Heavy metal contaminants removal by soil washing

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Abstract

The feasibility of soil washing for decontaminating a silty sand spiked with cadmium, chromium, lead, and zinc was evaluated in laboratory-scale batch and column experiments. Soil samples were subjected to chelant extraction using a solution of disodium salt of ethylenediaminetetraacetic acid (Na_2EDTA), sodium metabisulfite ($Na_2S_2O_5$) solution (an inexpensive reducing reagent), and a solution containing a mixture of the two reagents. Batch and column washing of the contaminated soil with deionized water (DI water) revealed that $\approx 70\%$ of the cadmium in the sample is weakly bound and readily mobilized in aqueous solution at neutral pH, followed by $\approx 25\%$–30% of zinc, $\approx 20\%$–25% chromium, and only $\approx 10\%$ of lead. Of the washing reagents tested, Na_2EDTA solutions were generally more effective than $Na_2S_2O_5$ for removing heavy metals from the soil samples. Na_2EDTA preferentially extracted lead over zinc and cadmium but exhibited little impact on chromium removal. Cadmium and, especially zinc, removal by a 0.01-M Na_2EDTA solution were enhanced considerably by inclusion of 0.1 M $Na_2S_2O_5$, suggesting that a mixture of the two reagents may provide an economically optimum solution for certain contaminated soils. © 1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

Toxic heavy metal contamination of soil and subsequent potential fouling of groundwater is a common problem at many hazardous waste sites. These include, for example, industrial or commercial sites on which production residues were improperly stored or buried. In other instances, the contamination may have occurred by leaks or mishandling

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in transportation of different hazardous materials. In addition to contributing to pollution of groundwaters, soil contamination often results in restricted utilization of the site and, in some cases, a complete prohibition on cultivation or other potential use of the area.

Major soil contaminant categories commonly reported at National Priority List (NPL) sites are volatile organics, hydrophilic and hydrophobic organics, heavy metals, and radioactive material. The most frequently found heavy metal contaminants include lead, mercury, arsenic, chromium, cadmium and copper [1]. The EPA estimates that over 20 million cubic yards of soil at current NPL sites are contaminated with metals [2].

There are four possible management options for contaminated soils:
· leave the contamination as is and restrict the use of the site in question;
· immobilize the contaminants at the site and enforce continuous monitoring, with the intent of restricting contaminant migration to other locations;
· remove the contaminated soil and store it in a special disposal site; and,
· decontaminate the soil on-or off-site.

Decontamination can be an economically competitive alternative, particularly in instances where site reutilization is deemed important. There are a variety of decontamination methodologies involving physical, chemical, thermal, and/or biological processes for soil treatment. Soil decontamination is usually performed by excavating the contaminated zone, above ground treatment by isolation and removal or destruction of the pollutants, and redepositing the cleaned soil. Decontamination can also be accomplished through in situ soil washing in which a washing solution is applied to the unexcavated contaminated zone by flooding or sprinkling in order to extract pollutants from the soil. The migration of contaminants into the groundwater must be prevented by using proper control measures specific to each location. In situ washing is a promising technology and one of the alternative treatment methods to reduce the quantity and the impact of soil pollutants. The effectiveness of in situ washing is limited by the permeability of the soil in its undisturbed state. Soils with permeability of less than 10^{-4} cm/s are considered unsuitable for in situ washing, in which cases excavation of the contaminated soil followed by on-site clean-up by washing can provide a viable alternative.

Several classes of chemical reagents have been investigated as to their effectiveness in extracting heavy metals from soils. A sampling of recent studies is summarized in Table 1 including the contaminants and washing solutions evaluated and the mode of application (batch vs. soil column). Most studies of this type have focused on comparing different chelating and extraction reagents in batch-mode tests. The results reflect a wide range of metal removal efficiencies depending on the soil type and the composition of the washing solution. Removal of many metals by reaction with chelating reagents is quite efficient, but the high cost of chelating reagents such as EDTA has precluded their use in remediation of metal contaminated sites [3]. Furthermore, permeability has been reported to be considerably reduced when EDTA is contacted with certain types of soil, indicating that in situ washing with EDTA may require extended clean-up time [4]. Acid washing will alter soil properties due to mineral dissolution and result in an increase in contaminant mobility [5]. The above mentioned approaches for soil washing were developed on a case by case basis, reflecting the absence of standardized clean-up criteria for contaminated soil.

Table 1
Soil washing investigations for heavy metals

Soil	Washing method	Agents	Metal	Concentration (mg/kg)	Removal (%)	Reference
Artificially contaminated	Column	$Na_2S_2O_5$	Pb	204	61	Abumaizar and Khan [4]
			Zn	79	94	
Artificially contaminated	Column	HCl	Pb	500–600	85	Reed et al. [5]
		EDTA			100	
		$CaCl_2$			78	
Contaminated soil	Batch	EDTA, NTA and citric acid plus reducing reagents: sodium borohydride, $Na_2S_2O_5$ and thiourea dioxide	Pb	21 560	99	Peters et al. [8]
			Cu	1241	99	
			Zn	3729	97	
Artificially contaminated	Batch	HCl	Pb	10–1000	65–100	Cline and Reed [19]
		EDTA			60–100	
		CH_3COOH				
		$CaCl_2$			0–85	
Artificially contaminated	Column	NaOCl Diethylenetriamine pentaacetic acid (ADTPA) Tetrasodium EDTA	Zn	4450	38–81	Davis and Singh [20]
Contaminated soil	Batch	S-carboxymethyl-cysteine (SCMC)	Cd	2	80–100	Chen et al. [12]
		N-2-acetamidiomindiacetic acid (ADA)	Cu	5	(for all metals)	
		Pyridine-2,6-dicarboxylic acid (PDA)	Pb	100		
			Ni	6		
			Zn	290		
Bank sediment	Batch	Na_2EDTA	Cu	970	55	Jianzhen and Klarup [21]
			Zn	2500	32	
Contaminated soil	Batch	EDTA	Pb	350	95	Allen and Chen [3]
Contaminated soil	Batch	HCl	Pb	1000	90	Cline et al. [22]
		EDTA				
Contaminated soil	Batch	EDTA	Pb	1509–51 100	85–97	Evangelista and Zownir [17]

