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Remediation of heavy metal contamination in calcareous soil by washing with reagents: A column washing

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Abstract

This paper presents an evaluation of different dose of HCl and Na₂EDTA for the removal of Cd and Pb contaminated calcareous soil in the column mode. The field soil contained high concentrations of DTPA-extractable Cd (12.82 mg kg⁻¹) and Pb (105.38 mg kg⁻¹). Both HCl and Na₂EDTA were found to be effective on removing DTPA-extractable Cd, but low concentration of HCl was ineffective on removing DTPA-extractable Pb and the highest removal efficiency of DTPA-extractable Pb washed by optimal dose of Na₂EDTA was only 45.39%. In order to effectively and economically remove both metals from the contaminated soil, a sequential use of the optimal dose of HCl followed by the optimal dose of Na₂EDTA was tested and 87.3% and 73.2% removal efficiency were obtained for DTPA-extractable Cd and Pb, respectively. Compared to using single washing agent, the removal efficiencies of DTPA-extractable Cd and Pb for the sequential washing with HCl followed by Na₂EDTA were increased more than 8.3% and 27.92%, respectively. Results of soil extractions experiments revealed that the predominant fraction of the removed Cd and Pb were Fe/Mn oxide fraction and carbonate fraction. Trace metals in leachate collected from sequential washing was successfully precipitated and the leachate was safe for discharge.

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Keywords: soil contaminated; Cd; Pb; DTPA-extractable heavy metal; sequential washing

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1. Introduction

Recently, the contamination of soil by heavy metals has been recognized as a significant environmental issue especially in the area of public health [1]. It is technically difficult and expensive to reduce the heavy metal content in soil to an extremely low level. But if a reasonable clean up goal is set, the decontamination would be much easier and more economical. Such a goal could be remove the fraction which may access to food chain [2]. The heavy metal redistributed in soil has increased the chances of people exposed to these metals through inhalation, ingestion and skin contact [3]. The itai-itai disease occurred in Japan was aroused by ingesting "Cd rice". Thus, the remediation of heavy metal contaminated soil is urgency especially for cultivated land.

To improve soil quality, various in-situ and ex-situ remediation methods have been employed, such as stabilization, solidification, soil washing, electroremediation and phytoremediation [4]. Among these techniques, soil washing is considered as one of the most suitable on-site techniques for removing metals by which the contaminant bonded to soil are eliminated effectively and transferred to the liquid phase by desorption and solubilization [5]. Soil washing can be practiced in two ways, batch washing and column washing. Compared to batch washing, column washing has many advantages. Firstly, the soil structure remains intact, which is not the case for batch extractions. Secondly, the process can minimize the chance of workers exposure to contaminants [6, 7]. What's more, column washing was proved to have better metal removal effects than batch washing [8].

Various column washing agents have been investigated such as mineral acid, organic acid, chelating agents, mineral salt and biosurfactant [2, 9-11]. Recently, increased attention has been focused on the use of acidic and chelating agents which are capable of desorbing heavy metal contaminants from soil into solution [12]. Acid washing mainly utilize ion exchange and soil matrix dissolution to solubilize metal and it effectively increase the mobility of heavy metals. HCl is the most common alternative suggested for cleaning polluted soils [13]. Certainly, a mass of work has been done with synthetic metal chelators with high metal stability constants. Because of the toxicity and potential carcinogen of NTA (Nitrilotriacetic acid) and DTPA [14], Na₂EDTA has become the first choice and widely used in column washing because Na₂EDTA has a low degree of biodegradability in soil and a strong chelating ability with a wide range of heavy metals [15]. The combination of acid and chelator can achieve a higher removal efficiency than any single acid or chelator selected. Washing with acid can enhance the mobility of heavy metal due to the low soil pH, which has a great contribution to forming complexes with metals and Na₂EDTA. However, there is little published report on the combination of acid and chelator and treatment of washing wastewater.

The object of this paper was to evaluate the removal efficiency of the DTPA-extractable heavy metal by using HCl and Na₂EDTA in treating a contaminated calcareous soil in laboratory columns and to select the optimal conditions. The study also focused on the dispose of leaching washing.

