



Evaluation of remediation process with plant-derived biosurfactant for recovery of heavy metals from contaminated soils

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Abstract

A washing process was studied to evaluate the efficiency of saponin on remediating heavy metal contaminated soils. Three different types of soils (Andosol: soil A, Cambisol: soil B, Regosol: soil C) were washed with saponin in batch experiments. Utilization of saponin was effective for removal of heavy metals from soils, attaining 90–100% of Cd and 85–98% of Zn extractions. The fractionations of heavy metals removed by saponin were identified using the sequential extraction. Saponin was effective in removing the exchangeable and carbonated fractions of heavy metals from soils. In recovery procedures, the pH of soil leachates was increased to about 10.7, leading to separate heavy metals as hydroxide precipitates and saponin solute. In addition recycle of used saponin is considered to be effective for the subsequent utilization. The limits of Japanese leaching test were met for all of the soil residues after saponin treatment. As a whole, this study shows that saponin can be used as a cleaning agent for remediation of heavy metal contaminated soils. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Saponin; Biosurfactant; Soil washing; Heavy metals; Removal; Leaching test

1. Introduction

Soils have been contaminated with heavy metals as the result of numerous industrial activities, including mining, smelting, automobile battery production, vehicle emission, and landfilling of industrial waste and fly ash from incineration process. The presence of heavy metals in soils leads to serious problems because they cannot be biodegraded: (1) toxicity on biological system (Morrison, 1983) and (2) groundwater contamination by leaching process. There are two fundamental technolo-

gies to remediate heavy metal contaminated soils. The first technology immobilizes heavy metals into tightly bound solid matrix to minimize migration. However, this technology is not a permanent solution. Site reuse of soils is limited and long-term monitoring is generally required. For these reasons, solidification is generally limited to radioactive or highly toxic wastes. The second technology promotes heavy metal mobility and migration to the liquid phase by desorption and solubilization. This technology is a permanent solution, providing recycle of remediated soils and improving future land-use option. Currently, soil washing with acid or chelating agent such as EDTA is the most prevalent method. However, acid washing leads to decreased soil productivity and adverse changes in the chemical and physical structure of soils due to mineral dissolution (Reed et al.,

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1996). Soil washing with EDTA has health and safety concerns due to minimal or slow degradation. The recovery of heavy metal from the heavy metal–EDTA complex is also difficult.

In previous work the authors demonstrated that saponin as a kind of biosurfactant complexed with Cd and Pb in aqueous solution (Hong et al., 1998). According to FTIR analysis, these complexations with heavy metals were caused by carboxyl group of saponin. Saponin seemed to be an attractive cleaning agent of soil washing because of its biodegradability (Kommalapati and Roy, 1996; Makkar and Becker, 1997), low toxicity, possibility of reuse, and easy isolation from plants. In addition saponin had potential to enhance the aqueous dispersion of organic contaminants that frequently occurred in heavy metal contaminated soils by solubilization and mobilization. Although biosurfactants produced by microbes have been used for the remediation of heavy metal contaminated soils (Herman et al., 1995; Torrens et al., 1998; Mulligan et al., 1999), no scientific research applying plant-derived biosurfactant has been found. The present study investigated the efficiency of saponin on remediation of heavy metal contaminated soils. Recovery of heavy metals from the soil leachates after saponin treatment was studied by alkali treatment with NaOH. In addition used saponin obtained through precipitation process was recycled for the subsequent soil treatment.

2. Materials and methods

2.1. Saponin

Saponin selected in this study was a triterpene glycoside type from quillaja bark and contained β -D-glu-

curonic acid with carboxyl group of sugar moiety in hydrophilic fraction (Hostettmann and Marston, 1995). Saponin was obtained from Sigma Chemical Co. (St. Louis, MO) and used without further purification. According to the elemental analysis of saponin, the percentage compositions of each element were 51% for oxygen, 44% for carbon, and 6% for hydrogen. The critical micelle concentration of saponin was 0.1% and surface tension was 36 mN m⁻¹. Saponin showed weakly acidic nature (pH 4.6) due to the hydrolysis of glycosides.