The purpose of this study is to investigate the utility of sodium metabisulfite ($Na_2S_2O_5$) as an alternative for decontamination of soils containing multiple heavy metals to counter the disadvantages of employing chelating reagents alone. $Na_2S_2O_5$ is a reducing reagent that has received its most extensive application in the treatment of inorganic wastes such as heavy metals, sulfides and cyanides. It is commonly employed in the reduction of chromium (VI) to the less hazardous chromium (III). The use of $Na_2S_2O_5$ as a reducing reagent provides a versatile and relatively inexpensive alternative to more costly chelating reagents [6,7]. Several reducing reagents including $Na_2S_2O_5$, were evaluated by Peters et al. [8] for their effectiveness in solubilizing heavy metal contaminants from a soil matrix as a pretreatment step prior to chelation. Batch tests indicated that lead and copper removal by chelant extraction with EDTA and citric acid were only nominally affected by the pretreatment step. Zinc removal using EDTA was slightly increased by each reducing reagent studied. However, reducing reagents significantly improved citric acid extraction of zinc, with the best overall pretreatment enhancement reported for $Na_2S_2O_5$. A solution of disodium salt of ethylenediaminetetraacetic acid (Na_2EDTA) an odorless, crystalline aminopolycarboxylic acid, is also tested in this study for comparison.

2. Materials and methods

2.1. Initial soil characterization

The test soil was obtained from the excavation material of a construction site in University Park, TX. The soil was passed through a No. 4 sieve (4.75 mm). Rocks and other large material not passing through the sieve were removed. The soil was then thoroughly mixed to ensure uniformity and stored in a plastic barrel at room temperature for subsequent use in experiments. Following evaporation at 103°C in a ventilated oven, the volatile organic content of the soil sample was determined from the mass differential before and after heating at 550°C in a muffle furnace according to Standard Method 2540-G [9]. The specific surface area was obtained by three point BET N_2 adsorption using a Quantasorb surface analyzer, while total pore volume (PV) was determined by N_2 adsorption using an autosorb Gas Adsorption System (Quantachrome). Sieve analysis, specific gravity test and classification of the soil was performed according to the procedures described by Bowles [10]. Soil properties are presented in Table 2.

2.2. Contamination procedure

About 1 kg of oven dry soil was thoroughly mixed with 1 l of deionized water (DI water) containing dissolved salts of cadmium nitrate, $Cd(NO_3)_2 \cdot 4H_2O$, potassium dichromate, $K_2Cr_2O_7$, lead nitrate, $Pb(NO_3)_2$ and zinc nitrate, $Zn(NO_3)_2 \cdot 6H_2O$. The slurry was allowed to age at room temperature for a period of about six months with frequent thorough mixing, at the end of which the mixture was oven dried to a constant mass. To determine the heavy metal content of the original soil, three soil samples were digested for total heavy metal concentration using EPA Method 3050 [11]; and to

Table 2
Characteristics of soil used in study

Property	Value
Coarse sand (ASTM classification)	3.4%
Medium-fine sand	67.7
Silt clay	28.9
Organic matter	1.6%
Specific gravity	2.65
Plasticity index	2.5%
Soil pH	7.9 ± 0.3
ASTM soil classification	Clayey sand
Total PV	2.4×10^{-2} cm^3/g
Surface area	17.6 m^2/g
Metal concentrations of the contaminated soil	
Cd	603 ± 53 mg/kg
Cr	1231 ± 110 mg/kg
Pb	742 ± 61 mg/kg
Zn	624 ± 22 mg/kg
Background concentrations of the original soil	
Cd	4 ± 2 mg/kg
Cr	13 ± 2 mg/kg
Pb	17 ± 1 mg/kg
Zn	32 ± 3 mg/kg

determine concentrations of the contaminated soil, nine soil samples were digested following the same procedure, the results of which are presented in Table 2.

2.3. Desorption batch tests

Batch agitation studies were performed to determine appropriate ranges of concentration and dosage of the washing solutions to extract the heavy metal pollutants from soil. Two washing reagents were selected for the decontamination studies; namely, $Na_2S_2O_5$ and disodium salt of Na_2EDTA. DI water washes were performed to provide a baseline for the removal obtained by chemical washing. The tests were accomplished by placing certain amounts of soil in 150 ml plastic bottles followed by addition of varying volumes of the washing solution. The samples were then placed on a shaker table operated at 175 rpm at room temperature. A 2-h reaction time was deemed sufficient based upon batch rate desorption tests conducted over a 48-h period. After mixing, the samples were allowed to settle for about 15 min and then filtered through a 0.45-μm membrane 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 metal analysis. Precision was established by preparing replicate (total of three bottles) for each test. It was assumed that the metal concentration of the filtrate represents that released from the contaminated soil. Removal efficiencies were determined by dividing the heavy metal release quantities by the initial

quantity in the soil. All heavy metal analyses were performed using a Horizon 5310 inductively coupled plasma (ICP) spectrometer. ICP calibration standards were prepared from stock solutions according to Method 6010 [11]. Standard concentrations bracketed the anticipated concentration range of the samples and included a calibration blank (metal concentration equal to 0). Accuracy of the calibration curve was confirmed by a check standard from an independent source (VHG LABS brand, ICP calibration solution, 5% HNO_3 matrix).

