

Removal of heavy metals from a contaminated soil using tartaric acid

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Abstract: This study reports the feasibility of remediation of a heavy metal (HM) contaminated soil using tartaric acid, an environmentally-friendly extractant. Batch experiments were performed to test the factors influencing remediation of the HM contaminated soil. An empirical model was employed to describe the kinetics of HM dissolution/desorption and to predict equilibrium concentrations of HMs in soil leachate. The changes of HMs in different fractions before and after tartaric acid treatment were also investigated. Tartaric acid solution containing HMs was regenerated by chestnut shells. Results show that utilization of tartaric acid was effective for removal of HMs from the contaminated soil, attaining 50%–60% of Cd, 40%–50% of Pb, 40%–50% of Cu and 20%–30% of Zn in the pH range of 3.5–4.0 within 24 h. Mass transfer coefficients for cadmium (Cd) and lead (Pb) were much higher than those for copper (Cu) and zinc (Zn). Sequential fractionations of treated and untreated soil samples showed that tartaric acid was effective in removing the exchangeable, carbonate fractions of Cd, Zn and Cu from the contaminated soil. The contents of Pb and Cu in Fe-Mn oxide fraction were also significantly decreased by tartaric acid treatment. One hundred milliliters of tartaric acid solution containing HMs could be regenerated by 10 g chestnut shells in a batch reactor. Such a remediation procedure indicated that tartaric acid is a promising agent for remediation of HM contaminated soils. However, further research is needed before the method can be practically used for *in situ* remediation of contaminated sites.

Keywords: tartaric acid; soil remediation; heavy metals; soil contamination

Introduction

The rapid development of industries and the use of chemical substances in many industries have caused a steady increase of heavy metal (HM)-pollution in soils (Tejowulan and Hendershot, 1998). Because HMs in the environment are posing significant threats to human health and ecological environment, therefore reliable remediation techniques are required for site clean-up (Abumaizar and Khan, 1996). There are generally two fundamental technologies to remediate soils (Hong, 2002). The first technology is to immobilize HMs into tightly bound solid matrix to minimize migration. However, this technology is not a permanent solution. Site reuse of soil is limited and long-term monitoring is generally required. For these reasons, solidification is generally limited to radioactive or highly toxic wastes. The second technology is to promote HMs mobility and migration to the liquid by desorption and solubilization. This technology is a permanent solution, providing recycle of remediated soils and improving land-use option in the future.

Soil washing, a water-based process that employs chemical and physical extraction processes to remove contaminants from the soil, has recently become a common *ex-situ* technique for remediating sites contaminated with organic and inorganic pollutants. This process has been proven successful in the remediation of various HM-contaminated sites in the US (Anderson, 1993).

Much of previous work on soil washing was mainly focused on using strong acids or chelating agents as extractants to remove HMs from contaminated soils. However, strong acid washing leads to decreased soil productivity and adverse changes in the chemical and physical structure of soils due to mineral dissolution (Reed *et al.*, 1996), despite ethylenediaminetetraacetic acid (EDTA) could extract very high percentages of HMs from contaminated soils (Steele and Pichtel, 1998; Papassiopi *et al.*, 1999; Garrabrants and Kosson, 2000; Kim and Ong, 2000; Sun *et al.*, 2001; Lim, 2005). But it is very stable and could remain adsorbed in the soil after extraction, this can make the soil unfit for further use because residual EDTA can slowly leach nutrients from the soil. Therefore, it can also disturb the physical, chemical, and biological properties of soils.

With the aforesaid problems in mind, we are trying to find an environmentally-friendly extractant, which has additional advantages of being readily available, non-toxic and relative low in cost for the efficient *in situ* remediation of HM contaminated soils. Many laboratory studies have shown that low molecular weight organic acids could solubilize HMs from contaminated soils through complexation reactions (Krishanmurti *et al.*, 1997; Poulsen and Hansen, 2000; Taniguchi *et al.*, 2000; Wu *et al.*, 2003; Qin *et al.*, 2004; Liao and Xie, 2004). Wasay has compared the extractability of HMs by 12 different organic ligands, including 10 different organic acids and two chelating agents, in a laboratory-scale batch

and column experiments. Results show that citric acid and tartaric acid could remove the HMs from the contaminated soils, as effective as EDTA and DTPA (diethylenetriaminepentaacetate) (Wasay *et al.*, 1997, 2001; Wasay, 1998). While compared to EDTA and DTPA, tartaric acid is reasonably inexpensive, biodegradable, less destructive to soil structure, relatively easy to handle, and has a comparatively lower affinity for alkaline earth metals (Ca, K, and Mg), so it is a suitable environmentally-friendly extractant for soil washing (Raman and Shiv, 2000).