2.2. Soils

Three different types of soils were used in this study. Soil samples were collected from Japanese soil that had been contaminated by heavy metals for more than two years. Soils were air dried and sieved to remove coarse sand and stone by a 2 mm sieve. The soil samples were homogenized and stored in a plastic container for subsequent experiment. The content of heavy metals contained in soils was determined by acid digestion (1 HNO₃ + 3 HCl) at boiling temperature (ASTM, 1993). The digested liquid was filtered with 0.45 μ m nitrocellulose membrane filter and filtrate was analyzed for heavy metals by ICP spectrometry (ICPS 7500; Shimadzu Corp., Kyoto, Japan). The selected chemical and physical characteristics of soil samples are presented in Table 1.

2.3. Batch test

A washing process with saponin was performed in a batch experiment as the function of concentration, pH, and time. To determine optimum concentration of saponin for soil treatment, 1 g of soil was taken in a series

Table 1
Chemical and physical characteristics of heavy metal contaminated soils

Characteristics	Soil A	Soil B	Soil C
Type	Andosol	Cambisol	Regosol
Texture	Clay loam	Loam	Sandy caly loam
pH-water	4.6	4.3	5.4
pH-CaCl ₂	4.9	4.5	5.4
Water (%)	6.5	4.4	0.3
EC (mS cm ⁻¹)	1.03	1.12	0.16
CEC (meq 100 g ⁻¹)	5.2	4.8	15.4
Organic matter (%)	7.22	11.25	0.07
Surface area (m ² g ⁻¹)	58.8	37.2	5.5
<i>Heavy metals (mg kg⁻¹)</i>			
Cd	1484	1026	701
Cu	2155	2181	1521
Pb	7288	7161	5253
Zn	692	551	472

of polycarbonate centrifuge tubes and 25 ml of solution containing various saponin concentrations was added. The pH of soil A and B suspensions was adjusted with 0.1 M NaOH in the pH range of 5.0–5.5. The suspensions were shaken in a 20 °C thermostat. After 24 h, the mixture was centrifuged with a refrigerated centrifuge. The supernatant was withdrawn and filtered through 0.45 µm nitrocellulose membrane filter. The composition of heavy metals was analyzed by ICP spectrometry. The pH effect of saponin solution (3%) was studied in the pH range of 3.0–7.0. As the control, deionized water was prepared in the same way and compared with the result of saponin treatment. The pH of suspensions was adjusted with 0.1 M HNO₃ or 0.1 M NaOH. For kinetic study, 5 g of soil was added to 100 ml of saponin solution (3%) in the pH range of 5.0–5.5. The removal of heavy metals from soils was measured at different time intervals. Thereafter the same procedure as above was followed.

2.4. Speciation of heavy metals in soils

The soil residues obtained from saponin treatment at pH around 3 were fractionated by the sequential extraction procedure (Tessier et al., 1979), which were compared with the result of soils untreated with saponin. One gram of soil was used and three replicates were carried out for each sample. The fifth residual fraction was calculated from the difference between heavy metal concentration determined by hot acid digestion and the total quantity of heavy metals removed in the preceding extraction procedures.

2.5. Recovery of heavy metals from the soil leachates

Precipitation method using caustic soda (NaOH) was adopted for the treatment of soil leachates containing heavy metals. For this experiment, the leachate from soil A (pH 3.2) was used as a sample. The soil suspension was centrifuged with a refrigerated centrifuge. The supernatant was withdrawn and filtered through 0.45 µm nitrocellulose membrane filter. The filtrate was analyzed for heavy metals by ICP spectrometry. After determining the content of heavy metals, the pH of soil A leachate was gradually increased with 3 M NaOH for precipitating heavy metals as hydroxide solids. The solution was allowed to stand for 24 h before it was analyzed for heavy metals by ICP spectrometry. Moreover, the solubility of saponin was measured in alkaline pH ranges. The concentration of saponin was finally made up to 0.3% and analyzed by UV–visible spectrophotometer (UV-160A; Shimadzu Corp., Kyoto, Japan). For this measurement, each sample was appropriately diluted to ensure that saponin content could be analyzed by this instrument.

2.6. Recycle of used saponin

Efficiency of used saponin on removal of heavy metals from soils was studied in a batch experiment described in Section 2.3. The supernatant was collected from the sample obtained through precipitation procedure. The concentration of saponin in supernatant was determined by UV–visible spectrophotometer. Thereafter saponin solution was adjusted with 3 M HNO₃ in the pH range of 5.0–5.5. A soil washing procedure with used saponin was followed.

