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Removal of heavy metals and arsenic from a co-contaminated soil by sieving combined with washing process

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ABSTRACT

Batch experiments were conducted with a heavy metals and arsenic co-contaminated soil from an abandoned mine to evaluate the feasibility of a remediation technology that combines sieving with soil washing. Leaching of the arsenic and heavy metals from the different particle size fractions was found to decrease in the order: <0.1, 2–0.1, and >2 mm. With increased contact time, the concentration of heavy metals in the leachate was significantly decreased for small particles, probably because of adsorption by the clay soil component. For the different particle sizes, the removal efficiencies for Pb and Cd were 75%–87%, and 61%–77% for Zn and Cu, although the extent of removal was decreased for As and Cr at <45%. The highest efficiency by washing for Pb, Cd, Zn, and As was from the soil particles >2 mm, although good metal removal efficiencies were also achieved in the small particle size fractions. Through SEM-EDS observations and correlation analysis, the leaching regularity of the heavy metals and arsenic was found to be closely related to Fe, Mn, and Ca contents of the soil fractions. The remediation of heavy metal-contaminated soil by sieving combined with soil washing was proven to be efficient, and practical remediation parameters were also recommended.

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Introduction

In recent decades, the intensification of human activities such as mining, smelting, electroplating, and coal combustion has resulted in a broad range of new environmental problems. Among these has been the widespread generation of enormous quantities of complex, heavy metal-contaminated soils, which constitute a major health challenge of global concern (Boularaba et al., 2006). Many heavy metal-contaminated sites have been identified (Dermont et al., 2008). In the United States, heavy metals are prevalent at 77% of the Superfund sites, 72% of the Department of Defense sites, and 55% of the

Department of Energy sites, and over 50 million m³ of heavy metal-contaminated soil exist at current National Physical Laboratory sites (USEPA, 2004). In Europe, heavy metal-contaminated soils encompass several million hectares, accounting for about 37.3% of the total contaminated soil (EEA, 2014). Similar trends are also found in China, where 16.1% of the soil has been proven to be contaminated, primarily by heavy metals, and in regions characterized by heavily polluting enterprises, industrial wastelands, industrial parks, and mining areas, the contamination levels can be as high as 30% (Ministry of Environmental Protection and the Ministry of Land, 2014).

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The mobility and bio-availability of metals are significantly affected by the particle's size and composition of the soil. Fine soil fractions can adsorb more contaminants than coarse sand because of their larger specific surface areas. In general, elemental adsorption (particularly heavy metals) increases with decreasing aggregate size (Zhang et al., 2003). Anderson et al. (1999) pointed out that contaminants were concentrated in the finer (0.05 mm or less) silt and clay fractions. In addition, metal accumulation in the clay fraction is attributed to the presence of clay, organic matter, minerals, and Fe/Mn oxides in the micro-aggregates, which act as delivery vehicles for metals (Rodriguez-Rubio et al., 2003; Quenea et al., 2009). As a result, heavy metals and arsenic in clays are difficult to remove due to their strong adsorption. Cheng et al. (2008) indicated that the concentration of Cu in clays was as high as 670.6 mg/kg, 4.77 times the concentration achieved in gravel. Gong et al. (2013) drew a similar conclusion in a soil survey in Hainan, wherein the smallest fraction (<0.053 mm) had the highest heavy metal concentrations.

Soil washing is one of the few treatment alternatives for the elimination of heavy metals from contaminated soils, which can be applied to pilot/full-scale field remediation (Dermont et al., 2008). The advantages of the technology are: high adaptability, a wide range for effective concentration of the contaminants, simple operation, strong regulation, short repair cycle period, lower cost, wide applicability, and huge practical value. Juwarkar et al. (2007) used 0.1 mol rhamnolipids to wash Cd-contaminated soil and obtained 91% Cd removal at pH = 10. Torres et al. (2012) demonstrated that Cd, Zn, and Cu could be washed with efficiencies up to 85.9%, 85.4%, and 81.5%, respectively. Maity et al. (2013) proved that soil washing can achieve high efficiencies, with the removal of 98% Pb, 95% Cu, and 56% Zn.