2.4. Column testing

Soil column studies were conducted to more closely simulate in situ clean-up conditions using a plexiglass column with a 1.9-cm internal diameter and a total length of 5.8 cm. Contaminated soil was packed in three layers to a total height of 3.0 cm in the middle of the column. The top and bottom portions of the column were filled with clean R-50 glass beads in order to enhance uniform flow distribution of the washing solution into and out of the column. In all columns, the dry weight of soil was about 9.25 g, which produced a bulk density of 1.1 g/cm^3 (empty bed volume = 8.5 cm^3, void volume $\approx$ 4.85 cm^3 or a void fraction of 0.57). Approximately 300 PVs were passed through each column with the average flow rate maintained at about 1.2 ± 0.1 ml/min.

The washing solutions were introduced from the bottom of the column to saturate the soil using a B-100-S Eldex piston pump. The configuration of the soil column apparatus is shown in Fig. 1. Column effluent was collected as continuous composite samples (40 ml per sample) using an Eldex Universal fraction collector. The samples were acidified
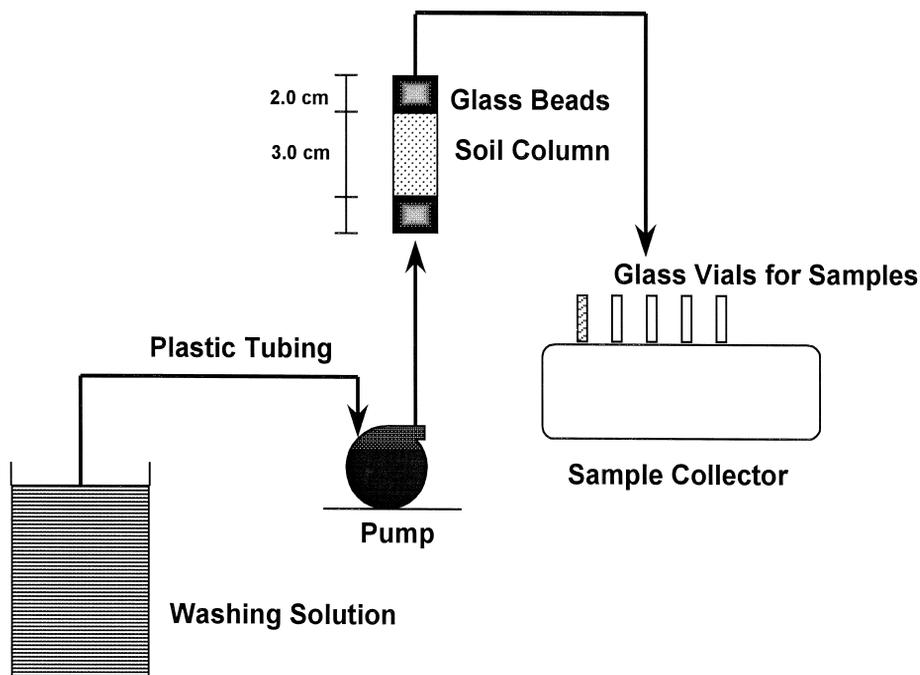
Fig. 1. Diagram of soil column and apparatus used for extraction of heavy metals.

and analyzed as described previously after the pH was measured and recorded. Precision in this case was established by replicate (total of 3) integrations when performing ICP concentration readings of each sample. Each data point represents the average of the three readings.

3. Results and discussion

When metal-containing compounds are dissolved in water, the metallic component exists normally as mobile ions in solution. Unless they are complexed by inorganic or organic ligands, metal ions such as those of interest in this study will be present in aqueous solution only at very low concentrations in the pH range of natural surface and subsurface waters. When the concentrations of these metals exceed the solubility of their corresponding hydroxide or carbonate phase at a given pH value, metal precipitates will intermingle and become an integral part of the soil matrix [12]. Many soils contain mineral and humic constituents that carry hydroxyl and carboxylic surface functional groups. The acid–base characteristics of these functional groups contribute to the formation of a characteristic surface charge that plays an important role in metal retention. Thus, in addition to physical entrapment of metal hydroxide or carbonate solids, the speciation of metals in soil is complex and may include one or more of the following fractions: ion exchangeable, adsorbed, precipitated, organically bound, or trapped in an insoluble form within the soil matrix [12,13].

