

In situ Soil Washing on Metal-Contaminated Sandy Soil by Sedimentation Method: A New Approach on Soil Remediation

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ABSTRACT

We propose a new approach of in situ soil remediation called in situ soil washing by sedimentation method, by injecting high air pressure into mixing water-sandy soil ground and hydraulically separate soil particles based on their particle size and density. This physical separation exploits the distribution of contaminant in soil by physically separating a select, contaminant rich fraction. The advantage of this method is on the washing and separation processes that are carried out simultaneously during remediation process. The suitability of the method for heavy metal remediation was examined by batch sedimentation column experiment. Laboratory experiment was effective to produce a distinct size separation of the soil into coarse, fine and wash water and indicate significant reduction in heavy metal level (90%). The coarse fraction had the least level of heavy metal contaminant while the fine fraction contained the highest heavy metal concentration and a very small amount of the original contaminant was retained in the coarse fraction. The experimental results show that the removal efficiencies depend on the initial concentration of metal in the soil sample, the duration of washing and the addition of biosurfactant in the washing solution.

Keywords: in situ soil washing, heavy metal contamination, sedimentation method, removal efficiencies

1. BACKGROUND

We propose a new approach of in situ soil washing method that works based on air-water flow that hydraulically separates soil particles based on their particle size [1]. This approach is called sedimentation method or gravity separation of solids from liquid by settling [2]. Soil washing was conventionally performed ex situ in treatment plants that employ extracting chemical to remove contaminant from soil into aqueous solution [3][4][5][6]. Few studies of in situ soil washing have been conducted, even though in situ soil washing could be suitable for certain contaminated soil in the field, such as described by Nash and Traver, 1993 [7]; Niven and Khalili 1998 [8]; and Makino, 2006 [9]. Prior to developing experimental design, a conceptual model was developed, which was based on sedimentation phenomenon describe in part by

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Stokes Law, in which particle of uniform shape settle through water as rate proportional to their density and to the square of their diameter.

We tried to make in situ soil washing by injecting high air pressure into mixing water-sandy soil ground on certain depth (D) and hydraulically separate soil particles based on their particle size and density (Figure 1). Chemical agents, such as surfactants can be also added to the water solution to enhance removal efficiency of contaminant from soil fraction. This physical separation exploits the distribution of contaminant in soil by physically separating a select, contaminant rich fraction. Several researches indicate that the finest parts of soil are particularly active in the sorption processes of organic as well as inorganic contaminant [10]. Ideally, the treated fraction will require no further treatment and the concentrated fraction can be more effectively processed.

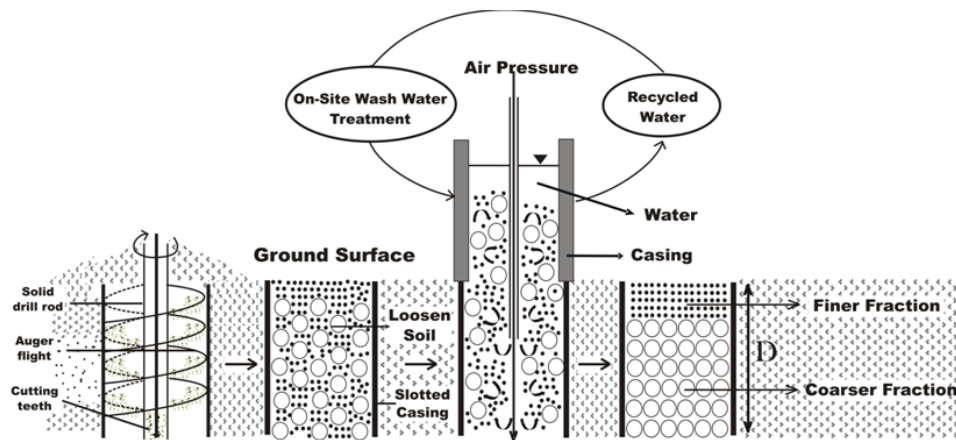


Figure 1. In-situ Soil Washing by Sedimentation Method

For practical purposes, the two soil fractions are considered in our experiment. We used the terminology "fine" and "coarse" particles as the results of separation of particles by the difference in settling velocity. The upper layer is assumed to be fine particles (silts and clays) and the bottom layer is assumed to be coarse particles (fine-coarse sands and gravels) (Figure 1). In this method, wash water will also be generated as part of sedimentation process.