Physical separation technologies are primarily applied in the mining and mineral processing industries to separate particulate forms of metals. These technologies include sieving, centrifugation, flocculation, hydrocyclone classification, magnetic separation, and flotation. As these technologies concentrate contaminants into smaller volumes, they have been applied in the field of soil remediation in recent years (Dermont et al., 2010; FRTR, 2007). Lin et al. (2001) removed 84%–88% Pb from soil by jigging and density separation, and achieved the efficient removal of Pb by soil washing. Reynier et al. (2013) adopted soil washing combined with flotation to eliminate heavy metals in four soils, and removal efficiencies of 82%–93%, 30%–80%, and 79%–90% were obtained for As, Cr, and Cu, respectively.

Previous studies have shown that physical separation and soil washing can both result in the effective removal of heavy metals from soil, and even the combined technology has been attempted to remediate heavy metal-contaminated soil. Considering that soil washing is insensitive to the type of contaminant and suitable for sandy soils (Impellitteri et al., 2002), and that separation technology can reduce the volume of waste (Anderson et al., 1999), we plan to use sieving combined with soil washing to treat heavy metal-contaminated soil. The objectives of the research are to: (1) discover the occurrence, distribution characteristics, and influence of heavy metals in soil particles; (2) evaluate the removal efficiency and potential volume reduction of contaminants in the soil fractions; (3) probe the

mechanism of heavy metal adherence to soil particles during the process of soil washing.

1. Materials and methods

1.1. Soil samples and main physicochemical properties

Soil sample was collected from the 0–50 cm surface layer of a metallurgical industry disposal site (E113°04'24"; N27°52'38") located in Hunan Province, China. The sample was air-dried and homogenized at room temperature in the laboratory, and the coarse debris and visible plant materials were removed before further processing. The primary physical and chemical properties of the soil were as follows: pH 6.65; organic matter, 66.9 g/kg; total nitrogen, 0.13%; total phosphorus, 0.11%; Fe, 3.47%; Ca, 5.42 mg/kg; and cation exchange capacity (CEC), 15.7 cmol/kg.

1.2. Soil particle separation and metals distribution according to particle size

For the separation procedure, the air-dried sample (250 g) was weighed and dry-sieved. The soil was subjected to 3 × 10 min automatic shaking in a series of graded sieves positioned in a vibrating screen instrument (ZBSX-92A, Lei Yun Test Equipment Manufacturing Co., Ltd., China). The sieved material was divided into six graduated fraction sizes, >2, 2–1, 1–0.25, 0.25–0.1, 0.1–0.053, and <0.053 mm, which corresponded to 14.63%, 12.33%, 32.05%, 17.62%, 15.07%, and 8.30% of the total original sample. The distribution of the soil was determined by the weight of each size after sieving. The sample was classified as a sandy soil according to the particle size definition by the American Society for Testing and Materials (Fig. 1).

The concentrations of trace elements (including heavy metals, Ca, and S) were analyzed by inductively coupled plasma-optical emission spectrometry (ICP-OES, Perkin-Elmer Optima 5300DV) after complete sample (0.05 g) decomposition by mixed acid digestion (HF–HNO₃–HClO₄) (a modification of the GB-T 17141-1997 method, NSPRC (National Specifications of the People's Republic of China), 1997). Two reference standard soils

Fig. 1 – Particle-size distribution in the bulk soil sample.

and reagent blanks were used as quality control samples to validate the accuracy and performance of the equipment during the analytical procedures. The relative standard deviations ($n = 3$) of duplicate and blank samples were less than 10% and 5%, respectively.

1.3. Sample prescreening for soil washing

A pilot study confirmed that a mixture of 1.0% rhamnolipids in 2.0 mol/L HCl was suitable for treating the contaminated soil. Thus, batch experiments were run with the mixed solution as the flushing solution. The handling process is depicted in Fig. 2. Leaching experiments using different particle-size fractions were conducted in triplicate. The washing process was performed with 100 g of each soil fraction mixed with 1000 mL washing solution in a 2 L plastic bottle. The bottles were mixed in a rotary agitator (TCLP-12A, Bo Ke Test Equipment Institute, China) at 30 r/min for 2 hr; then, the supernatant was separated from the slurry by centrifugation at 3000 r/min for 15 min. The recovered solution was filtered through a 0.45 μm membrane before further measurement. The moisture in the soil separated from the slurry was removed with a vacuum freeze dryer (LGJ-10D, Four-Ring Science Instrument Plant, Beijing, Co.). Then, all the samples were well ground and digested. The washing supernatants and the digested soil samples were evaluated by ICP-OES for heavy metal content.