Exposure of a soil–metal system to a reducing reagent, such as $Na_2S_2O_5$, can provide conditions that maximize the solubilities of the ion exchangeable fraction of the metal by reduction to a lower oxidation state or by weakening the bond of metal–soil attachment, thereby rendering the sorbate more likely to be extracted by the washing solution. Chelation, on the other hand, follows an alternate mechanism. A chelating reagent such as Na_2EDTA is capable of a six-fold coordination with metals (i.e., hexadentate ligand) and, like many organic chelants, behaves as a weak acid in aqueous solution. If sorbed metals are sufficiently accessible to aqueous-phase chelant, EDTA can form metal complexes that are thermodynamically ''stronger'' than the metal–soil interactions, with the complexes being water soluble. This allows the metal–chelant complex to be flushed away with the washing solution. The action of metal and ligand may be expressed by the following equation and simplified mass action expression:

$$Me + L \Leftrightarrow MeL, \quad K = [MeL]/[Me][L] \tag{1}$$

where Me represents a metal cation, L represents a ligand anion, and K is the formation constant [4,14]. In order to be effective at extracting metals from soil and concomitantly forming soluble complexes, a ligand must overcome competing processes including (i) metal precipitation as hydrous oxide and/or carbonate precipitates, and (ii) surface complexation and precipitation on soil particles [12].

3.1. Batch washing tests

Removal efficiencies using DI water, $Na_2S_2O_5$ solution, Na_2EDTA solution, and a mixture of $Na_2S_2O_5$ and Na_2EDTA are summarized in Table 3. Three different sets of data representing three levels of soil to washing solution ratios (by weight) are listed in

Table 3
Soil washing efficiencies for batch tests

Washing solution	Mass of soil (g)	Soil:solution (mass)	Solution pH	Filtrate pH	Removal efficiency (%)			
					Pb	Zn	Cd	Cr
DI water	2.00	1:5	6.3 ± 0.4	7.6 ± 0.1	17.3 ± 0.8	30.9 ± 5.1	70.1 ± 1.0	18.3 ± 1.1
0.1 M SM[a]	2.00	1:5	3.9 ± 0.1	5.1 ± 0.7	24.9 ± 4.1	54.5 ± 3.1	84.2 ± 4.2	10.3 ± 0.5
0.1 M EDTA	2.00	1:5	5.1 ± 0.0	8.2 ± 0.2	67.8 ± 4.6	49.5 ± 3.1	89.3 ± 7.9	26.9 ± 4.8
0.01 M EDTA	2.00	1:5	5.2 ± 0.2	8.2 ± 0.0	47.6 ± 2.9	42.9 ± 3.1	81.9 ± 7.4	25.4 ± 2.3
0.1 M SM + 0.01 M EDTA	2.00	1:5	4.2 ± 0.3	7.4 ± 0.2	60.3 ± 1.4	70.1 ± 3.1	101.9 ± 4.9	15.9 ± 1.0
DI water	2.00	1:12.5	6.3 ± 0.4	8.0 ± 0.0	14.2 ± 1.4	29.4 ± 5.1	65.3 ± 4.9	16.7 ± 2.1
0.1 M SM	2.00	1:12.5	3.9 ± 0.1	3.5 ± 0.1	23.4 ± 3.3	57.3 ± 6.5	78.2 ± 9.2	25.4 ± 5.8
0.1 M EDTA	2.00	1:12.5	5.1 ± 0.0	4.6 ± 0.2	104.6 ± 7.4	81.8 ± 4.4	112.1 ± 4.4	40.7 ± 3.8
0.01 M EDTA	2.00	1:12.5	5.2 ± 0.2	7.6 ± 0.2	54.4 ± 1.4	44.9 ± 5.7	83.0 ± 3.7	23.8 ± 3.8
0.1 M SM + 0.01 M EDTA	2.00	1:12.5	4.2 ± 0.3	4.1 ± 0.1	56.1 ± 4.7	71.0 ± 8.6	92.3 ± 5.1	25.2 ± 2.5
DI water	2.00	1:25	6.3 ± 0.4	7.5 ± 0.8	15.2 ± 0.8	30.4 ± 2.4	77.2 ± 7.9	23.3 ± 6.2
0.1 M SM	2.00	1:25	3.9 ± 0.1	4.5 ± 0.1	28.8 ± 5.4	61.1 ± 6.3	84.6 ± 11.5	26.0 ± 4.6
0.1 M EDTA	2.00	1:25	5.1 ± 0.0	4.9 ± 0.1	94.1 ± 2.5	75.9 ± 1.2	96.5 ± 1.0	35.1 ± 1.4
0.01 M EDTA	2.00	1:25	5.2 ± 0.2	7.4 ± 0.1	41.8 ± 4.2	39.6 ± 1.9	79.8 ± 8.1	19.9 ± 4.1

[a] Sodium metabisulfite.

the table. The significance of washing with DI water is to provide information about the fraction of the metal that is weakly bound to the soil particles and readily available for mobilization due to the lack of applying the normal drying and wetting and heating processes which actually incorporate the metal. As evident in the three data sets, the fraction of each metal that is weakly bound is virtually independent of the soil to DI water ratio. Cadmium is the most weakly bound metal for this case, with approximately 70% of its mass from the artificial contamination removed by DI water. Lead appears to be the most strongly bound to the soil matrix of the four metals in this study. The remaining fractions of the metals are considered to be strongly bound and immobilized within the soil matrix under natural-water conditions.