2. Materials and methods

2.1. Soil sampling

The moist soil sample of the upper soil layer (0-10 cm) of a Dystric Cambisol (FAO-UNESCO,1994) was collected from an actual contaminated field site located in northwest China (104°35'E, 36°48'N). The Dystric Cambisol was a typical soil in Northwestern China. The soil was heavily contaminated by Pb and Cd because of long-term irrigation of heavy-metal containing wastewater. The general chemical properties of the tested soil were: organic matter 2.16%, CEC 240.40 mmol kg⁻¹, total Cd 33.93 mg kg⁻¹, total Pb 550.10 mg kg⁻¹, DTPA-extractable Cd 12.82 mg kg⁻¹, DTPA-extractable Pb 105.38 mg kg⁻¹ and

pH(H₂O) 7.0. Soil samples were air-dried at room temperature (20-30°C) and sieved (< 2 mm) for the column washing experiment.

The soil was analyzed physically and chemically. The total metal content was determined after acid digestion (HF/HClO₄/HNO₃). The DTPA-extractable concentration of heavy metals was analyzed with 0.005mol/l DTPA. Soil pH was measured by using a 1:5 soil to water ratio and pH meter. The cation exchange capacity of the sample was determined by the ammonium acetate (NH₄OAc) /sodium acetate (NaOAc) method. Organic matter was analyzed by walkley-black titrations. All the heavy metal analyses were performed using an atomic absorption spectrophotometer (AAS).

2.2. Column washing experiment

Column washing studies were carried out at bench scale to examine the removal efficiency of the DTPA-extractable heavy-metal by using different dose of HCl and Na₂EDTA in a contaminated calcareous soil.

Firstly, to evaluate the effect of HCl and Na₂EDTA concentrations on the removal of DTPA-extractable Cd and Pb, the column washing experiments were conducted with a soil to solution ratio of 1:10. Briefly, 300 grams of contaminated soil was placed in soil column with 5-cm in diameter and 30cm in height. A plastic mesh (D=0.2mm) was placed at the bottom of the column to retain the soil. Then, 3L of washing solutions were passed through the corresponding soil columns by using a peristaltic pump. The concentrations of HCl and Na₂EDTA used in the experiment were 0.01M~0.8M and 0.01M~0.12M, respectively. The Column washing were performed in duplicates to ensure reproducibility of the results.

Secondly, to optimize their soil to solution ratio for the remediation of the experimental soil, the optimal concentration of HCl and Na₂EDTA were tested in column experiments at soil to solution ratio of 1:2~1:12 and 1:2~1:10, respectively. The washing process was conducted as it was mentioned above.

Then, the optimal dose of HCl solution washing followed by the optimal dose of Na₂EDTA solution were employed to remove both Cd and Pb. The washing process was conducted as it was mentioned above, the optimal dose of HCl and Na₂EDTA were added successively through peristaltic pump.

2.3. Leachate treatment

The leachate from washing processes were collected to analyze for Cd and Pb concentrations and then were treated by using different precipitants. A portion leachate of HCl was tested to adjust its pH to 11 and 12 with 10 mol/l calcium hydroxide and the suspended liquid was filtered respectively, the filtrate was analyzed for Cd and Pb. The pH level of the filtrate was adjusted to 7 to discharge. The leachate of Na₂EDTA was tested to adjust its pH to 12 with 10mol/L calcium hydroxide. Cd and Pb were precipitated for 40min with Na₂S•9H₂O in a series of flasks containing 50ml of leachate that were dosed over a range of ratio of Na₂S•9H₂O to total Cd and Pb from 10 /1 to 20/1. 0.1%~0.3% PAM was added to flocculate Cd and Pb precipitants and the suspended liquid was filtered, the filtrate was analyzed for Cd and Pb. The pH level of the filtrate was adjusted to 7 to discharge.

3. Results and discussion

3.1. Effects of single washing agent on heavy metal removal

Fig.1 shows the removal efficiency of DTPA-extractable Cd and Pb in soil after washing with HCl and Na₂EDTA. The removal rate of Cd varied from 0~85.76% for HCl and 24.96~89.98% for Na₂EDTA and that of Pb were range from 0~90.92% and 0~52.09%, respectively. Both HCl and Na₂EDTA exhibited

high removal efficiencies for DTPA-extractable Cd, while only Na₂EDTA and high concentrations of HCl were found to be effective on removing DTPA-extractable Pb. The results illustrate that Cd was easier to remove from soil than Pb when HCl and Na₂EDTA was used as washing agents within the tested concentrations. The result was in agreement with the result of Lafuente who reported that Pb was the most difficult to liberate while Cd was the most easily liberated [16]. This phenomenon could be explained by that Pb has great affinity for the surface of sorbates than Cd [3, 17]. Lead in the soil matrices was therefore not very soluble except at low pH (<3) when washing with HCl. Na₂EDTA was much more effective at removing Pb than HCl. This may attribute to the strong chelating ability of Na₂EDTA.