2.7. Leaching test

The soil residues obtained from saponin treatment were subjected to the leaching test specified in the notification no. 25 of Ministry of the Environment of Japan (1997). A 50 g of soil was mixed with 500 ml of water (pH 5.8–6.3 with HCl). The suspension was shaken for 6 h at room temperature and filtered with a 0.45 µm nitrocellulose membrane filter. The filtrate was analyzed for heavy metals by ICP spectrometry.

3. Results and discussion

3.1. Efficiency of saponin on removal of heavy metals from soils

Effect of saponin concentration (Fig. 1) was expressed in terms of percentage of removed heavy metal to their content (Table 1). The concentration was stepwise changed from 0.1% to 10% which is near saturation. The removal efficiency of heavy metals was found to be dependent on saponin concentration. The removal of heavy metals abruptly increased with increasing saponin concentration to 3%. As the concentration of saponin was further increased from 3% to 10%, the removal of Cd, Pb, and Zn from only soil A continuously increased but at a slower rate. Therefore, the optimum saponin concentration seems to be approximately 3% for soil treatment to avoid introduction of excess saponin into soils. For the following experiment, 3% concentration of saponin was used to investigate the effect of other parameters such as pH and time.

Effect of pH on removal of heavy metals from soils is shown in Fig. 2. The amount of saponin sorbed onto soils increased with decreasing pH due to the increased electrostatic attraction between saponin and soil surface (Hong, 2000). Thus, the pH effect of saponin solution was investigated over pH 3 for minimizing saponin sorption to soils. The removal efficiency of heavy metals was dependent on pH. Cadmium was not removed from soils by the control at final pH > 6, while 50–75% of Cd

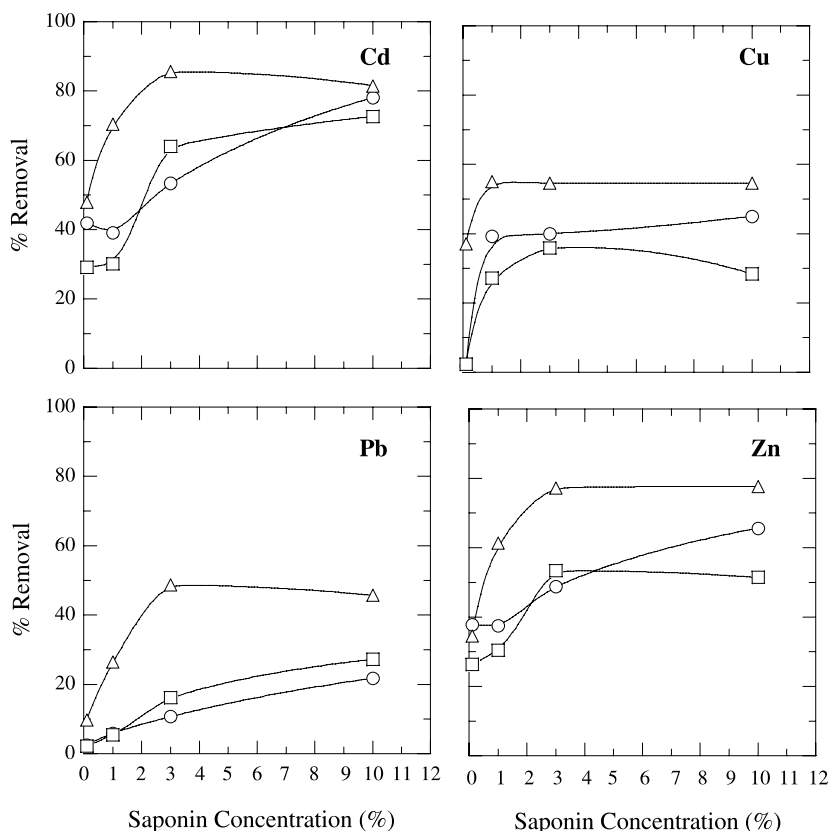


Fig. 1. Effect of saponin concentration on removal of heavy metals from soils in the pH range of 5.0–5.5 at 20 °C. Each point is the average of duplicate samples (○: soil A, □: soil B, △: soil C).