There is little in the existing literature concerning the extraction kinetics of heavy metals from contaminated soils. In an attempt to determine whether there is an optimum reaction time for the release of heavy metal from soil matrix, the removal efficiencies as a function of time for 0.1 M $Na_2S_2O_5$ and 0.1 M Na_2EDTA solutions for 2.0 g soil samples and a soil to solution ratio of 1:25 are presented in Fig. 2. The data revealed a rapid initial release rate of all metals into the washing solution. This is consistent with the release rate using DI water alone, suggesting the dissolution of weakly bound metals sorbed at easily coordinated sites on the outer surfaces of soil grains or the fast dissolution of fine precipitates [15,16]. A slow ongoing release of metal, as in the case of zinc, may be due to reaction with sorbed or precipitated metal species more strongly bound to interior surface sites (Fig. 2a and b), and/or extraction by excess chelating reagent after preferential complexation of other cations (e.g. lead) nears completion (Fig. 2b). A rapid uptake of lead from contaminated soil by Na_2EDTA was observed by Evangelista and Zownir [17]. They reported an optimum soil–chelant contact time of 15 min. Based on this study and the results shown in Fig. 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.

The 0.1-M $Na_2S_2O_5$ solution extraction results listed in Table 3 show only very slight improvement in chromium removal over flushing with DI water and moderate enhancement in lead and cadmium extraction (a range of 10%–15%). Zinc removal, on the other hand, was doubled to achieve more than 61% recovery using $Na_2S_2O_5$ solution. The best results for $Na_2S_2O_5$ were obtained using a 1:25 soil to solution ratio.

Na_2EDTA (0.1 M concentration) extraction test results indicate higher removal efficiencies than those of $Na_2S_2O_5$ in most cases, with complete removal of cadmium and lead, and about 25% more removal of zinc for a soil to solution ratio of 1:12.5. There was little improvement in chromium removal above the DI water wash. The highest removal percentage of chromium was achieved using 1:12.5 soil to 0.1 M Na_2EDTA solution. For a 10-fold increase in Na_2EDTA solution concentration (0.01–0.1 M), the increase in removal efficiency over that achieved by DI water washing alone is about 60% at 1:5 soil–solution ratio, and increases to two- to three-fold for a ratio of 1:12.5. For the 1:25 soil–solution ratio, the increase in removal efficiency for 0.1 vs. 0.01 M Na_2EDTA is about three-fold for lead, and five- to six-fold for zinc and cadmium.

To study the effect of combining the two mechanisms of reduction and chelation, a set of batch experiments was conducted with a washing solution containing a mixture of
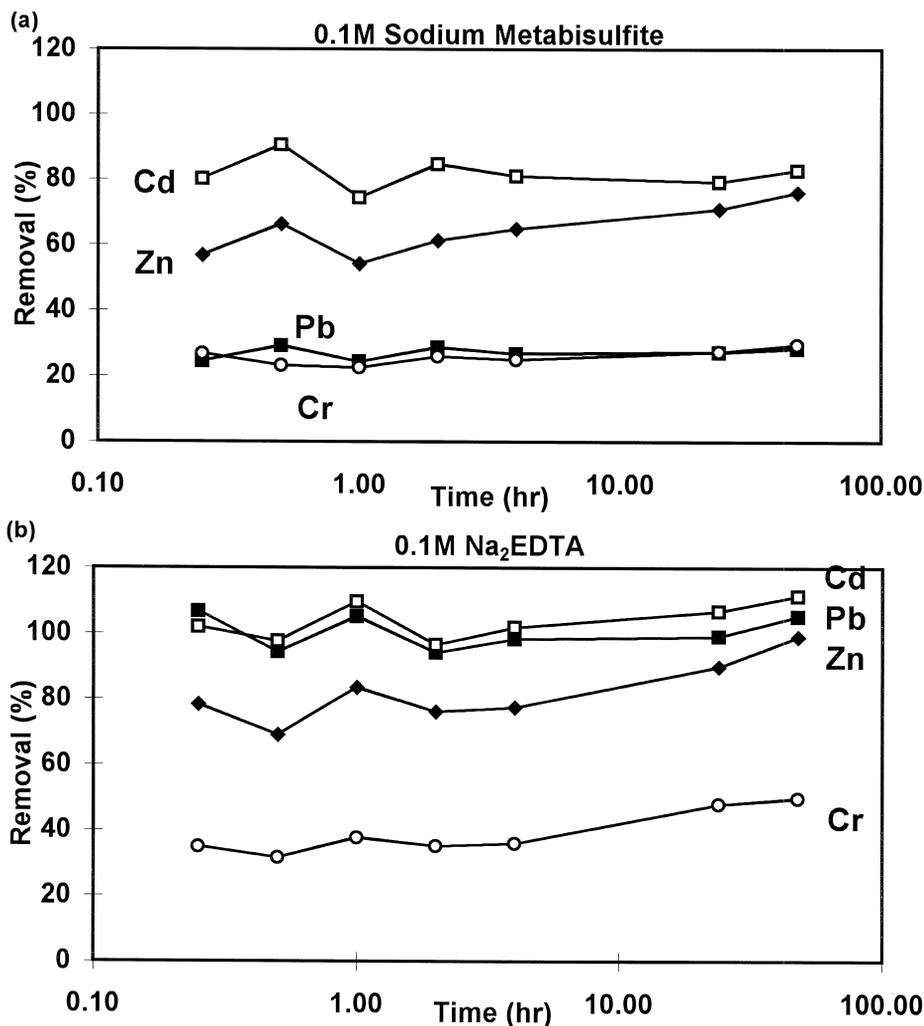
(a)

(b)

Fig. 2. Removal efficiency vs. reaction time for 2 g soil samples using (a) 0.1 M SM and (b) 0.1 M Na_2EDTA.