The advantage of this method was attributed to the washing and separation processes that simultaneously occur when the pressure exerted by the water present in the saturated soil results to the soil particles being suspended in water. One promising method for enhancing the efficiency of the processes under consideration was based on creation of a suspended soil for accomplishing the interaction of the liquid (gaseous) medium with the ground solid materials. When the water pressures become sufficiently high to counteract the gravitational pull on the soil particles, the soil particles effectively float, or suspended. The soil particles can then move freely with respect to each other, throughout the height of water column or sediment suspension concentration.

Furthermore, when air pressure is introduced, this will automatically separate the fine particles from the coarser particles and after going through *in situ* sedimentation, it will effectively separate and concentrate the contaminants into a smaller volume of soil that can

be further treated or disposed of. Air can be injected into the soil using a compressor at high pressure. The groundwater level should be determined and include the depth of the seasonal high groundwater level and the type of water table. Creating a borehole and addition of water solution is required in the soil ground before *in situ* soil washing to be performed. To prevent borehole collapse, a slotted casing can be introduced into the borehole (Figure 1). The main advantage of our method is to produce vertical column sedimentation which separate contaminated soil into coarse and fine fraction and wash water. In situ soil washing by sedimentation method using on site wastewater treatment system has not been applied before for contaminated site as illustrated in Figure 1.

For *in situ* application as shown on Figure 1, the water solution used for washing may be leaked to the surrounding the site. It is necessary to isolate the site being remediated by wall installation prior to *in situ* soil washing. Considering the volume of water need to be added to the soil column or soil-water ratio in order to obtain appropriate separation, it is necessary to fix wall installation in the ground surface to protect water solution as illustrated in Figure 1. Soil remediation by sedimentation method seems to be effective, quick and cheap since there are no costs for excavation of contaminated soil from the site. The fine fraction is recovered for further treatment or disposal. The process water is completely collected, treated and recycled. In the field, physical separation by sedimentation method and on site water wash treatment is performed as an integrated process (Figure 1).

2. OBJECTIVE

This research had two objectives. The first is to simulate laboratory scale experiment and the future research objective is concentrate on the application making *in situ* washing into soil in the field. Laboratory experiment was conducted to evaluate the potential success of the *in situ* soil washing by sedimentation method by introducing air pressure to water-soil column in laboratory scale which separates soil particles as a function of size and density.

3. EXPERIMENTAL DESIGN

3.1. Soil Sample Characterization, Preparation and Analysis

Uncontaminated soil sample of this study was collected from Ota District Tokyo in 1.5 m depths. The average pH of the soil suspension was 6.65. Determination of the cation exchange capacity (CEC) used the $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ compulsive exchange described by Gillman and Sumpter (1986) [11] was 6.8. The result of grain-size distribution indicated that the original soil sample contained approximately 10-20% clay-silt size particles and the remaining was sand (sandy soil). Surface area measured by BET method was $8.0\text{m}^2/\text{g}$. X-Ray diffraction analysis (powder method) revealed that the sample contained kaolinite, illite, chlorite, quartz and feldspar. Cu, Pb, Zn and Cd were selected as representative heavy metals. Three artificial contaminated soils were used, prepared by dissolving an appropriate quantity of heavy metal as described by Hong, 2004 [12]. In brief, uncontaminated soil sample was spiked with solution of nitrate salts $\text{Cu}(\text{NO}_3)_2$, $\text{Cd}(\text{NO}_3)_4$, $\text{Pb}(\text{NO}_3)_2$ and $\text{Zn}(\text{NO}_3)_2$ for 20 days. They are as follows: (A) soil with high concentration of heavy metal; (B) soil with intermediate concentration of heavy metal;

(C) soil with low concentration of heavy metal, by spiking uncontaminated soil sample with 20 millimolar (mM) solution of nitrate salts for soil A, 10 mM for soil B and 2,5 mM for soil C, respectively. The resulting synthetic contaminated soils had a final concentration of 2225, 1101, 5102, 1393 mg/kg of Cu, Zn, Pb, Cd on soil A and 438, 230, 1305, 286 mg/kg of Cu, Zn, Pb and Cd on soil B and 315, 124, 786, 25 mg/kg Cu, Zn, Pb, Cd on soil C, respectively. Heavy metal concentration was determined after acid digestion by Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES 7500; Shimadzu Corp., Kyoto, Japan) under optimal operating conditions.