being removed by saponin treatment. At final pH 3, 90–100% of Cd was removed from soils by saponin treatment. The percentage removal of Cu was 42% for soil A, 36% for soil B, and 62% for soil C at final pH 3. For Pb, the percentage removal was 58% for soil C at final pH 3. The percentage removal of Zn was 85–98% for soils at final pH 3. As shown in Fig. 2, the percentage removal of heavy metals significantly decreased at final pH 7. Saponin solution showed weakly acidic nature as the pH value was 4.6. In this study NaOH was added to adjust the pH of saponin solution. Sodium may compete with heavy metals for saponin, thereby leading to Na-saponin complex. In comparison to Cu and Pb, soil treatment with saponin was more effective in removing Cd and Zn from soils. This result was due to the electronegativity of heavy metals. Therefore, the mobility of Cu and Pb was obviously lower than that of Cd and Zn, consistent with its strong chemisorption on clays, oxides, and humus of soils. Saponin was effective for removal of heavy metals from soil C in comparison to soil A and B. High content of organic matter in soil A and B made removal of heavy metals very difficult by its high sorptive capacity.

3.2. Kinetic study

In Fig. 3, the residual concentration of heavy metals in soils was plotted against time. The kinetic experiment indicated that in most cases equilibrium was almost attained within 6 h for maximum removal of heavy metals. Generally comparison of the rate constant gives better understanding for kinetic study. In every case, removal of heavy metals followed a first-order reaction within 30 min, which could be described as below:

$$\log(C_t/C_0) = -(k/2.303)t, \quad (1)$$

where C_t = residual concentration of heavy metals in soils (mg g^{-1}) at time t , C_0 = initial concentration of heavy metals in soils (mg g^{-1}), k = rate constant (min^{-1}), t = time (min).

The order of rate constant was $\text{Zn} > \text{Cd} > \text{Cu} > \text{Pb}$ (data not shown). Although the order of Cu and Pb was interchanged, this order was a reverse tendency to that obtained by soil adsorption (Lo et al., 1992). Among the soils, the rate constant of heavy metals was highest in soil C.

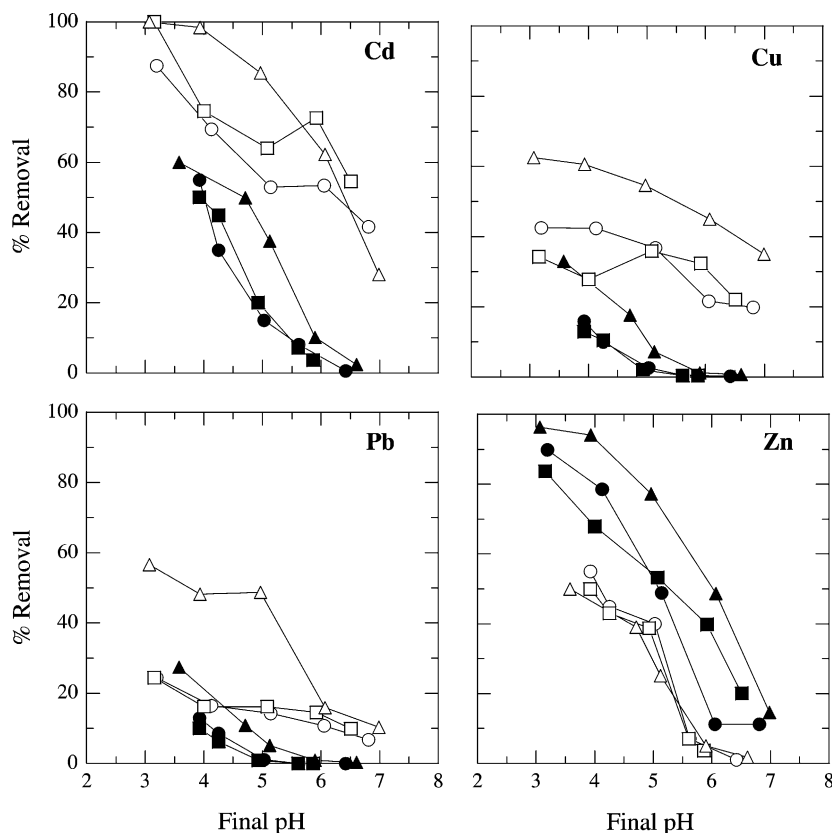


Fig. 2. Effect of pH on removal of heavy metals from soils. Each point is the average of duplicate samples (●: soil A blank, ○: soil A saponin, ■: soil B blank, □: soil B saponin, ▲: soil C blank, △: soil C saponin).