0.01 M Na_2EDTA and 0.1 M $Na_2S_2O_5$, with the results included in Table 3. For 1:5 and 1:12.5 soil–solution ratios, removal efficiencies of lead, zinc, and cadmium were improved, in some instances as much as two-fold, over those achieved by either solution alone. The data indicate in particular, that zinc and cadmium removal by 0.01 M Na_2EDTA was significantly improved by the presence of 0.1 M $Na_2S_2O_5$ in solution. The improvement in the removal of cadmium and zinc may indicate that a considerable fraction of these two metals exists in an ion exchangeable form in the soil matrix and is modified by the action of $Na_2S_2O_5$. The predominant forms of lead, however, may be

adsorbed at higher energy sites and thus relatively unaffected by the reducing reagent, but preferentially complexed by Na_2EDTA. Chromium is likely in the hexavalent bichromate form ($HCrO_4^-$) under the conditions of interest and therefore not readily complexed by Na_2EDTA. Evidently, a large fraction is strongly adsorbed at high energy sites and not readily reduced to Cr(III) by $Na_2S_2O_5$ at the pH values of operation.

3.2. Soil column tests

The purpose of the column tests on the same contaminated soil was to further evaluate the performance of Na_2EDTA solution vs. a mixture of $Na_2S_2O_5$ and Na_2EDTA solution, and to determine the removal efficiencies in soil columns that simulate in situ washing or heap-leaching process. An initial run (Fig. 3) determined the cumulative removal efficiency vs. PVs for DI water washing alone. As in the batch tests, the results provide useful information concerning the fraction of the metals that could be considered readily mobile. The removal efficiencies obtained from this column are almost identical to those achieved previously in the batch experiments for DI water. The rapid initial rate of metal removal and approach to a steady state pattern are also consistent with the results of batch rate studies. Fig. 4 represents the removal efficien-
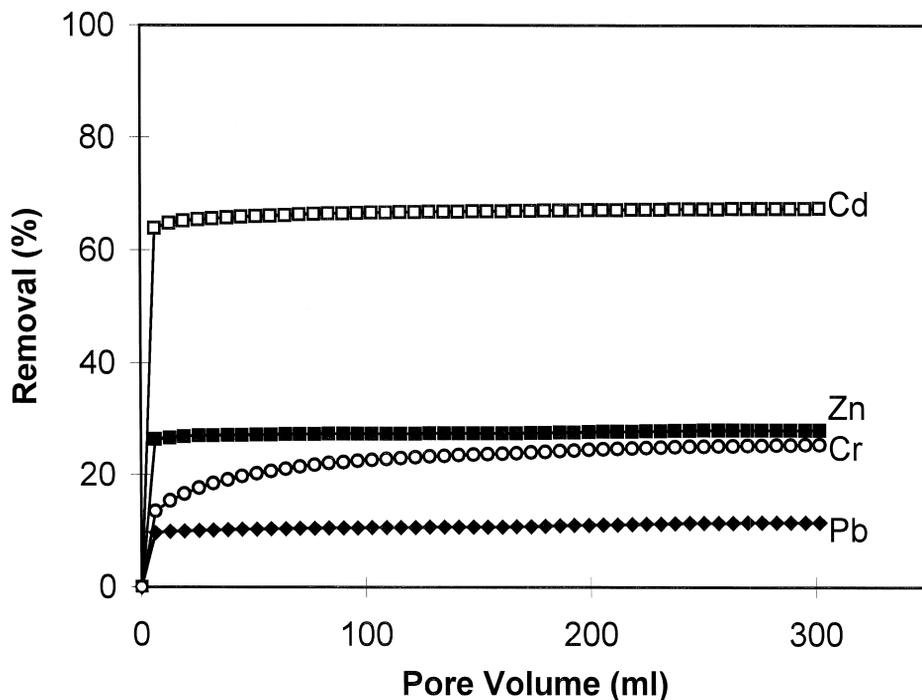

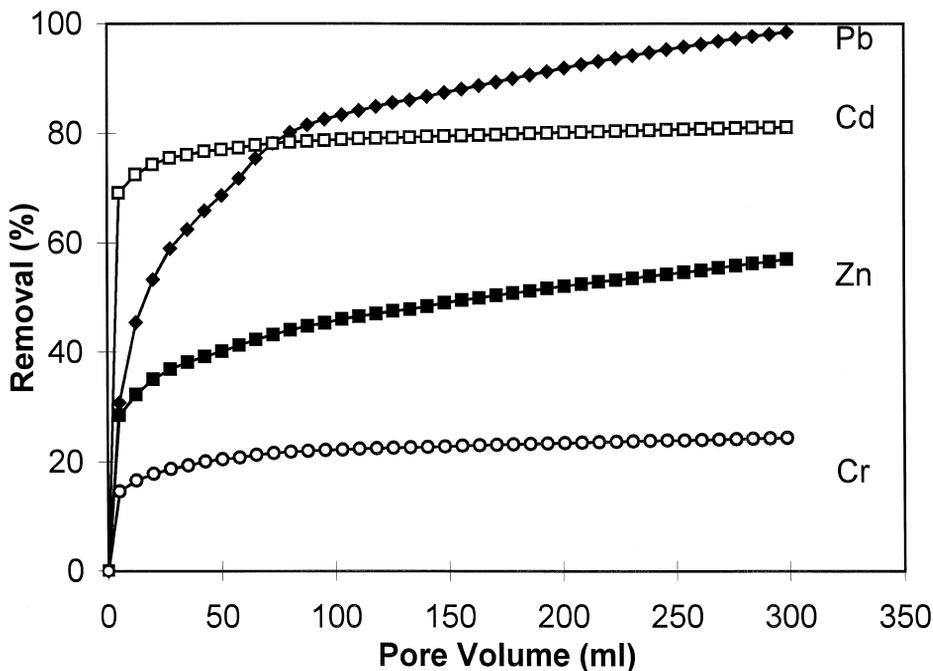Fig. 3. Cumulative removal efficiency vs. PVs of DI water.

