

# Concentration and Chemical Speciation of Heavy Metals in Sludge and Removal of Metals by Bio-surfactants Application

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**Abstract:** The concentration and chemical speciation of heavy metals including REEs (rare earth elements), Th (thorium) and U (uranium) in domestic sludge and electroplating sludge were investigated, and those of the domestic sludge were compared with those of natural soil. Removal of heavy metals in electroplating sludge was studied with bio-surfactants (saponin and sophorolipid) by batch and column experiments. The results suggested that heavy metals have greater concentrations and exist as more relatively unstable fraction in sludge than those in Natural soil. Nonionic saponin is more efficient than sophorolipid for the removal of heavy metals from the electroplating sludge, and mainly reacts with carbonate state (i.e., F3) and Fe-Mn oxide state (i.e., F5) fractions. The recovery efficiency of heavy metals in leachates from the electroplate sludge was attained 88%-97%. Saponin can be reused and be a promising and cost-effective material for the removal of heavy metals in sludge.

**Key words:** Sludge, chemical speciation, heavy metals, bio-surfactant, column washing.

## 1. Introduction

With the rapid development of economy and the increasing population in city, the sludge contaminated by heavy metals has been a hot issue of common concern in the world. Heavy metals in sludge can accumulate and migrate in soil, or permeate into the ground water, or be absorbed by plant, and then pose risks to human health by food chain. Heavy metals in sludge exist as six kinds of forms: water soluble state, exchangeable state, carbonate state, organic state, Fe-Mn oxide state and residual state [1, 2]. The first four states are less stable and available by living beings; the latter two states are relatively stable and difficult to be released into the environment. Thus, it is very significant to evaluate the concentration and

chemical speciation of heavy metals in sludge. Furthermore, it is urgent to remove heavy metals in sludge efficiently, still more by eco-friendly method (if possible) for the effective utilization of sludge. On the other hand, the demand for trace metals such as REEs (rare earth elements) in modern society has increased markedly in recent years. The shortage of trace metals including REEs and U (uranium) has been of concern, and the investigation of new sources of these trace metals is important from the viewpoint of resources recovery.

Domestic wastewater sludge is produced between  $7.602 \times 10^4 \text{ m}^3 \cdot \text{d}^{-1}$  and  $1.267 \times 10^5 \text{ m}^3 \cdot \text{d}^{-1}$  in China [3]. Most of domestic sludge is usually treated simply by landfill and dumping. These methods not only occupy arable land and contaminate environment, but also may waste the usable sources in sludge. Thus, it is necessary to study and find the rational use of

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domestic sludge. Currently, the part of domestic sludge is provided to use as the soil modifier or the soil fertilizer due to its nutrient-rich (N, P, K, Ca and organic matters) after the compost in China [4]. However, it is noteworthy that the use of sludge is still limited because it may contain hazardous inorganic substances such as heavy metals and radioactive elements, although the amount of organic matter and micro-organisms is reduced and the nutrient materials are easily absorbed by plant after compost.

In addition, electroplating sludge is well known as the hazardous wastes containing a large quality of heavy metals, such as Cr, Cd, Ni and Zn. Then, the sludge needs to be treated or disposed properly with effective and eco-friendly treatment technologies.

In recent years, the concentrations and distribution of heavy metals in sludge has been extensively studied. Nonetheless, most research has been mainly focused on toxic heavy metallic elements such as Cd, Pb, Cu and Cr as subject elements [5-9], on the bioavailability and toxicity of heavy metals in sludge [5, 6], and on the differences and characteristics of these elements according to different types of sludge or different treatment processes [7-9]. However, few reports have been published about the behavior and distribution of REEs, Th and U, and about comparisons between the concentrations of heavy metals in sludge and those in Natural soil. It is also important to compare the concentration and distribution of metals in sludge with those in natural soil when considering the utilization of sludge as agricultural soil in the future.