Sequential extraction analysis described by Tessier 1979 [13] was also conducted for three artificial contaminated soil samples for knowing of how heavy metal partition among the various phases allows for a better insight into the mechanism of retention and release involve the process of migration and decontamination, especially before *in situ* soil washing was performed. The results of the sequential extraction analysis for heavy metals in the three contaminated soil sample generally show that cadmium was mostly associated with the exchangeable fraction. The amount of Cd in Fe-Mn oxide and organic matter fraction were found to be negligible. Therefore, cadmium is considered to be easily leached from the soil. Copper was found predominantly in Fe-Mn oxide fraction followed by the carbonate and organic matter fraction. Lead was irregularly found in the all fraction. Zinc was primarily partitioned in the carbonate fraction followed by exchangeable fraction.

3.2. Batch Sedimentation Experiment

The objective of batch laboratory scale of our work was to test a sedimentation column model for hydraulic separation by injecting air pressure through pipe to soil-water column which separates soil particles as a function of size and density, in which heavy metal contamination is removed from contaminated sandy soil by the proposed technique. The specific objective of this batch sedimentation experiment is (1) to perform vertical column sedimentation of heavy metal contaminated soil, (2) to determine particle fraction distribution, heavy metal concentration, heavy metal distribution from the separated fraction, (3) to determine the effect of washing time and removal efficiencies.

A tube cylinder tube with 200 millimeters height and internal diameter 50 millimeter equipped with inlet and outlet pipe was used as batch sedimentation apparatus as shown in Figure 2. Fifteen similar apparatus were constructed and tested for series of test washing time. Air was pumped into the tube through inlet pipe to obtain finely dispersed gas bubbles, which migrated upwards to the surface. The air forced through the water produced air bubbles in the tube containing water and soil sample. The water pressures build below the water surface to the point that the water breaks through the surface much like bubbles in boiling water. Air was introduced into the fifteen tubes for 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14 and 15 minutes in order to determine the effect of washing time.

The air pressure flow rate started with the position of inlet pipe reaching the surface soil sample inside the tube. The air pressure flow rate was increased as the inlet pipe penetrated to the soil sample. After the final depth was reached, air pressure flow rate was constant until the inlet pipe almost reaching the bottom of the cylindrical tubes. Flowing air pressure will separate the soil particles as a function of size and density. Theoretically, soil grains in the water will settle in a descending order of particle sizes with the top part of the soil layer consisting of smaller grains. The separation of soil into nominal size fraction depends on settling

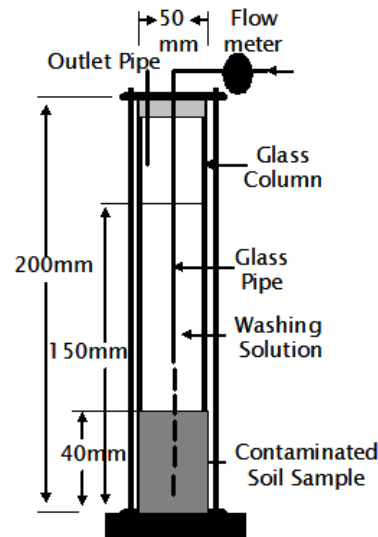


Figure 2. Laboratory Experimental Setup

phenomenon on hindered settling describe in part by Stokes Law developed by Kynch 1952 [14], McRoberts and Nixon 1976 [15], Coulson 1991 [16]. Although this experimental method was not exactly similar from field condition, for initial observation it was considered to conduct column experiment with uniform distribution contaminant in the soil.

4. RESULTS AND DISCUSSION

4.1. Separation of Soil Particles by Sedimentation Method

The soil inside the tube was allowed to settle, to obtain clear water above the settled solids. The fractions separated by our fifteen column using sedimentation method were therefore analyzed on particle size analysis to determine the percentage of grains of expected size in each granulometric class. In our work, we observed each column experiment to observe the effect of washing time on particle size separation.

The data shown in Table I indicated that the result of separation by sedimentation method is reliable, and the accuracy of separation increased depending on duration of washing, in fact after 15 minutes of washing, 92.2% of particles in the coarse fraction separated as >0.075 mm particles size diameter (fine to coarse sand) and 7.8% remain of fine fraction separated as <0.075 mm particles size diameter (clay-silt). Perfect separation was expected in this method, but it showed that only about 90% of its grains were separated.