Fig. 4. Cumulative removal efficiency vs. PVs of 0.01 M Na$_2$EDTA solution.

cies of 0.01 M Na$_2$EDTA solution. To evaluate the extent of improving the performance of Na$_2$EDTA in soil column washing, a third run was conducted using a mixture of Na$_2$S$_2$O$_5$ (0.1 M) and Na$_2$EDTA (0.01 M). The results of this run are presented in Fig. 5.

3.2.1. Cadmium

DI water washing of cadmium resulted in a total of about 67% removal after 300 PV. The cumulative removal efficiency curve also shows that about 66% removal was obtained after only 25 PV. The DI water washing removed that fraction of cadmium which is readily desorbed and present in the void space of the soil matrix. Washing with 0.01 M Na$_2$EDTA solution resulted in a moderate increase in cumulative removal to about 80% after 300 PV. Nearly all of this was achieved after just 25 PV, indicating a fast reaction rate. Using a mixture of Na$_2$S$_2$O$_5$ and Na$_2$EDTA, as shown in Fig. 5, substantially enhanced cadmium removal to nearly complete recovery after 300 PV. The mixture had little impact on the shape of the elution profile, i.e. a rapid reaction rate is observed with about 90% of the cadmium removed in the first 25 PV. Cadmium removal from soil, therefore, is likely controlled by rapid desorption/dissolution of weakly coordinated Cd–soil surface complexes and/or loosely held metal precipitate in the soil interstices. Some further removal is achieved by the chelation or reduction–chelation reactions.
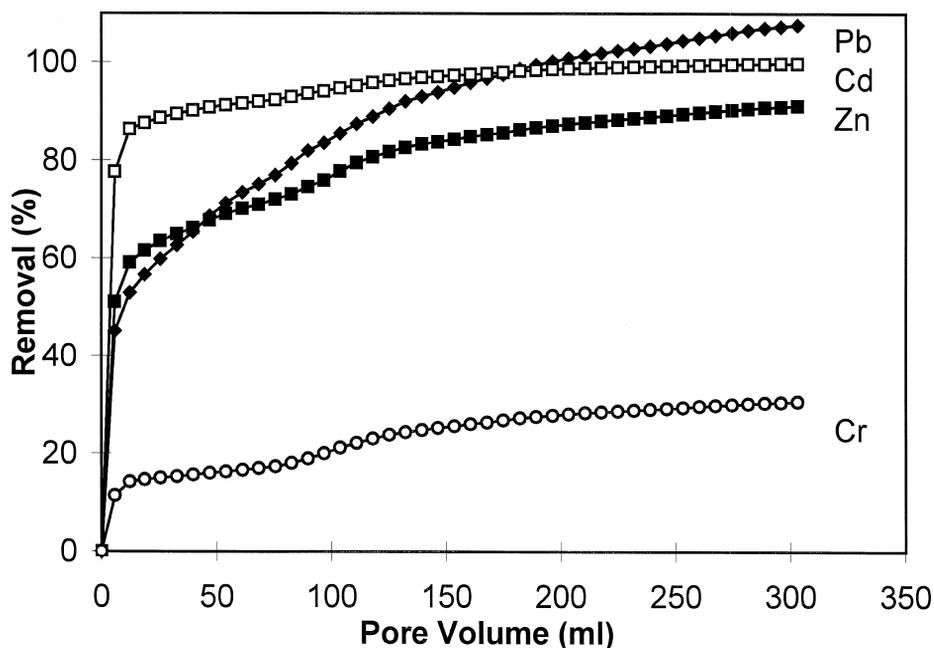
Fig. 5. Cumulative removal efficiency vs. PVs of 0.1 M $Na_2S_2O_5$ and 0.01 M Na_2EDTA solution.

3.2.2. Chromium

For the DI water and Na_2EDTA only washes (Figs. 3 and 4, respectively), the chromium removal profiles are nearly identical, approaching a steady state pattern and $\sim 20\%$–25% cumulative removal by 300 PVs. The pattern for chromium release in DI water is not as abrupt as for the other three test metals, exhibiting a more gradual approach to steady state. This could be due to small-scale, rate-limited reduction of hexavalent to trivalent chromium by soil organic matter, with subsequent formation of weak Cr(III) hydroxide complexes or fine precipitates that are washed from the soil surface [18]. While Na_2EDTA has no observable impact on chromium removal, there may be a small, though arguable, enhancement by the presence of $Na_2S_2O_5$ as evidenced by a cumulative removal of 30% that appears to be increasing still at 300 PVs (Fig. 5). The enhancement may be a result of an ongoing, slow reduction of hexavalent to trivalent chromium that is subsequently complexed by Na_2EDTA. In general, the chemistry of chromium may be expected to be different than the other metals in the study. Chromium removal is small due to its likely existence in the anionic bichromate form ($HCrO_4^-$) for the pH range of the study.