1.4. SEM-EDS analysis of the soil samples

The particles in the freeze-dried samples recovered after the soil washing experiments were also characterized by scanning electron microscopy (SEM, S4800, Hitachi, Japan) coupled

with energy dispersive spectroscopy (EDS) analysis, to determine their chemical compositions and mineralogical characteristics (size, shape, and associated, enclosed, or liberated nature of the metal-bearing phase). The selected area for soil mapping (10 μm) was rigorously kept the same for all samples.

2. Results and analysis

2.1. Heavy metal enrichment and particle size distribution

The distribution of heavy metals according to the six particle sizes is given in Table 1. The concentrations of Pb, Cd, and Zn in the soil increase with decreasing particle size, with the highest levels observed in the <0.053 mm fraction. As the particle size decreases, the concentrations of As, Cu, and Cr decrease at first and then subsequently increase. The lowest concentrations of all the metals were present in the 1–0.1 mm particles.

To estimate the contribution of different particle-size fractions to the total contents of contaminants in the original soil, mass loadings were calculated, as shown in Fig. 3. The 1–0.25 mm particle had the largest mass loadings of metals, with total contents of 32.5% Pb, 30.6% Cd, 30.7% Zn, 29.6% As, 27.5% Cu, and 28.0% Cr. The second largest mass loadings of As, Cu, and Cr were found in the coarse aggregates (>2 mm), although smaller particle fractions (0.25–0.1 and 0.1–0.053 mm) also contributed large mass loadings. The <0.053 mm fraction comprised the smallest percentage of the total soil, resulting in a low mass loading.

Fig. 2 – Experimental flow diagram.

Table 1 – Concentration distribution of heavy metals and arsenic according to particle size (mg/kg).

	Origin soil	>2 mm	2–1 mm	1–0.25 mm	0.25–0.1 mm	0.1–0.053 mm	<0.053 mm
Pb	3623.79	2514.40	3247.00	3761.68	3604.63	4378.40	5355.64
Cd	234.58	127.04	217.83	222.42	249.27	290.43	341.55
Zn	9091.50	6587.70	9282.19	8581.77	8871.77	10277.25	11848.38
Cr	249.75	393.96	361.68	267.80	271.63	298.78	302.54
As	555.79	520.54	448.39	414.13	398.03	452.67	546.66
Cu	1220.65	1141.93	697.26	621.42	591.36	691.60	762.48

2.2. Leaching dynamics of the metals by particle-size fraction

Similar trends for the leaching dynamics of Pb, Cd, Zn, and Cu for each particle size were found in the washing process (Fig. 4). The fraction (>2 mm) had the lowest concentration of metals in the effluent; the concentration increased over the first 100 min and then began to decline. The three particle-size fractions in the 2–0.1 mm range had minimal Pb, Cd, Zn, and Cu concentration differences, and their variations with time were small, in the ranges 300.3–395.4 (Pb), 17.6–23.6 (Cd), 535.4–636.6 (Zn), and 42.5–58.1 (Cu) mg/L, respectively. After 40 min soil washing, the <0.053 mm fraction afforded the maximum total heavy metal leachate, with concentrations of Pb, Cd, Zn, and Cu of 693.5, 35.9, 803.5, and 74.5 mg/L, respectively. The second highest level was observed in the 0.1–0.053 mm fraction. During the 40–50 min time period, a dramatic fall in the concentrations of the metals was observed, which began to level off at 60 min and achieved a concentration similar to the 2–0.1 mm fraction. The Cr concentration in the solution was not significantly different from the behaviors of the aforementioned metals except for the <0.1 mm fractions.