This inaccurate result is reflected as the lack homogeneity in particle size distribution in each fraction. This may be related to the application of Stokes Law, which shows a good application to suspensions of particles with size ranging from 0.001 mm to 0.050 mm [17], reflected by the presence of fine particles in the coarse fraction. Another factor that may

Sample (observed fraction)	Washing Time (minutes)	Sand % (0.850mm-0.250mm)	Fine sand % (0.250mm-0.075mm)	Silt % (0.075mm-0.005mm)	Clay % (<0.005mm)
Original	0	42.1	33.7	12.8	11.4
Coarse	1	40.1	49.2	6.1	4.5
Coarse	2	42.7	47.3	6.0	3.9
Coarse	3	42.9	47.5	5.9	3.5
Coarse	4	45.2	45.6	5.3	3.5
Coarse	5	43.1	48.4	5.3	3.0
Coarse	6	44.8	47.5	4.1	3.5
Coarse	7	44.8	47.0	4.4	2.8
Coarse	8	43.2	49.0	5.0	2.7
Coarse	9	44.4	47.7	5.0	2.7
Coarse	10	44.7	47.6	5.0	2.6
Coarse	11	44.8	47.5	5.0	2.5
Coarse	12	43.5	49.1	4.9	2.3
Coarse	13	44.8	48.2	4.7	2.1
Coarse	14	44.2	49.7	4.0	2.0
Coarse	15	44.7	48.5	4.6	2.1

Table I. Values Obtained by Particles Size Analysis to Different Size Fraction Separated by Sedimentation Method

influence the result was that the concentration of the suspension during washing process. The sedimentation process is more complicated if many bodies are present and the system becomes a sediment suspension in hindered settling [18][19], reflected when the concentration of the suspension decrease consequently the homogeneity of the separated fraction will increase and therefore impossible to exclude small amounts of finer grain particle in successive size fraction. Although the result of separation processes during sedimentation was not perfect, the first important point of this research is the process of the invention to separate the soil into a coarse fraction and a fine fraction by sedimentation method. The separation into coarse and fine fraction will reflect the high and low content contaminant in each fraction.

As mentioned earlier, particles size distribution can influence the level of contamination in soil, because of the presence of fine particle such as silt and clay which has a large specific surface area of the soil provides numerous active sites for adsorption reactions of contaminant. Coarse particle size separated by sedimentation method (Table I) then was measured on surface area by BET method and the result was shown in Figure 3. The results obtained showed by the surface area of coarse fraction plotted as a function of washing time. As expected, the surface area decreased with washing time reflected by decreasing content of fine particle.

4.2. The Effects of Washing Time, Addition of Chemical Agent on Washing Solution and Removal Efficiency of Heavy Metals in Soil

As mentioned earlier, the accuracy of separation of particle size increases depending on duration of washing, and consequently it will influence the removal efficiency of contaminant from original soil sample. The results obtained showed by the heavy metal content plotted

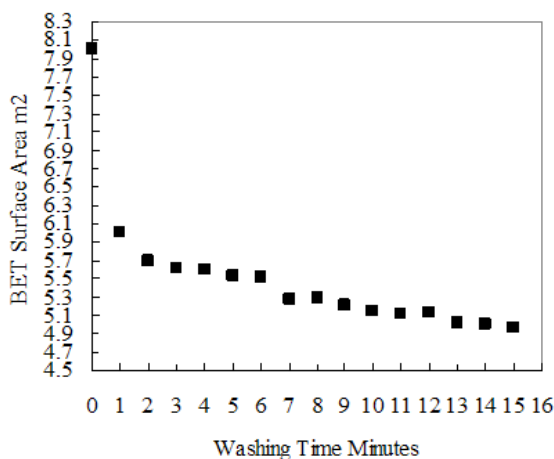


Figure 3. Surface Area of Coarse Fraction vs. Washing Time

as a function of washing time. In this experiment, the heavy metal removal efficiency of the contaminated soil was determined from the following equation:

$$\text{Removal efficiency (\%)} = \frac{(\text{Concentration heavy metal in initial sample} - \text{after washing})}{\text{Concentration heavy metal in initial sample}} \times 100$$

The three different of artificial contaminated soil samples and the deionized (DI) water were fed into each of the tube and air was introduced into the each tube for 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14 and 15 minutes. In each observation, coarse particle was sampled in order to observe the decreasing concentration of heavy metal in soil sample. As expected, the heavy metal removal increased with washing time. Generally the concentrations of heavy metal in the coarse samples were high at the beginning, then gradually decreasing. The wash water and the fine particles were sampled through pipe by suction. The coarse particles were sampled using small spoon after wash water and the fine material was removed and then was sampled for the heavy metal analysis.