3.2.3. Lead

Lead is known to adsorb strongly to soil surfaces with binding by chemisorption and inner layer surface complexed with mineral surface oxides expected in contaminated soils [13]. This is attested by the results of Fig. 3 in which lead removal was the least for

washing with DI water. The total amount of readily mobilized lead was only 12% after 300 PV. The gradual increase in lead removal by the Na_2EDTA solution throughout the run (Fig. 4) is indicative of a slower removal kinetics compared to cadmium. Van-Benschoten et al. [13] reported rapid lead removal in the first few hours, followed by a slower, more gradual removal from contaminated soil using HCl solution. Fig. 4 suggests that Na_2EDTA forms strong and preferential complexes with lead relative to cadmium, zinc, and chromium, with essentially complete removal achieved at 300 PVs. Fig. 5 illustrates that the addition of $Na_2S_2O_5$ to the washing solution has little, if any, impact on the extent or rate of lead removal for this soil.

3.2.4. Zinc

The cumulative removal curves for zinc display trends similar to those of lead in the three columns; namely, (1) fast removal and approach to steady state for the mobile fraction in the case of DI water column (Fig. 3); and (2) a gradual increase in the cumulative removal throughout the advance of the washing process in the cases of Na_2EDTA and Na_2EDTA–$Na_2S_2O_5$ mixture solutions as shown in Figs. 4 and 5, respectively. As in the case of lead, zinc adsorption to soil surface sites is relatively strong, but the continuous contact of ''fresh'' Na_2EDTA washing solution with soil layers in a plug-flow type reactor system provide a thermodynamically favorable conditions for continuous, albeit slow, Na_2EDTA extraction of zinc molecules from the soil. As noted previously, Na_2EDTA preferentially chelates lead over zinc; however, consistent with batch studies, zinc extraction is considerably enhanced by the inclusion of $Na_2S_2O_5$. Although the enhancement is not as great as that observed in batch studies, it is evident that the presence of the reducing reagent serves to weaken the zinc–soil bond, rendering the metal more amendable to Na_2EDTA extraction. The exact nature of the reduction–chelation mechanism requires further study.

4. Summary and conclusions

Extraction of heavy metals from contaminated soil is a process that is highly controlled by the dissolution of the metal–mineral bond followed by the dispersion of the pollutant metal in the washing liquid as an emulsion, complex, or suspension. The results of batch and column washing experiments completed in this study indicate that cadmium, lead, zinc, and, to a lesser degree, chromium, can be extracted from artificially contaminated soil using a reducing reagent solution, chelating reagent solution, and a mixture of the two. Metal extraction kinetics were 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.

As evidenced in the DI water wash experiments, $\approx 70\%$ of the cadmium in the contaminated sample is weakly bound and readily mobilized in aqueous solution at neutral pH, followed by $\approx 25\%$–30% of zinc, $\approx 20\%$–25% of chromium, and only $\approx 10\%$ of lead. The fraction of the respective metals that is weakly bound is approximately the same in both experimental systems and is independent of the soil to DI water

ratio or, with the possible exception of chromium, the PVs of water passed through a soil column.

A 0.1-M $Na_2S_2O_5$ solution exhibited good removal efficiencies for cadmium and zinc in batch experiments, but did not offer significant potential for lead or chromium extraction. The soil to washing solution ratios did not appear to affect the performance of $Na_2S_2O_5$ in most cases. For both 0.1 and 0.01 M washing solutions of Na_2EDTA, however, batch studies revealed that an intermediate washing solution to soil ratio of 12.5:1 provided higher percent metal extraction than tests using either 5:1 or 25:1 ratios. Na_2EDTA extraction resulted in higher removal efficiencies than those for $Na_2S_2O_5$ at the same reagent concentration. A 0.1-M concentration of Na_2EDTA exhibited complete removal of cadmium and lead for a soil to solution ratio of 1:12.5. For the best solution to soil ratio of 12.5:1, a 10-fold increase in Na_2EDTA concentration (0.01–0.1 M) resulted in a two- to three-fold increase in metal removal over that achieved by DI water washing. A mixture of 0.1 M $Na_2S_2O_5$ and 0.01 M Na_2EDTA resulted in near complete removal of cadmium, more than 70% removal of zinc, and about 56% removal of lead in batch tests for a 1:12.5 soil to solution ratio. More importantly, the inclusion of $Na_2S_2O_5$ resulted in a two- to three-fold increase in zinc removal and substantial increase in cadmium removal above DI water wash levels than when 0.01 M Na_2EDTA is used alone.

Column experiments resulted in generally better metal removals than those obtained in batch tests. Column runs often involve higher soil to solution ratios (e.g. 25 PV is equivalent to 1:15 soil:solution ratio). Therefore, more extraction reagent is available to react with the metal contaminant. The continuous flow of the washing solution in the soil column promotes the flushing of the reaction reagent–metal complex, thereby inhibiting the opportunity for complex re-adsorption on the soil surfaces and further contributing to greater removal efficiencies in column experiments. Complete removal of lead, $\approx 80\%$ of cadmium, $\approx 55\%$ of zinc, and $\approx 25\%$ of chromium was accomplished by 300 PVs of 0.01 M Na_2EDTA solution. For the same number of PVs, cumulative zinc removal and, to a less extent, cadmium and chromium removal were enhanced when a mixture of 0.1 M $Na_2S_2O_5$ and 0.01 M Na_2EDTA was used. These results suggest that the contribution of $Na_2S_2O_5$ in the washing solution is directed toward the relatively insoluble, ion-exchangeable sorbed metal fraction in the soil matrix.

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