3.3. Fractionation of heavy metals in soils before and after saponin treatment

The chemical forms of heavy metals in soils can greatly influence their fate in terms of leaching and subsequent transport (Clevenger, 1990). The sequential extraction procedure has been used to evaluate the chemical forms of heavy metals in soils (Yarlagadda et al., 1995). In this study, heavy metals remained in soil residues were separated to several fractions to investigate the effect of saponin on each fraction of heavy metals. The results are presented in Fig. 4, showing the percentage of each fraction of heavy metals in soils. Although the characteristics of soil samples varied substantially, fractionation of heavy metals was similarly distributed among soils. Cadmium in soils was primarily found in exchangeable and carbonate fractions followed by Fe–Mn oxide fraction. The amount of Cd in organic matter fraction was found to be negligible. The exchangeable and carbonate fractions of Cd were almost removed from soils by saponin treatment. Cadmium in exchangeable fraction can be desorbed through

the addition of saponin containing exchangeable secondary cation (H^+). As described above, weakly acidic nature of saponin also leads to dissolve the carbonate fraction of Cd. Copper and lead was predominantly found in Fe–Mn oxide fraction followed by carbonate fraction. Zinc was primarily partitioned to carbonate fraction followed by exchangeable fraction. For Cu, Pb, and Zn, the effect of saponin was almost similar to that of Cd. Although Fe–Mn oxide and organic matter fractions were also mobilized by saponin treatment, the removal efficiency was significantly lower than exchangeable and carbonate fractions.

3.4. Recovery of heavy metals from the soil leachates after saponin treatment

To separate heavy metals from the soil leachates by alkali treatment, investigation on the solubility of saponin is a very important factor in the alkaline pH ranges. Although the solubility of saponin slightly decreased with decreasing pH, alkali treatment had no influence on the solubility of saponin. Thus, the precipitation

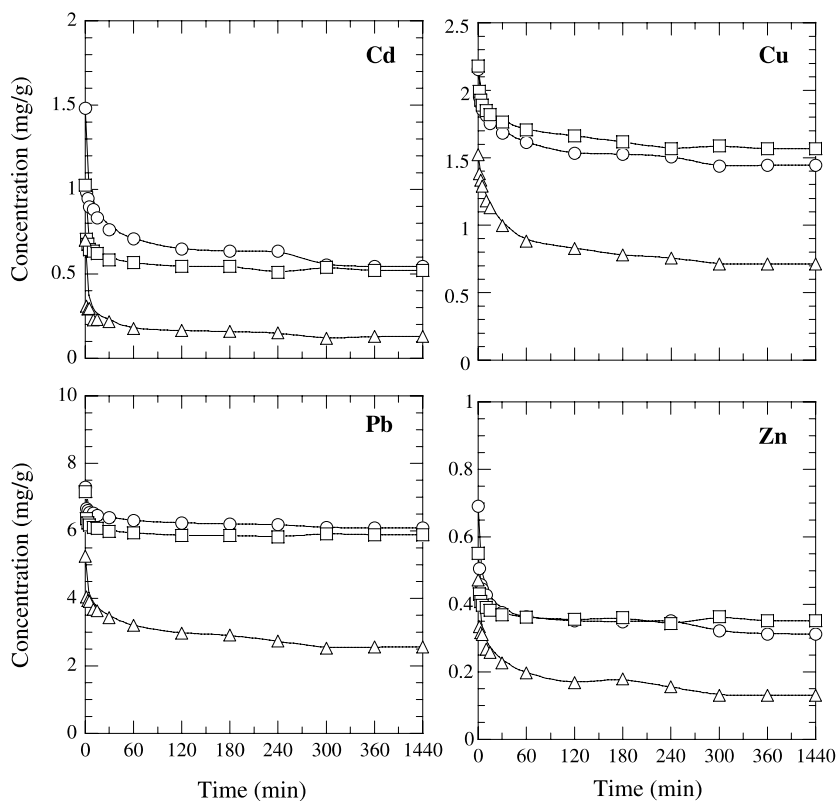


Fig. 3. Kinetics for removal of heavy metals from soils. Each point is the average of duplicate samples (O: soil A, □: soil B, △: soil C).