Fig.1.a shows that when the concentration of HCl increased from 0.01 to 0.8M the removal efficiency of Cd increased from 0~85.76% and the removal efficiency of Pb increased from 0 ~90.46%, respectively. A significantly increase in Cd removal occurred at HCl concentration range from 0.01M to 0.05M. This may be caused by the decrease of soil pH. Soil pH has been proved as one of the most significant factors that affect leaching processes through a soil profile [18, 19]. The mobility of Cd increased with the pH value of soil decreased from neutral to acidity. In fact, the amphoteric properties of some functional groups like the hydroxyl groups on the sides and edges of the clay minerals determine the charges on the inner and outer surfaces of the swellable three-layer minerals such as illites and smectites. These groups can be charged positively or negatively according to the pH of the surrounding solution [19]. Hydroxyl groups tend to absorb protons in acidic pH. As a result, the concentration of effective anion in soil surface decreased and the ability of adsorbing heavy metals was weakened. Low concentration of HCl was proved to be ineffective at removing Pb from the soil while a high concentration was proved to be effective. Kuo reported that the concentration of HCl used for soil washing should be >0.1M [20].

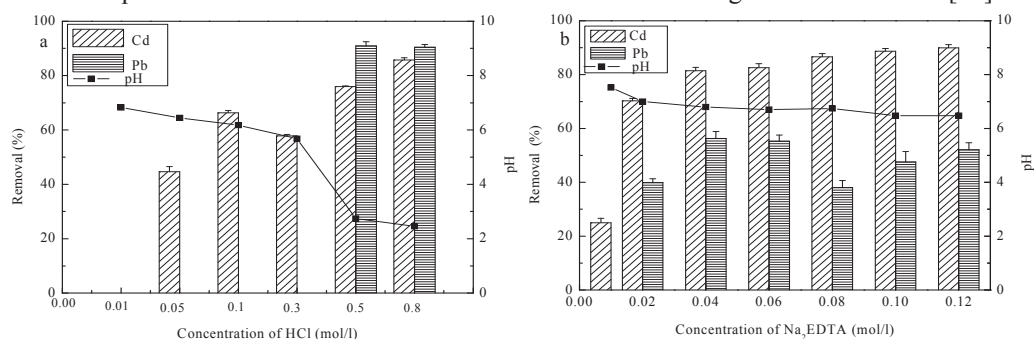


Fig.1. (a, b) Effect of concentration on removal of DTPA-extractable cadmium and lead from the contaminated soil using HCl and Na₂EDTA and the various of soil pH

Previous studies have shown that Na₂EDTA was effective for removing Cd and Pb from contaminated soils due to its high stability constants with heavy metals, although the extraction efficiency depends on many factors, such as the dose of Na₂EDTA, pH and soil matrix [21]. The removal efficiency of Cd by Na₂EDTA increased with the increasing Na₂EDTA concentration. The removal percentage was in the range of 24.98%~89.98% (Fig.1.b). Abumaizar reported that Na₂EDTA can form strong and preferential complexes with Pb relative to Cd [22]. The percentage of washed-out Pb from contaminated soil had a declined tendency when the Na₂EDTA concentration vary from 0.04~0.12M. This phenomenon could be explained by that the presence of large concentrations of ions without participation in chelation process (such as the large quantity of sodium ions present in the Na₂EDTA solutions) can lower the stability of metal–chelant complexes. Papassiopi [23] have reported that Na₂EDTA concentration has no effect on the removal rate of lead from contaminated soils while Lo [24] consider that the varying of

Na₂EDTA concentration obviously affected Pb removal from contaminated soils.

In order to investigate whether the dose of washing agents per kilogram of soil can be reduced, a series of leaching tests were conducted. Taking cost-effectiveness and environmental impacts into consideration, 0.1M HCl and 0.06M Na₂EDTA were selected to investigate the optimum dose and the results presented in fig.2.

Fig.2.a indicated that 0.1M HCl was efficiency for removing Cd and with the increasing of the dose the removal efficiency was increased from 12.41~64.30%. As expected, varying the dose of 0.1M HCl was ineffective for removing Pb.