Being different from the other metals, the concentration of As for the various particle sizes remained within a small range as time elapsed. The fraction (<0.053 mm) was consistently superior with a concentration on the scale of 33.9–39.9 mg/L, and was closely followed by the 0.1–0.053 mm fraction with the range 29.9–34.4 mg/L. There were minor differences among the As concentrations in the 2–0.1 mm fractions, which had an average level of 10.8 mg/L. The minimum concentration was observed in the fraction of >2 mm at 3.9 mg/L.

Fig. 3 – Heavy metal mass loadings for the six particle-size fractions.

2.3. Metal leaching efficiency in different size particulates

According to the results presented in Table 2, the removal efficiencies of the different particle sizes in decreasing order of: Pb, Cd > Zn, Cu > As, Cr. There was a distinct difference among heavy metal removal efficiencies from the soil depending on soil particle diameters. A larger particle size did not necessarily result in greater removal efficiency for arsenic and heavy metals. The highest removal efficiencies by washing for Pb, Cd, Zn, and As were obtained in the fraction of >2 mm. However, these results differ from prior studies, because the small particle size fractions can also achieve high heavy metal removal efficiencies. Compared with the original efficiency, the equivalent efficiencies for Pb, Cd, and Zn had been enhanced, whereas the equivalent efficiencies for As and Cu were lower.

2.4. SEM-EDS analysis and mobilization correlation

The composition, surface topography, and element distribution of the soil samples were analyzed by SEM-EDS (Fig. 5). Using these results and correlation analysis (Table 3), we studied the relationship between the heavy metal distribution and Ca, Mg, Al, S, P, Fe, and Mn contents in the soil. In this study, we found that the heavy metal distribution was related to Fe, Mn, and Ca contents, but independent of the Mg, Al, S, and P distribution (data not shown).

Aggregates are formed during treatment and appear on the surfaces of the soil particles. Comparing the images and peaks both before and after processing, we found that arsenate and zinc slags can be found in almost every fraction before treatment, whereas the arsenic slag disappears after processing and the zinc is reduced. At the same time, the content of Fe in the particles of >2 and 0.1–0.053 mm declined, whereas the concentration of Ca tended to increase overall, with the exception of the grain size of 0.1–0.053 mm. Mn was detected only in the 1–0.25 and 0.1–0.053 mm fractions and obtained a decreased concentration after treatment. The As content exhibited a remarkable positive linear correlation ($p < 0.01$) with Fe both before and after treatment, whereas in the process of soil washing, it was significantly and positively correlated with Ca. Before processing, Zn was significantly and positively correlated with Ca, although it became significantly and positively correlated with Fe after processing. For the other elements, there were highly significant correlations between Cu and Fe, Cd and Ca, and Cd and Mn before treatment, but less significant correlations occurred between Cu and Ca, Cu and Mn, and Cd and Fe after treatment.

Fig. 4 – Average of Pb, Cd, Zn, Cr, As, Cu concentrations in the effluents from the batch tests with 1 mol/L HCl and 0.5% rhamnolipids.

3. Discussion

3.1. Evaluation of soil washing combined with sieving technology

Soil washing combined with sieving is an effective method for removing heavy metals in soil. The maximum removal efficiencies for Pb, Cd, Zn, and As were obtained for the grain sizes >2 mm, although the small size grains also exhibited

very high levels of efficiency. The grains <0.053 mm removed larger amounts of Pb, Cd, and Zn, and produced higher leaching losses of As and Cu. Previous studies indicated that soil washing is suitable for porous sandy soils with high permeability. Once the soil has a high content of organic matter or clays (>30%), soil washing is considered ineffective for heavy metal remediation. Kuhlman and Greenfield (1999) showed that soil particles finer than 0.02 mm can also be washed, but only if the contaminants can be solubilized in water or a suitable extractant, or separated by flotation.

Table 2 – Removal efficiency of the variously sized soil particles.