Although effect of tartaric acid pH, concentration and contact time on removal of HMs from contaminated soils has been studied (Wasay *et al.*, 1998), there is limited information on the changes of HMs speciation during soil washing. The term speciation is related to the distribution of an element among chemical forms or species. HMs can occur in several forms in water and soils. Interest has been increased in sequential extraction techniques to relate the degree of mobility with risk assessment (i.e. the more mobile the metal is, the more risk associated with it) (Bourg, 1995). Not only is total HM concentration of interest, but it is now accepted that understanding the environmental behaviour by determining its speciation is of paramount importance (Mulligan *et al.*, 2001). Based on the HM speciation in contaminated soils, the most appropriate method for soil remediation can be determined. Selective sequential extraction can potentially be used to determine if the HMs can be removed by remediation techniques such as soil washing or to predict removal efficiencies. Mulligan *et al.* (1999) demonstrated that sequential extraction techniques could be used prior to soil washing to design and monitor the remediation process for a contaminated soil sample. However, so

far few attempts have been made to correlate sequential extraction results with soil washing results.

The aims of this paper were: (1) to determine the changes of HMs in different fractions before and after tartaric acid treatment; (2) to investigate the effect of contact time on the transport and removal rates of HMs; (3) to test the influence of tartaric acid pH, concentration on the removals rates of HMs; (4) to observe the regeneration of tartaric acid solution containing HMs for recycling by chestnut shells.

1 Materials and methods

1.1 Chemicals

Tartaric acid of reagent grade was used as an extractant for heavy metal (HM) removal from contaminated soil.

Chestnut shells were dried at 65°C during 24 h until moisture content was negligible and then sieved. The fraction between 2 and 10 mm was kept at 4°C to minimize biodegradation.

1.2 Soil sample

The soil used in this study was collected from the Shenyang Zhangshi Irrigation Area, located in the western suburbs of Shenyang (122°25'—123°48'E, 41°12'—42°17'N). This area is well known in China for its notorious Cd polluted farm. Soil sample was air dried and sieved through a 2-mm sieve. The soil sample was homogenized and stored in a plastic container for subsequent experiments. The contents of HMs in the soil were determined by an acid digestion method (HNO₃+HClO₄+HF). The digested liquid was filtered through Whatman No. 42 paper, and the filtrate was analyzed for HMs measurement using ICP spectrometry (OPTIMA 3000, USA). The selected chemical and physical characteristics of the soil sample are presented in Table 1.

Table 1 Physical-chemical characteristics of the contaminated soil

Organic matter, %	pH	CEC, cmol/kg	Clay, %	Loam, %	Sand, %	Cadmium(Cd), mg/kg	Lead (Pb), mg/kg	Copper (Cu), mg/kg	Zinc(Zn), mg/kg
1.9	6.2	16.4	39.2	41.6	19.3	3.4	68.3	43.9	211

Note: CEC. Cation-exchanged capacity

1.3 Extraction of HMs from soil with tartaric acid

A series of batch extraction experiments were performed with tartaric acid as an extractant to test the effects of concentration, pH and contact time on HM removals.

To determine optimum concentration for soil treatment, 1 g of soil was put into a series of polycarbonate centrifuge tubes, and 25 ml of tartaric acid solutions with different concentrations was added to each centrifuge tube. The pH of the tartaric acid was adjusted with 0.1 mol/L NaOH in the range of

3.5—4.0. The suspensions were shaken for 24 h in a 20°C thermostat. After this, the suspensions were centrifuged with a refrigerated centrifuge. The supernatants were filtered through a Whatman No. 42 paper, and the filtrates were analyzed for HM contents.

