on the Extraction of Pb**

The leaching effect of five kinds of organic acids on Pb was shown in Fig. 3. The Pb content at each leaching content of organic acids were higher compared with the control (0.20 mg·kg\(^{-1}\)). Pb content of citric acid at each treated content (1.35-5.93 mg·kg\(^{-1}\)) were obviously higher than the other four organic acids. The Pb content extracted by oxalic acid of 40 mmol·kg\(^{-1}\) was 3.36 mg·kg\(^{-1}\), the Pb contents leached by the remaining treatments of oxalic acid and all treatments of succinic acid, tartaric acid and acetic acid were ranged from 0.45-1.26 mg·kg\(^{-1}\). However, the extraction rate of organic acid was 0.13-0.56%. The order of Pb maximum extraction content in soil was: Citric acid>oxalic acid>tartaric acid> acetic acid>succinic acid.
The five kinds of organic acids had significantly different effect on activating three kinds of heavy metals (Pb, Zn, Cd). Overall, the ability of organic acids on mobilization of heavy metals followed the order of Zn> Cd> Pb. Citric acid had the extraction rate of activating Zn (28%). The highest extraction rate of 7% that used citric acid to mobile Cd, and the remaining four acids was almost 3%. The highest extraction rate of five organic acids on Pb was 0.5% in citric acid of 40 mmol·kg\(^{-1}\). Compared with Zn and Cd, the proportion is much smaller. These results suggested the kind of heavy metals significantly affected the activating effect of organic acids.

**Effect of Organic Acids on Soil pH**

As shown in Fig. 4, after applied organic acids to the soil, the pH was decreased apparently. And after 24h, pH had a certain degree of rebound. The reduction degree of pH was proportional to the content of organic acids, and inversely proportional to the extraction concentration of heavy metals in the soil filtrate. Soil pH with citric acid application had the maximum reduction of all treatment (8.07-5.31), it was consistent to that citric acid made the largest mobilization of heavy metals. Otherwise, the ability of tartaric acid to lower the pH only after citric acid (8.07-5.60), but it didn’t have the outstanding ability to activate heavy metals. That suggested that the mobilization of heavy metals was not only associated with the
reduction of soil pH, but also with other factors, such as the complex stability of organic acid with heavy metals, the charge characteristics of soil surface, soil physical and chemical properties, etc. And after 24h, soil pH had rebounded, closed to the original soil pH (8.07). One hand, that might be gradually reach equilibrium after adding organic acids to the soil. On the other hand, that might be the degradation of organic acids in the soil. In addition, the complexes that formed with organic acids and heavy metal were not stable. Its decomposition might lead to the rebound of soil pH.

Discussion

Currently, phytoremediation of heavy metals still have to deal with some problem such as phytotoxicity, a limited contaminant uptake[8]. And successful phytoremediation are also of great challenges due to the lower solubility and availability of heavy metals to plant uptake caused by the strong fixation of heavy metals by soil organic matter, clays and oxides[9]. It has been reported that the root exudates, especially low molecular weight organic acids are capable of forming soluble complexes and chelates with metals, and may modify the mobility and fixation of heavy metals in soil. In this study, applied different concentrations of organic acids o leach heavy metals of Pb, Zn, Cd in soil, the result suggested the experimental application of five organic acids are in varying degrees, increased solubility of three kinds of heavy metals and reduced the soil pH, and the reduction of soil pH was proportional to the concentration of organic acids. Thus, the application of organic acids lowered the pH of the soil may be one reason that increased the solubility of heavy metals in soil. Organic acids changed the surface charge of soil to decrease the soil pH through proton acidification. It released the heavy metals that fixed by Fe and Al oxides fixed, while activated the heavy metals bound with humus, to increase the solubility of heavy metals in soil.

Different types of organic acids had significant differences in activating heavy metals in soil. Citric acid in every concentration showed the advantage of the other four kinds of organic acids.

Some studies[10] showed that the activation effect of low molecular weight organic acids on heavy metals was concerned with the number and location of carboxyl and phenolic groups in these. After adding organic acids into the soil, the mainly reaction was the complexation with heavy metals and functional groups (such as -COOH and -OH). Generally, tricarboxylates had the greater ability to activate heavy metals than dicarboxylic acid. Among five acids in this study, citric acid was the only one of tricarboxylates, acetic acid is a monobasic acid, and the others were dicarboxylic acids. Therefore, citric acid showed obvious advantage to increase solubility of heavy metals. In addition, the ability of mobilization of heavy metals of low molecular weight organic acids was related to the magnitude of the stability constants of complexes that organic acids and heavy metal ions formed. The greater stability constants might have the stronger adsorption capacity for heavy metal ions, heavy metals were more likely released from the soil colloidal system.

Conclusion

Citric acid, oxalic acid, acetic acid, succinic acid and tartaric acid leached soil of Pb, Zn, Cd compound pollution. Our results suggested a possibility of organic acids had a certain ability to activate heavy metals in soil. As the increasing concentrations of organic acids, the Zn and Cd concentration in soil filtrates also increased, while Pb did not appear a clear rule. Citric
acid showed a clear advantage on activation of heavy metals in soil, the remaining four kinds of organic acids showed not obvious difference of the ability to activate heavy metals. We had chosen to citric acid to assist phytoremediation to conduct further experiments. Application of five kinds of organic acids had lowered the soil pH. This result indicated decreased soil pH might be a possibility to increase the solubility of heavy metals.

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References