	Pb	Cd	Zn	Cr	As	Cu
>2 mm	87.4%	87.3%	76.5%	10.4%	45.5%	64.9%
1–2 mm	74.7%	80.0%	66.7%	37.1%	26.5%	61.7%
0.25–1 mm	84.3%	80.6%	67.4%	25.0%	21.8%	65.5%
0.1–0.25 mm	84.3%	81.7%	60.9%	34.7%	23.5%	65.3%
0.053–0.1 mm	85.4%	78.1%	60.7%	25.9%	10.2%	62.4%
<0.053 mm	87.2%	79.5%	66.0%	25.1%	27.2%	66.6%
Equivalent efficiency	84.0%	80.7%	65.9%	25.4%	25.9%	64.5%
Original efficiency	79.1%	79.6%	63.7%	25.4%	38.5%	76.9%

Removal efficiency = $(c_b m_b - c_a m_a) / c_b m_b$.
Equivalent efficiency = $(c_1 m_1 f_1 + c_2 m_2 f_2 + \dots + c_6 m_6 f_6) / (c_1 m_1 + c_2 m_2 + \dots + c_6 m_6)$.
Original efficiency: the removal efficiency of origin soil.
b: before washing; a: after washing; c: concentration of the contaminants; m: mass; f: removal efficiency.

Soil washing combined with particle separation can concentrate the metals in smaller volumes of soil, and thus considerably reduce the volume of contaminated media. A soil washing procedure via magnetic separation proved effective at removing a significant amount of some of the contaminants present in the soil, affording the recovery of 59.83% Cu, 22.38% Pb, 92.44% Zn, 49.87% As, and 74.17% Fe (Sierra et al., 2014). The combination of soil washing and separation, which recovered 42%–52% of the total metals and reduced soil volume by over 80%, has also received attention by Dermont et al. (2010). Based on our work, optimal grading standards and washing times for practical remediation were selected to achieve the goals of high efficiency, reduced energy consumption, and cost-effectiveness, which the original soil should be sieved into three grades (>2, 2–0.1, and <0.1 mm) with washing times of 80, 25, and 40 min, respectively.

3.2. Washing Pb, Zn, and Cd from different particle sizes

We noticed that the grains in the size range of 2–0.1 mm, which comprised about 60% of the total soil, enriched about 60% of the heavy metals, whereas the fraction of <0.1 mm, constituting about 20% of the soil, concentrated about 30% of the contaminants. This indicated that heavy metals were more likely to be enriched in the smaller particle-size fractions, and a higher leaching concentration and a larger amount of leached metals may be achieved in these fractions. The concentrations of Pb, Cd, and Zn in the eluent increased with decreasing grain size, and the maximum recoveries appeared in the fraction <0.053 mm, which were higher than those of the coarse aggregates. Metals tend to concentrate as micro-aggregates (<0.25 mm), forming in relationship to the types and contents of the clays, organic matter, and Fe–Mn oxides in the soil (Rodriguez-Rubio et al., 2003). Small particles, because of their larger surface areas and the characteristics of the oxides produced by Si–OH and Al–OH, can act as cementing materials to enrich the metals in soils (Qian et al., 1996). By comparing the results of SEM-EDS, we speculate that the occurrence of metals in the grains >0.1 mm is influenced by iron oxide and calcium oxide, whereas adsorption in the grains <0.1 mm is associated with iron oxide or manganese

oxide. Some studies have indicated that clay minerals, organic matter, and Fe–Mn oxides usually act as adsorption vehicles, implying a robust adsorption mechanism with the toxic elements (Matera et al., 2003; Kumpiene et al., 2008).

The removal of heavy metals from the soil in the presence of rhamnolipids and HCl occurs through a series of interactions that can be considered mechanistically from two perspectives. In one case, the heavy metal binding sites in soils are destroyed by hydrochloric acid, releasing the metals into the liquid phase from the electrical double layer in the form of ions where they can then combine with the rhamnolipids. Alternatively, the hydrophilic groups of the rhamnolipids can interact with metals at the surface of the soil particles or as free species in the liquid (Mulligan et al., 2001; Wang and Mulligan, 2004). Rhamnolipids can form micelles at concentrations above the critical micelle concentration (CMC), with an increase in the mobilization of metals from soils (Mukhopadhyay et al., 2013). In addition, rhamnolipids are likely to precipitate under acidic conditions (Wang and Mulligan, 2004), resulting in a release of a portion of the metals from the complexes and adsorption onto the clay minerals, which can explain the sudden drops in concentration during the leaching process.