The pH effect of tartaric acid solution (0.4 mol/L) was studied in the pH range of 3.0—7.0. As a control, deionized water was prepared in the same way as the tartaric acid treatment and compared with the results of tartaric acid treatments. The pH of tartaric acid was adjusted with 0.1 mol/L NaOH. 1 g of soil was put

into a series of polycarbonate centrifuge tubes, and 25 ml of tartaric acid solutions with different pH values (3.0, 4.0, 5.0, 6.0, 7.0) was added to each centrifuge tube. The suspensions were shaken for 24 h in a 20°C thermostat. After this, the suspensions were centrifuged with a refrigerated centrifuge. The supernatants were filtered through a Whatman No. 42 paper, and the filtrates were analyzed for HM contents.

For kinetic study, 5 g of soil was added to 100 ml of 0.4 mol/L tartaric acid solution with pH in the range of 3.5–4.0. The removals of heavy metals from soil were measured at different time intervals (0.5, 2, 4, 8, 12, 24, 48 h). Thereafter the same procedure above mentioned was used.

1.4 Speciation of HMs in soil before and after tartaric acid treatment

The soil residues obtained from tartaric acid treatment, together with untreated soil sample, were fractioned by the sequential extraction procedure (Tessier *et al.*, 1979). One gram of soil sample, sieved to 0.2 mm, was used in three replicates. The sequential extraction procedure was as follows:

(1) Exchangeable fraction: 15 ml of 1 mol/L MgCl_2 was added, shaken continuously at room temperature for 2 h. The mixture was centrifuged at 4000 r/min for 10 min and the supernatant was analysed using ICP spectrometry.

(2) Carbonate fraction: 15 ml of 1 mol/L CH_3COONa (adjusted to pH 5.0 with CH_3COOH) was added, shaken continuously at room temperature for 2 h. The mixture was centrifuged at 4000 r/min for 10 min and the supernatant was analysed using ICP spectrometry.

(3) Fe-Mn oxide fraction: 20 ml of 0.04 mol/L hydroxylamine hydrochloride ($\text{NH}_2\text{OH}\cdot\text{HCl}$) in 25% (v/v) acetic acid was added, shaken occasionally at $(96 \pm 3)^\circ\text{C}$ for 5 h, then another 10 ml of 0.04 mol/L $\text{NH}_2\text{OH}\cdot\text{HCl}$ in 25% (v/v) acetic acid was added. The mixture was centrifuged at 4000 r/min for 10 min after cooling, and the supernatant was diluted to 10 ml and analysed using ICP spectrometry.

(4) Organic fraction: this extraction is divided into three phases: phase (I). 3 ml of 0.02 mol/L HNO_3 and 5 ml H_2O_2 (30%) (adjusted to pH 2.0 with 0.1 mol/L HNO_3) was added, standing at room temperature for 1 h; phase (II). 3 ml H_2O_2 (at pH 2.0), intermittently agitated for 2 h at 85°C , another 3 ml H_2O_2 was added, and continue agitated for 3 h at 85°C ; phase (III). 5 ml of 3.2 mol/L NH_4Ac was added after cooling, diluted to 20 ml with deionized water, shaken continuously for 1 h. The mixture was centrifuged at 4000 r/min for 10 min, and the supernatant was diluted to 25 ml and analyzed using ICP spectrometry.

(5) Residue fraction: this fraction was calculated from the difference between HM concentration determined by hot acid digestion and the total quantity

of HMs removed in the preceding extraction procedures.

1.5 Regeneration of tartaric acid solution containing HMs

The feasibility of tartaric acid regeneration was investigated using chestnut shells for adsorption of HMs from used tartaric acid by means of batch experiment in an Erlenmeyer flask (250 ml nominal volume). A total 100 ml of used tartaric acid solution was poured into the flask, in each flask 10 g of chestnut shells were added, a flask without chestnut shells served as a control. The flasks were placed on the flat bed orbital shaker rotating at 150 r/min for 12 h. The mixture was centrifuged at 5000 r/min for 20 min and the supernatant was analysed using ICP spectrometry.