Figures 4A to 6A show several experimental data representing soil washing experiment using DI water as washing solution. Those figures show that significant decrease of heavy metal in the soil sample start from 1 minute to 15 minutes. Removal efficiencies were obtained by comparing heavy metal concentration on coarse particles of soil sample to the initial concentration of heavy metal in original artificial contaminated soil sample. Figures 4B to 6B show that the removal efficiencies for soil A was 27% for Cu, 41% for Pb, 59% for Zn and 82% for Cd, while for soil B it was 64% for Cu, 65% for Pb, 62% for Zn and 70% for Cd and for soil C was 74% for Cu, 69% for Pb, 73% for Zn and 72% for Cd. The heavy metal in the contaminated soil sample must be converted to wash water and fine particles as well. The importance of washing using DI water was to reveal the heavy metals that are weakly bonded to the soil particles or adsorbed in the easily coordinated sites on the surface of the soil particles.

In this step, fine fraction in fifteen tubes was collected from glass column experiment for heavy metal concentration analysis. The results of the ICP-AES analysis on fine particles

showed that the concentrations of the heavy metals in the fine particles were very high. The accumulations of metals in the clay or fine fractions are attributed to the high specific surface area, the presence of clay minerals such as illite, and the high organic content. The weight and volume of this fine fraction was very small compared to coarse fraction in the original soil sample. This means that removing the fine fraction will reduce the contaminant in the soil sample significantly.

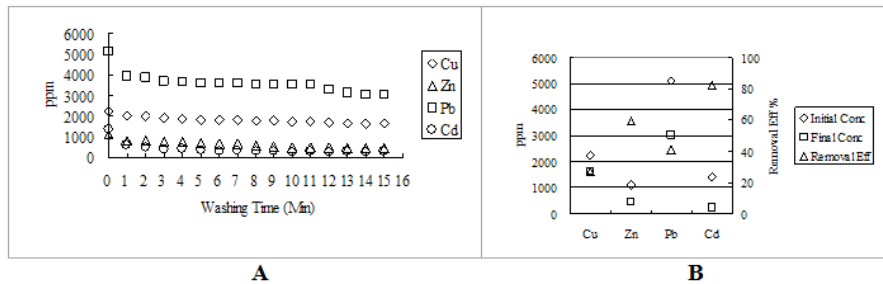


Figure 4. (A) Concentration heavy metal in soil sample vs washing time for soil A. (B) Removal efficiency DI water washing for soil A

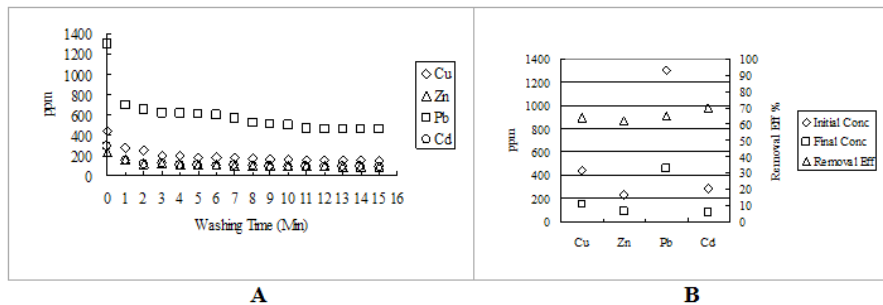


Figure 5. (A) Concentration heavy metal in soil sample vs washing time for soil B. (B) Removal efficiency DI water washing for soil B

The effectiveness of washing efficiency using DI water with an addition of biosurfactant was also observed in this experiment, by adding 0.25% by weight saponin in the water solution. Saponin is a type of biosurfactant produced by various plants and microorganisms and biodegradable, environmentally safe with a low toxicity, easily produced and can be reused. It is also known as capable of removing heavy metals in soil [20]. In the current experiment, after fine fraction was removed on previous experiment, wash water used on previous experiment was returned to the glass column, and air pressure was introduced at 1 to 15 minutes for each glass column, the same as previous experiment.

Coarse particle was sampled in order to observe the decreasing concentration of heavy metal in soil sample after saponin was added. As expected, the concentration of heavy metal removed decreased with washing time. Generally the concentrations of heavy metal in the coarse were high at the beginning, then gradually decreasing (Figure 7A-9A).