method was considered to be useful for recovery of heavy metals from the soil leachates. Before the leachate from soil A was subjected to the subsequent precipitation process, the concentration of heavy metals contained in that was analyzed. Their contents (C) were 1.30 mg l^{-1} of Cd, 0.92 mg l^{-1} of Cu, 1.78 mg l^{-1} of Pb, and 0.62 mg l^{-1} of Zn, respectively. Table 2 shows the precipitation ratio of heavy metals from soil A leachate by adding NaOH. Under alkaline pH ranges, heavy metals rapidly decomposed into hydroxide precipitates. The release of heavy metals was completed in less than 10 min at pH 11.6 (data not shown). Precipitation of heavy metals from soil A leachate containing saponin solution occurred at different pH values for each heavy metal. The order of heavy metal precipitation (judging at pH 10.7) was $\text{Zn} > \text{Pb} > \text{Cd} > \text{Cu}$, reflecting increase in basicity. Due to the amphoteric nature of lead, redissolution of lead compounds occurred at pH 11.6. This illustrates the importance of establishing optimal separation pH for the specific conditions encountered in actual practice. An excessively high pH for precipitation of heavy metals resulted in reduced recovery efficiency as well as greater costs for alkalization. Therefore, the optimal separation pH was considered to be about 10.7 for recovery and cost efficiency.

3.5. Efficiency of used saponin for recycle

Efficiency of used saponin on removal of heavy metals from soils was investigated for the subsequent recycle. The concentration of saponin in soil A leachate was about 2.9%. In other words, 3.7% of initial saponin concentration (3%) used for soil treatment sorbed to soil A. Used saponin was effective for removal of heavy metals from soil A. Due to the sorption of saponin onto soil A, the removal efficiency of used saponin was slightly lower than that of saponin. This result indicated that recovery of used saponin from soil A leachate was accomplished during the precipitation process of heavy metals. As a result, recycle of used saponin is considered to be effective for the subsequent utilization.

3.6. Leaching test

Table 3 shows the result of leaching test for soil residues after saponin treatment. The concentrations of heavy metals leached from soils were compared with the guideline values. Only 0.002 mg l^{-1} of Cd dissolved from soil A. For soil B and C, Cd was undetectable level. Copper was detected from 0.005 to 0.027 mg l^{-1} in soil A and B and undetectable in soil C. The concentration of