2 Results and discussion

2.1 Effect of tartaric acid concentration on removals of HMs from the contaminated soil

The effect of tartaric acid concentration on the removals of HMs from the soil is shown by plotting concentrations of tartaric acid solution vs. HM removals (Fig.1). The concentrations of tartaric acid solution stepwise changed from 0.01 to 0.8 mol/L with an interval of 0.01, 0.02, 0.04, 0.08, 0.1, 0.4, 0.8 mol/L. The removals of HMs were found to be dependent on the tartaric acid concentration. The removals of HMs abruptly increased with the tartaric acid concentration up to 0.4 mol/L. As the concentration of tartaric acid was further increased from 0.4–0.8 mol/L, the removal of Cd, Pb, Cu, and Zn from the soil did not increase. Therefore, the optimum tartaric acid concentration is 0.4 mol/L for soil treatment to avoid introduction of excess tartaric acid into soil. The maximum removals of Cd, Pb, Cu and Zn were 53.5%, 43.6%, 41.4% and 21.0%, respectively. The reason why tartaric acid has different removal capability for Cd, Pb, Cu, and Zn was mainly due to its speciation in soil. The predominant forms of zinc in soil was adsorbed at higher energy sites and this was relatively unaffected by the tartaric acid. The desorption of zinc from soil became more difficultly than that of other three HMs. Therefore, tartaric acid was more effective in removing cadmium, lead and copper than zinc.

2.2 Effect of tartaric acid pH on removals of HMs from the contaminated soil

The pH is an important parameter affecting the efficiency of HMs desorption from the soil (Naidu and Harter, 1998). Effect of tartaric acid pH on removal of HMs from the contaminated soil is shown in Fig.2. Results show that the removal efficiency of HMs was dependent on tartaric acid pH. Tartaric acid removed 50%–60% of Cd at pH 3.0–5.0, 40%–50% of Pb at pH 3.0–6.0, 40%–50% of Cu at pH 3.0–5.0 and

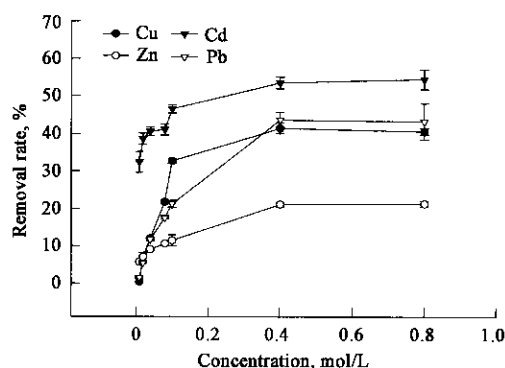


Fig.1 Effect of tartaric acid concentration on removal of heavy metals from the contaminated soil

20%–30% of Zn at pH 3.0–4.0. In this study NaOH was added to adjust the pH of tartaric acid solution. Sodium may compete with HMs for tartaric acid, thereby leading to Na-tartaric complex. In comparison to Zn, soil treatment with tartaric acid was more effective in removing Cd, Pb and Cu from the contaminated soil. This result was due to the chemical property of tartaric acid.

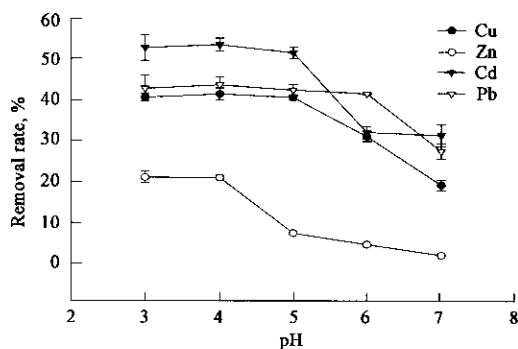


Fig.2 Effect of tartaric acid pH on removal of heavy metals from the contaminated soil

Tartaric acid carries two negatively charged carboxyl group and hydroxyl group which form more than one bond between the HM and the tartarate. The multiple bonds form a tight ring structure around the metal ion enabling the tartarate to solubilize the HMs and leach them from the contaminated soils. Wasay has demonstrated that the coordination of tartaric acid to a metal ion involves one carboxyl groups and two hydroxyl group (Wasay *et al.*, 1998). Negatively charged carboxyl groups and hydroxyl groups react with HMs cations when these groups become deprotonated. pH is the determining factor which controls this reaction. The dissociation of carboxyl group takes place at a pH 3.0–5.0 whereas dissociation of the hydroxyl group takes place at a pH above 5.0. Therefore, Cd, Pb and Cu reacts more

efficiently with the dissociated molecules of tartaric acid than Zn.