It was obvious that removal efficiency increased for both Cd and Pb when the dose of Na₂EDTA/soil increases from 2:1~6:1 and the removal rate for Cd and Pb varied from 49.57~78.67% and 0~45.39%, respectively. But no further increase was observed at the range of 6:1 to 10:1. This is in accordance with the result reported previously by Fonseca [25]. It was assumed that Na₂EDTA is not selective for the contaminants. The tested contaminated calcareous soil was also included a great quantity of other metals such as Cu, Zn Ca. It was proved that Ca can bind more than 89% of the available Na₂EDTA, while other metals utilize only small part of the chelate ions [21, 23].

3.2. Effects of sequential washing with HCl and Na₂EDTA

Although Na₂EDTA was proved to be effective for both Cd and Pb, the removal efficiency was not satisfied. Na₂EDTA is a costly extractants thus the decrease in the dose of Na₂EDTA is crucial. In order to effectively and economically remove both Cd and Pb from the contaminated soil, a combination of washing agents was selected to sequentially remove both metals. Low pH condition favors the mobility of heavy metal and then complex with organic agents. Thus, the 0.1M HCl followed by 0.06M Na₂EDTA was conducted based on their optimal concentration.

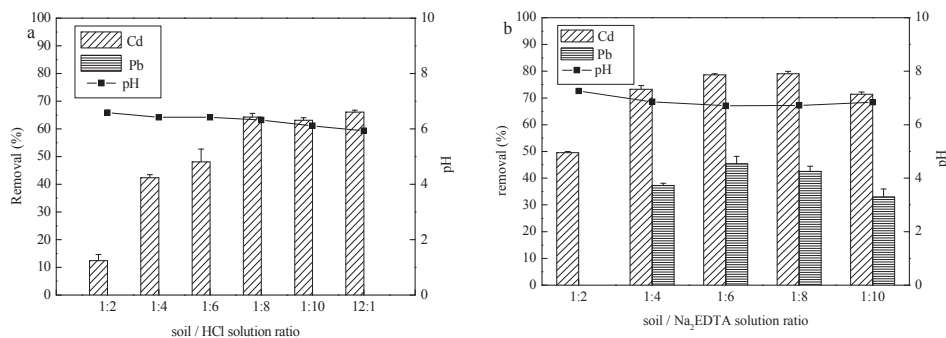


Fig.2. (a, b) Effect of the dose of HCl and Na₂EDTA on removal of DTPA-extractable cadmium and lead from the contaminated soil and the various of soil pH

Table 1 shows the removal efficiency of Cd and Pb using the combinations of HCl and Na₂EDTA. The sequential washing achieved 87.75% and 73.23% removal efficiency for DTPA-extractable Cd and Pb respectively. Obviously, some additional Cd and Pb removal was observed comparing with single column extraction with HCl and Na₂EDTA. This additional Cd and Pb removal is attributed to the presence of residual acids from the first-step extraction process.

Table 1 the contents and the removal of trace metal after treatment

Heavy metal	Fraction	0.1M HCl		0.06M Na ₂ EDTA		0.1MHCl+0.06M Na ₂ EDTA	
		Concentration (mg/kg)	Removal (%)	Concentration (mg/kg)	Removal (%)	Concentration (mg/kg)	removal (%)
Cd	Total	10.58	68.63	10.10	70.06	7.29	78.38
	DTPA-extractable	6.31	50.78	2.73	78.70	1.57	87.75
Pb	total	547.90	6.82	306.50	47.87	209.90	64.46
	DTPA-extractable	116.4	-10.46	59.26	43.76	28.21	73.23

3.3 The removal of Cd and Pb in leachate

The leachate from washing processes were collected to remove Cd and Pb and safely discharged. Chemical precipitation is the most generally applied to treat heavy metals in the wastewater [26]. Table 2 shows the results of metal separation from the leachate collected. The neutralization with lime is a prevailing method to dispose the very acidic leachate which produced during soil decontamination by a chemical leaching process using HCl because of its relative simplicity and low cost of precipitant. In the study, a satisfied result was obtained when the pH in leachate collected from HCl washing was adjusted to 11. The concentrations of Cd and Pb in leachate were decreased from 2.90 mg/l and 0.69 mg/l to 0.04 mg/l and 0.41 mg/l, respectively. In the present study, Na₂S•9H₂O was employed to separate metals from the leachate of Na₂EDTA and it was demonstrated to be effective. To improve metal separation, Ca(OH)₂ was usually applied to adjust the pH of the leachate before Na₂S•9H₂O was added. The addition of Ca(OH)₂ resulted in the precipitation of 97.1% and 98.6% of the Cd and Pb in solution. Both of the leachates are neutralize before discharge. As shown in table 2, Cd and Pb in the treated leachates met the allowable levels suggested by the Chinese Ministry of Environment [27].