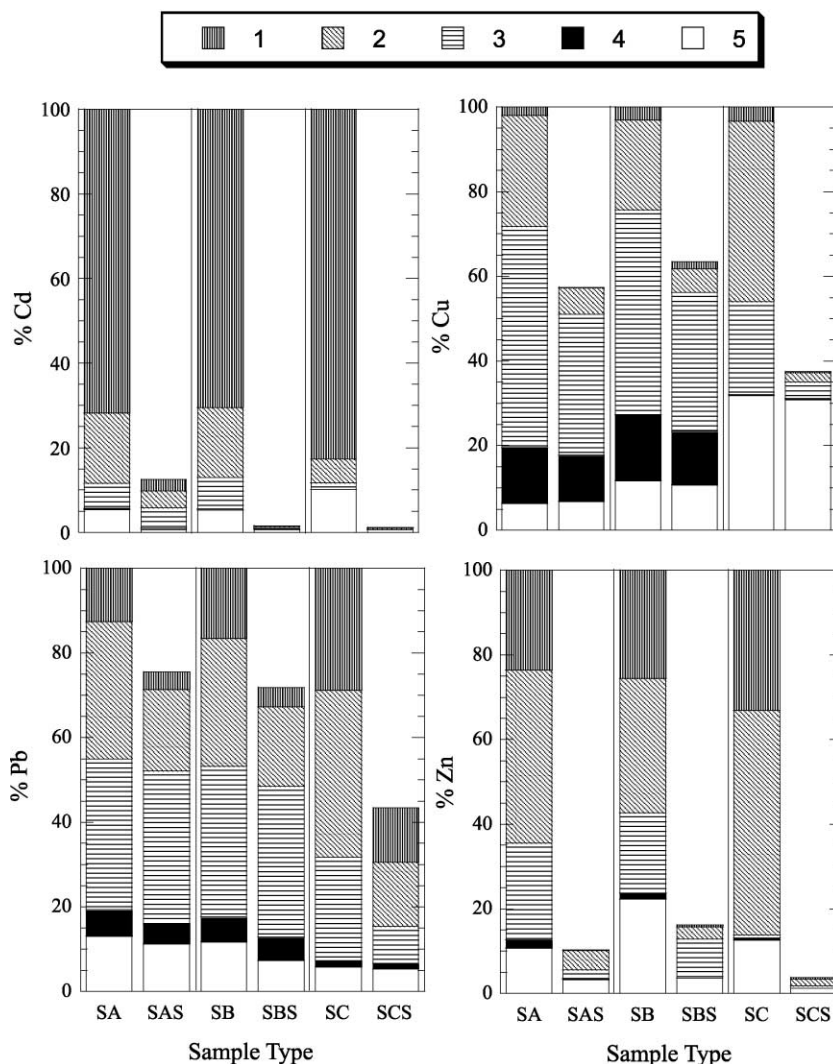


Fig. 4. Fractionation of heavy metals in soils before and after saponin treatment. Each value is the average of duplicate samples (SA: soil A before saponin treatment, SAS: soil A after saponin treatment, SB: soil B before saponin treatment, SBS: soil B after saponin treatment, SC: soil C before saponin treatment, SCS: soil C after saponin treatment, 1: exchangeable, 2: carbonate, 3: Fe–Mn oxide, 4: organic matter, 5: residual).

Pb and Zn leached from soils was undetectable level. As a whole, the concentration of heavy metals leached from the soil residues was much lower than those of the guideline values.

4. Conclusions

Utilization of saponin was effective for removal of heavy metals from contaminated soils. The optimum concentration of saponin for soil treatment seemed to be approximately 3% to avoid introduction of excess saponin into soils. The removal of heavy metals from soils increased with decreasing pH of saponin solution.

Practical treatment of soils is desirable in weakly acidic pH ranges because of less impact on the physical and chemical properties of soils. Thus, soil treatment with saponin was considered to be suitable in the pH range of 5.0–5.5. The maximum removal of heavy metals was attained within 6 h in soils. Efficiency of saponin on removal of heavy metals from soils was directly related to the chemical and physical characteristics of soils and speciation of heavy metals in soils. As a result, saponin treatment was most effective in removing the exchangeable and carbonate fractions of heavy metals from soil C. By precipitation method, heavy metals could be successfully recovered from the soil leachates after saponin treatment. The precipitation ratio of heavy metals

Table 2
Recovery of heavy metals from soil A leachate by adding NaOH^a

pH		Cd	Cu	Pb	Zn
3.2	C (mg l ⁻¹)	1.30	0.92	1.78	0.62
7.1	C_a (mg l ⁻¹)	1.27	0.88	1.64	0.60
	C_p (%)	2	4	8	3
9.6	C_a (mg l ⁻¹)	0.74	0.62	0.68	0.14
	C_p (%)	43	32	62	78
10.7	C_a (mg l ⁻¹)	0.28	0.39	0.18	0.06
	C_p (%)	86	80	90	91
11.6	C_a (mg l ⁻¹)	0.13	0.11	0.32	0.04
	C_p (%)	90	88	82	93

C (mg l⁻¹): initial concentration of heavy metals in soil A leachate.

C_a (mg l⁻¹): concentration of heavy metals in soil A leachate after precipitation process.

C_p (%): precipitation ratio of heavy metals.

^a Values are the average of duplicate samples.

Table 3
Results of the leaching test for the soil residues after saponin treatment^a

Soil	Leachate pH	Heavy metals (mg l ⁻¹)			
		Cd	Cu	Pb	Zn
A	5.1	0.002	0.027	nd	nd
B	5.1	nd	0.005	nd	nd
C	5.0	nd	nd	nd	nd
Guideline value	5.8–6.3	0.01 (1 mg kg ⁻¹ -rice)	*(125 mg kg ⁻¹ -soil)	0.01	*

Detection limit: 0.002 mg l⁻¹ of Cd, 0.002 mg l⁻¹ of Cu, 0.03 mg l⁻¹ of Pb, 0.004 mg l⁻¹ of Zn; *: guideline is not set; nd: not detected; (): for agricultural soil.

^a Values are the average of duplicate samples.

was 86% of Cd, 80% of Cu, 90% of Pb, and 91% of Zn at pH around 10.7. In addition the recycle of used saponin obtained through precipitation process was effective in removal of heavy metals from soils. The leaching test on the soil residues after saponin treatment showed that soils successfully met the environmental standard of Japan.

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