2.3 Kinetics of HM dissolution/desorption

In order to describe the kinetics of HMs dissolution/desorption, an empirical first order model was employed. This model can be used when dissolution/desorption arises out of equilibrium partitioning and mass transfer phenomena take place between two phases, one of which is a liquid phase and the other is a solid phase. The theoretical basis of this model is that at equilibrium, there is no net transfer between two phases and partition coefficients can be used to represent the ratio of the concentration of the same chemical species in two phases. Relative concentrations of HMs between two distinct phases provide an explicit measure of the property of HMs existing in each phase. In this study, the kinetics of HMs dissolution/desorption and equilibrium was plotted, mass transfer theory was used to derive first-order mass transfer coefficients and equilibrium tartaric acid phase concentration by fitting the data to the flowing equation.

$$C_0 = C_e [1 - \exp(-kt)] \quad (1)$$

Where C_0 is the HMs concentration of tartaric acid phase at time t , k is the lumped mass transfer coefficient, C_e is the equilibrium tartaric acid-phase concentration and t is the contact time with tartaric acid (Woolgar and Jones, 1999). Fitting of the data to the equation was achieved using a nonlinear curve fitting of software Sigma.

Kinetics of HMs dissolution/desorption from soil are shown by plotting the concentrations of HMs released from the soil vs. extraction time. Transport and mass transfers of HMs from the contaminated soil might be a key process responsible for reducing HMs from the soil. To achieve maximum HM removal, a specific period of time is required. Our results demonstrate a rapid dissolution/desorption process for Cd and Pb. During the initial phase (0–10 h), the dissolution/desorption rate of Cd and Pb was more rapid than Cu and Zn, and the equilibrium could be approached within 12 h. The desorption equilibrium of Cu and Zn could be approached within 24 h (Fig.3). The correlation coefficients (R^2) of individual HMs were highly significant and varied between 0.89–0.96 (Table 2). Using the model, we also can obtain the equilibrium HMs concentrations (C_e) and mass transfer coefficients (k). The order of mass transfer coefficients was Cd > Pb > Cu > Zn (Table 2). Table 2 shows that cadmium was most easily extracted from the soil to tartaric acid solution, followed by lead then copper and zinc. This result may be due to strong chemisorption by clays, oxides and humus of soil on zinc and copper. Therefore, the mobility of Cu and Zn was obviously lower than that of Cd and Pb.