Table 2 Concentration of metals in leachate collected from sequential extractions

leachate	Cd(mg/l)	Pb(mg/l)	After optimized precipitation with Na ₂ S•9H ₂ O+Ca(OH) ₂ or Ca(OH) ₂ (mg/l)	
			Cd	Pb
0.1M HCL (1g:8ml)	2.90±0.11	0.69±0.01	0.04±0.00	0.41±0.01
0.06M Na ₂ EDTA(1g:6ml)	1.04±0.08	51.31±0.71	0.03±0.00	0.70±0.04

3.4. The change of heavy metal fractions

Metals in soils can exert different reactivities toward acidification and chelation. In the original soil, the relative abundance of the different fractions of Cd was in the order of Fe/Mn oxide-bonded > carbonate-bonded > residual > exchangeable > organic-bonded > water soluble. As shown in fig.3.a Cd was almost equally distributed between the carbonate, exchangeable and residual, while the water soluble Cd content was below detection limits. The lower organic Cd fraction concentration corresponds to the low organic matter content since organic matter content in soil was 2.16%. The fractionation of Cd and Pb in the washed soils was also determined. For all the treatment, the content of Cd in exchangeable, Fe/Mn oxide-bonded, organic- bonded were decreased, while Cd in Fe/Mn oxide-bonded fractions that formerly presented in high amount in soil was removed by 71%. More than 42% carbonate-bonded fraction was removed except the treatment of washing with 0.1M HCl. The organic-bonded fraction,

even though presented in a small amount, was removed from soil entirely. For water-soluble and residual fractions, the amount of Cd in the treated soil were even higher than that in the original soil. This may be due to the changing of Cd from other fraction into this fraction. The most possibility fractions that can be changed were Fe/Mn oxide-bonded fraction and exchangeable fraction.

Fig.3.b shows more than 54% of the total concentration was presented in Fe/Mn fraction, 7.3% of lead was bonded to carbonates and hence could be altered by pH change. Due to the low content of organic matter in the sample, only 5.5% of lead is found in this fraction. The proportion of water soluble and exchangeable lead did not exceed 1%. Finally, up to 32% of lead is presented in the residual fraction, which might be difficult to remove. Most of the Pb was removed from the fractions bonded to carbonates and Fe/Mn oxides especially the treatment of washing with 0.1M HCl combining 0.06M Na₂EDTA. The amounts of Pb in water soluble, exchangeable and residual fractions in the treated soils were even higher than that in the original soil. The percentage of Pb in organic fraction was increased when soil was washed with 0.1M HCl and 0.06M Na₂EDTA. Whereas it was decreased when washed with 0.1M HCl combined 0.06M Na₂EDTA.

Fig.3. solid phase fractionation of (a) cadmium, (b) lead as affected by the following treatment: (1) native soil, (2) washing with 0.1M HCl (1g: 8ml), (3) washing with 0.06M Na₂EDTA (1g:6ml), (4) washing with 0.1M HCl (1g:8ml) by followed 0.06M Na₂EDTA (1g:6ml)

4. Conclusion

In the present work, the removal efficiencies of DTPA-extractable Cd and Pb in the calcareous soil by using HCl and Na₂EDTA at different dosages were evaluated. The concentration of the washing solution and soil to solution ratio were studied in order to identify the optimum operating parameters. Both HCl and Na₂EDTA exhibited good removal efficiencies for DTPA-extractable Cd in column washing experiment, while only Na₂EDTA and high concentrations of HCl were found to be effective in extracting DTPA-extractable Pb from the contaminated soil tested in the study. But high concentrations of HCl would result in adverse effects on the soil and increasing the dosage of Na₂EDTA did not produce a proportional gain in the DTPA-extractable Cd and Pb removing from soils. Sequential extraction indicated that the elements fraction that is weakly bonded to soil particles is insignificant. That is well explained the disproportional gain with the increasing concentration of washing solution.

Our study also clearly proved that sequential washing using HCl and Na₂EDTA is likely to be more efficient remediation strategy for the soil than any single HCl or Na₂EDTA treatment. This is important, since cost-effectiveness and relatively low environmental impacts are required in the on-site remediation.

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