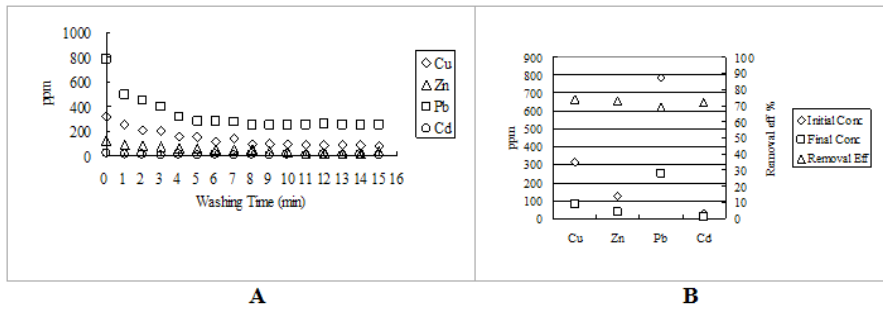


Figure 6. (A) Concentration heavy metal in soil sample vs washing time for soil C. (B) Removal efficiency DI water wash for soil C

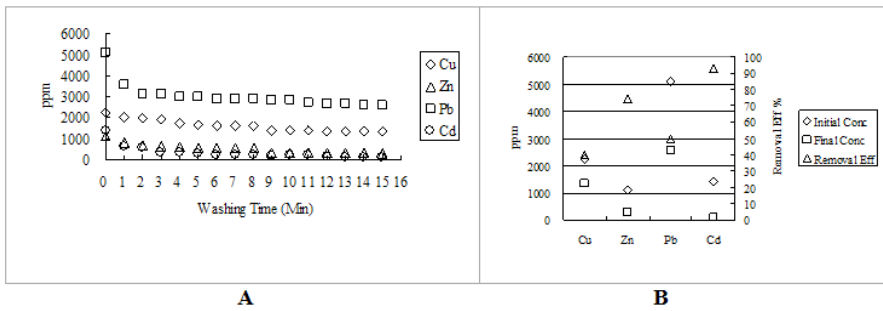


Figure 7. (A) Concentration heavy metal in soil sample vs washing time for soil A. (B) Removal efficiency biosurfactant washing for soil A

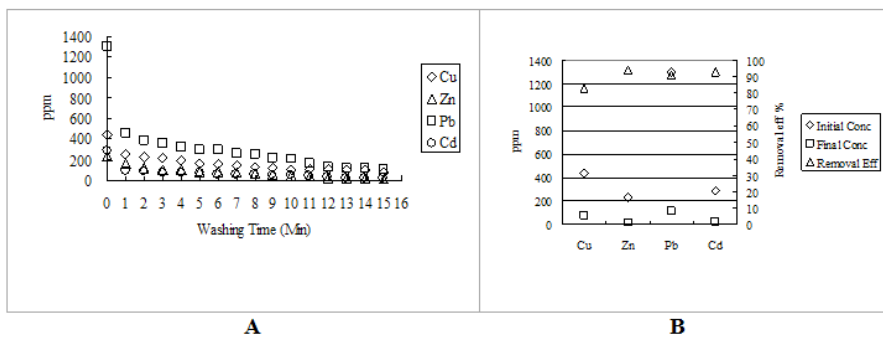


Figure 8. (A) Concentration heavy metal in soil sample vs washing time for soil B. (B) Removal efficiency biosurfactant washing for soil B

The removal efficiency for soil A was 40% for Cu, 50% for Pb, 74% for Zn and 93% for Cd; for soil B was 83% for Cu, 94% for Pb, 91% for Zn and 93% for Cd and for soil C was 92% for Cu, 94 for Pb, 91% for Zn and 88% for Cd (Figures 7B-9B).