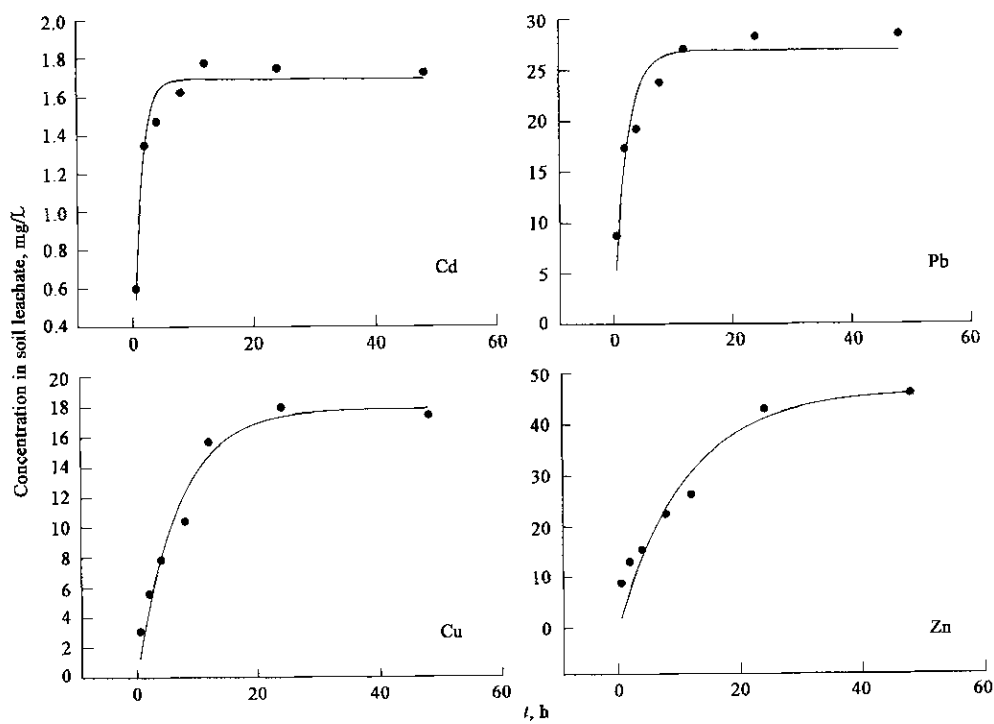


Fig.3 Desorption kinetics of HMs using a first-order model; Experimental desorption rates and model fitted curves of HMs from the contaminated soil

Table 2 Tartaric acid solution phase equilibrium concentrations of HMs (C_e) and mass transfer coefficients (k) derived by data fitting using a first-order model

Heavy metal	C_e	k	R^2
Cd	1.69 ± 0.04	0.77 ± 0.10	0.96
Pb	26.88 ± 1.37	0.44 ± 0.09	0.89
Cu	17.91 ± 1.07	0.15 ± 0.03	0.96
Zn	46.64 ± 4.59	0.09 ± 0.02	0.92

2.4 Fractionations of HMs in the soil before and after tartaric acid treatment

In this study, the soil sample was analysed to determine the speciation of HMs before and after tartaric acid treatment. Results are presented in Fig.4, showing that the amount of each fraction of HMs in soil. Before tartaric acid treatment, cadmium in soil was primarily found in exchangeable, carbonate and organic matter fractions followed by Fe-Mn oxide and residue fractions. Lead and zinc was predominantly found in Fe-Mn oxide fraction followed by residue fraction. Copper was primarily partitioned to organic matter fraction followed by Fe-Mn oxide and residue fractions. After tartaric acid treatment, the exchangeable and carbonate fractions of Cd, Zn and Cu were almost removed from the soil. The contents of Pb and Cu in Fe-Mn oxide fraction were also significantly decreased by tartaric acid treatment. Although Cd and Cu in organic matter fraction and Zn in Fe-Mn oxide

fraction were also mobilized by tartaric acid treatment, the removal efficiency was significantly lower than exchangeable and carbonate fractions.

Overall, the above results show a complex picture of HM removal from different fractions after tartaric acid treatment. These results were similar with Li *et al.*, who examined the use of the sequential extraction procedure with EDTA extraction of metals. They concluded that the organic phase and residue phase were very stable since HMs in these phases could not be removed by the EDTA and should not be considered in washing processes, since it would be uneconomical for treatment (Li *et al.*, 1995). Therefore, tartaric acid was suitable for soil washing and could be used as an environmentally-friendly extractant for remediation of HM contaminated soils.

2.5 Regeneration of tartaric acid solution containing HMs

Regeneration of tartaric acid is a vital step for the successful development of remediation process with tartaric acid as an extractant. Chestnut shell was considered as a sorbent applied to batch experiment. The overall efficiency of sorption process to achieve tartaric acid regeneration was determined based on concentrations of HMs in tartaric acid before and after the chestnut shells treatment. The remaining percentages of HMs in the tartaric acid after chestnut shells treatment are shown in Fig.5. After being treated with chestnut shell for 24 h at ambient temperature, more than 80% Cd, Pb, Cu and Zn were removed. The