3.3. Washing As from different particle sizes

Different from the behaviors of Pb, Cd, and Zn, the concentration of As in the particles decreased initially and then subsequently increased as the particle size decreased; high concentrations were found in both the >2 mm and <0.053 mm grains. The various distributions of As in the particles are primarily due to its high activity in the soil and significantly influenced by soil composition properties. Some arsenate slags can be observed in the coarse grains in images of Fig. 5 b-1 and c-1, which would explain the high As concentration in these particles. The occurrence of arsenic in the small particles is mainly influenced by Fe–Mn oxides, clay minerals, and organic matter. Iron oxide can adsorb metals by oxidation–reduction reactions and surface coordination due to its large surface area, low point of zero charge (PZC), high surface activity, and strong oxidizing potential (Ouvrard et al., 2005); then, bidentate binuclear inner-sphere complexes can be formed (Manning et al., 2002).

The removal of As proved to be less than ideal compared to metals such as Pb, Cd, and Zn. The As content in the leaching of coarse particles (>2 mm) slowly increased with time, whereas the concentration decreased in those of grains <0.1 mm. Lee et al. (2007) conducted a similar study with sediments from an abandoned coal mining site in which the concentration of As tended to increase with decreasing particle size; the As concentration of the particles <0.15 mm was 3.8–12.0 times higher than that of the particles of 4.76–2 mm. We concluded from the SEM-EDX results and correlation analysis that the concentrations of As demonstrate an outstanding positive linear correlation with Fe both before and after treatment, whereas during the process of soil washing, the As was independent of Fe. Iron oxide can combine with arsenate ions to form inner- and outer-sphere surface complexes because of a large number of hydroxyl sites (Miretzky and Cirelli, 2010; Wang and Mulligan, 2009). Yuan and Chiang (2007) drew the same conclusion for an acid environment, and

Fig. 5 – SEM micrographs and EDS chromatograms of the six particle-size fractions before and after treatment. (a) > 2 mm; (b) 1–2 mm; (c) 0.25–1 mm; (d) 0.1–0.25 mm; (e) 0.053–0.1 mm; (f) < 0.053 mm; 1: before treatment; 2: after treatment.

found that the As was strongly adsorbed on the surfaces of Fe(0) and FeOOH. Moreover, the rhamnolipids, which are negatively charged, compete with arsenic anions for adsorption sites, and therefore inhibit the mobilization of arsenic (Wang and Mulligan, 2009). The smaller particle-size grains are enriched with large amounts of Fe–Mn oxides, which have specific adsorption sites for As and result in low removal efficiency. Most of the As bound to Fe is difficult to wash

efficiently and this can be explained why As is less favorably transferred in the soil than the other metals.

4. Conclusions

The technology of sieving combined with washing for the remediation of soil co-contamination was evaluated through

Table 3 – Correlation analysis of heavy metal over process stages.

		Before process	In process	After process
Fe	Pb	–	0.204 ^a	–
	Cd	–	0.190 ^a	0.943 ^b
	Zn	–	0.733 ^b	0.860 ^a
	Cr	0.886 ^a	0.743 ^b	–
	As	0.886 ^a	–	0.943 ^b
Mn	Cu	1.000 ^b	0.668 ^b	–
	Pb	–0.657	0.361 ^b	–
	Cd	–0.829 ^a	0.341 ^b	–
	Zn	–0.543	0.792 ^b	–
	Cr	0.600	0.854 ^b	–
Ca	As	–	–	–
	Cu	0.600	0.743 ^b	0.829 ^a
	Pb	0.771	0.936 ^b	–
	Cd	0.829 ^a	0.953 ^b	–
	Zn	1.000 ^b	0.768 ^b	–
	Cr	–	0.704 ^b	–
	As	–	0.701 ^b	–
	Cu	–	0.850 ^b	0.943 ^b

^a A significant correlation.^b A highly significant correlation.

batch experiments. The approach was proven to concentrate the pollutants into smaller volumes of soil and effectively removed metals. The following conclusions were derived:

- (1) The concentrations of leached metals increased with decreasing particle sizes.
- (2) The dynamics of leaching were similar among Pb, Cd, Zn, Cr, and Cu, whereas As was different, presenting a decreasing trend with time.
- (3) The removal efficiency of the different particle sizes in decreasing order was Pb, Cd > Zn, Cu > As, and Cr.

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