These results also confirmed the increase of removal efficiency of heavy metals in the

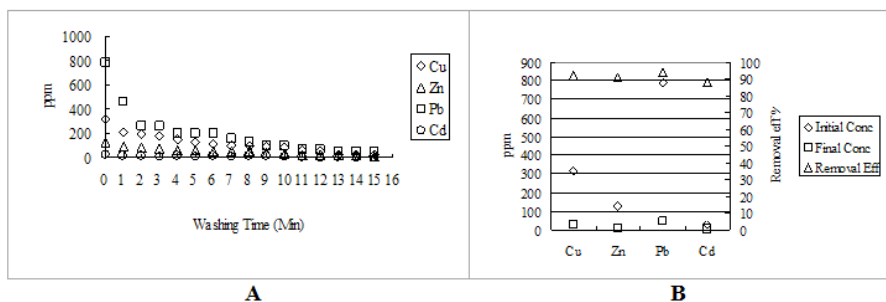


Figure 9. (A) Concentration heavy metal in soil sample vs washing time for soil C. (B) Removal efficiency biosurfactant washing for soil C

contaminated soil after the addition of saponin (Figures 7B-9B) compared to DI water washing only (Figures 4B-6B). The removal efficiency increased for soil A from 27 to 40% for Cu, from 41 to 50% for Pb, from 59 to 74% for Zn and from 82 to 93% for Cd, for soil B increased from 64 to 83% for Cu, from 65 to 91% for Pb, from 62 to 91% for Zn and from 70 to 93% for Cd and for soil C increased from 74 to 92% for Cu, from 69 to 94% for Pb, from 73 to 91% for Zn and from 72 to 88% for Cd. The heavy metal in contaminated soil sample must be converted or released to the wash water.

The percentage of heavy metal released to wash water in this experiment after the addition of saponin for 15 minutes washing was 3-5% for Cu and Pb and 17-37% for Zn and Cd (Table II). This means that the method used in our experiment significantly reduces only Zn and Cd in the contaminated soil sample recovered in the wash water. This was confirmed by sequential extraction analysis showing that the concentration of Cd in exchangeable fraction was the highest compared to the other fraction and the most easily leached from the soil. The highest release or desorption of heavy metal ion, especially Cd was confirmed by Kandpal *et al.*, 1999 [21], showing higher percent desorption of Cd relative to other heavy metals such as Ni and Cu. On the contrary, only about less than 5% of Cu and Pb were recovered in the wash water. These heavy metals must be remaining in the soil sample, either in the coarse or fine particles fraction. Pb, Zn and Cu appeared to be the more strongly bonded to the soil matrix among the four heavy metals used in this laboratory experiment. The remaining fractions of Cu, Pb and Zn were considered to be strongly bonded and immobilized within the soil matrix. This was consistent with an earlier observation on sequential extraction analysis, where partitioning of Cu, Pb and Zn was found to be low in the exchangeable fraction, and predominantly in the Fe-Mn oxide fraction, the carbonate and the organic matter fraction.

Heavy metal (%)	Soil A	Soil B	Soil C
Cu	3	5	4
Pb	3	5	5
Zn	17	32	33
Cd	28	37	32

Table II. Percentage of Heavy Metal Release to Wash Water after 15 Minutes Washing with Addition of Biosurfactant

Saponin was proven to be effective in heavy metal washing, indicated by the increasing removal efficiency of the heavy metals in the contaminated soil, especially for Cd and Zn. This was confirmed by a significant increase of heavy metal concentrations in the wash water after saponin was added, as shown by comparing Figures 4A-6A and 7A-9A. The increasing concentrations of the heavy metals in the wash water were known because this biosurfactant, added to the wash water, assisted the desorption of the heavy metals from the soil and the dissolution into the water. The biosurfactant was more effective at mobilizing Cd and Zn into the wash water than Cu and Pb. On the other hand, Cu and Pb were more concentrated in the fine particles. This was probably attributed to the initial high concentrations of these two metals in the artificially contaminated soil samples. In general, this result showed that addition of biosurfactant improved the efficiency of soil washing using deionized water.

5. CONCLUSION

This study has addressed *in situ* soil remediation of heavy metal contamination with emphasis on the washing and separation of particles by the difference in settling velocity. Further treatment for the fine materials and the wash water need to be further investigated. The following conclusions can be drawn from the result in this study:

1. The laboratory scale soil washing apparatus using sedimentation method was able to produce a distinct size separation of the soil into coarse and fine. Results from this study show that when flows are adequately controlled and mixing is sufficient, the up flow column and sedimentation processes are capable of providing particle size separation.
2. Removal efficiencies of remediation method proposed in this study depend on the concentration of metal in soil sample, duration of washing and the presence of biosurfactant in the washing solution.
3. The concentration of heavy metal contaminant was found to be a function of particle size with the fine fraction containing the highest concentration of heavy metal and small amount of the original contaminant retained in coarse fraction.

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