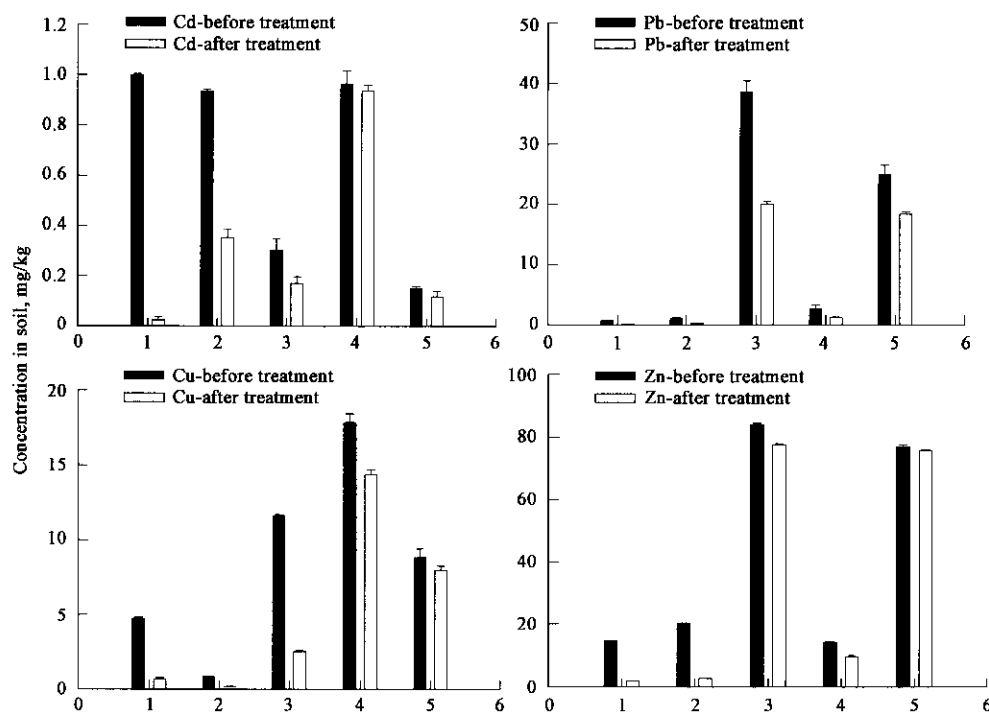


Fig.4 Fractionations of HMs in soil before and after tartaric acid treatment

1. exchangeable; 2. carbonate; 3. Fe-Mn oxide; 4. organic matter; 5. residual; error bars represent standard deviation of triplicate measurements

regeneration result was satisfactory. The control (without chestnut shells) showed slight variation from the untreated tartaric acid containing HMs, mostly by less than 5%. These results indicate that chestnut shell is a good sorbent for removal of HMs from tartaric acid solution which was used to extract HMs from the contaminated soil. However, further investigation is needed to optimize the regeneration process.

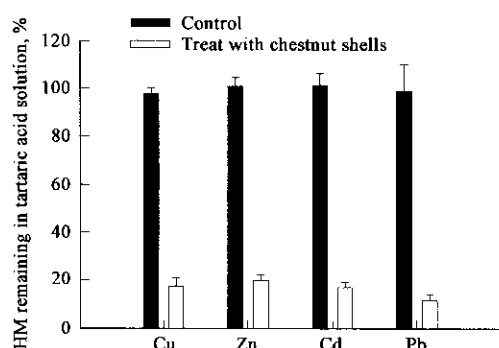


Fig.5 Regeneration of tartaric acid containing HM using chestnut shells

3 Conclusions

In conclusion, these results show that utilization of tartaric acid was effective for removal of HMs from the contaminated soil in Shenyang Zhangshi Irrigation Area. The optimum concentration of tartaric acid for soil treatment was 0.4 mol/L, optimum pH is in the range of 3.5–4.0. Practical treatment of soil was

desirable in weakly acidic condition because of less impact on the physical and chemical properties of the soil. Maximum removals of HMs were attained within 24 h in soil. Efficiency of tartaric acid solution on removal of HMs was directly related to the chemical and physical characteristics of soil and speciation of HMs in soil. As a result, tartaric acid was effective in removing the exchangeable, carbonate fractions of Cd, Zn and Cu from the contaminated soil. The contents of Pb and Cu in Fe-Mn oxide fraction were also significantly decreased by tartaric acid treatment. The tartaric acid solution containing HM could be regenerated by adsorption of HMs from tartaric acid solution using chestnut shells. Before this technique is applied to *in situ* or *ex situ* remediation on a full scale, a thorough assessment should be made involving costs and ecological risk related to the quality of tartaric acid solution, disposal of used tartaric acid and chestnut shells, the transport in soil, refill of contaminated site, and so on.

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