On the other hand, the investigations of methods for the removal of heavy metals from the electroplating sludge have been carried out [10-12]. Methods for the removal of heavy metal from sewage sludge include chemical extraction, bioleaching, electroreclamation and SFE (supercritical fluid extraction) [10]. Currently, there are two kinds of removal methods of heavy metals from the electroplating sludge interested, i.e., ultrasonic-assisted method and electrokinetic enhancement method. It has been proved that the two

methods are necessary and effective method for the improvement of heavy metal removal [11, 12]. However, the two methods affect the physical and chemical properties of sludge to some extent, and are energy-consuming.

Soil washing with bio-surfactants has also attracted many researchers' attention as a kind of effective and eco-friendly method for the removal of heavy metal in soil in recent years [13, 14]. The reason using bio-surfactants is primarily because of their diversity, environmentally friendly nature, higher biodegradability, possibility of large-scale production, selectivity, effectiveness under extreme conditions, and can be produced from industrial wastes and from by-products [15, 16]. However, until now researches on removal of heavy metals in sludge with this method are few. Maier et al. [17] tested the removal efficiency of rhamnolipid on Cu (copper) in artificially Cu-contaminated sludge. The results suggest that rhamnolipid-washing is an effective treatment to remove metals from sludge. In another study, Cr (chromium) recovery in actual contaminated tannery sludge was investigated with saponin solutions [18]. The results indicate that the extraction efficiency of saponin was strongly dependent on the organic matter content of the sample. The maximum Cr removal of 24.2% was obtained. Therefore, two kinds of nonionic bio-surfactants (saponin and sophorolipid) were collected, and the removal of heavy metals in electroplating sludge was performed with bio-surfactants washing in this work. Saponin is widely distributed in plants. Pure saponin is a mixture of triterpene-glycosides extracted from the bark of the tree *Quillaja saponari* [19]. It is soluble in water but not autoclavable. Saponin has been used for the removal of contaminants (organic compounds and heavy metals) in water and soil. On the other hand, sophorolipid is a kind of extracellular bio-surfactant produced by yeasts [20, 21]. It is also a mixture with differences in acetylated degree of sophorose, hydroxy fatty acid length, and hydroxyl group position on the

fatty acid. Sophorolipid is classified as lactonic form and acidic form. Generally, the lactonic form show better surface tension reducing property and biological activities [22]. It has been shown that the lactonic form is necessary, or at least preferable, for many applications [23]. Currently sophorolipid has been applied in many specific fields such as the cosmetics, detergent, petroleum, pharm-aceutical and environment industries.

The purpose of this paper is at first to investigate the behavior, distribution and characteristics of heavy metals including REEs, Th and U in domestic sludge and electroplating sludge. The second is to compare the characteristics of heavy metals including REEs, Th and U in domestic sludge with those in natural soil. The last is to study the removal/recovery process of heavy metals from electroplating sludge with bio-surfactants (saponin and sophorolipid) by batch and column experiments.

## **2. Experiments**

### *2.1 Apparatus and Reagents*

An ICP-MS (inductively coupled plasma mass spectrum) instrument (thermo scientific X-series) was used to determine the concentrations of REEs, Th and U, and an ICP-AES (inductively coupled plasma atomic emission spectrophotometer) instrument (SPS1500, Seiko Instruments Inc.) was employed to determine the concentrations of several heavy metals (Zn, Pb, Cd, Ni, Cr, Cu, Co, Mn and Fe). The operating conditions of the ICP-MS and ICP-AES are based on our other previous paper [24, 25].

Saponin was purchased commercially from Sigma-Aldrich, Inc. (Germany). It includes the carboxyl group (-COOH) based on the analysis of quillaja bark [39]. Sophorolipid was supplied by State Key Laboratory for Microbial Technology (Shandong University, China) [26].

Heavy metal standard solutions, including REEs, Th and U, were purchased from SPEX CertiPrep, Inc. (USA). Each working standard solution was prepared

by diluting the original standard solution. All other chemical reagents, purchased from Kanto Chemical Co., Inc. (Japan), were of analytical grade. Water (> 18.2 M $\Omega$ ), which was treated using an ultrapure water system (Advantec aquarius, RFU 424TA), was employed throughout the work.

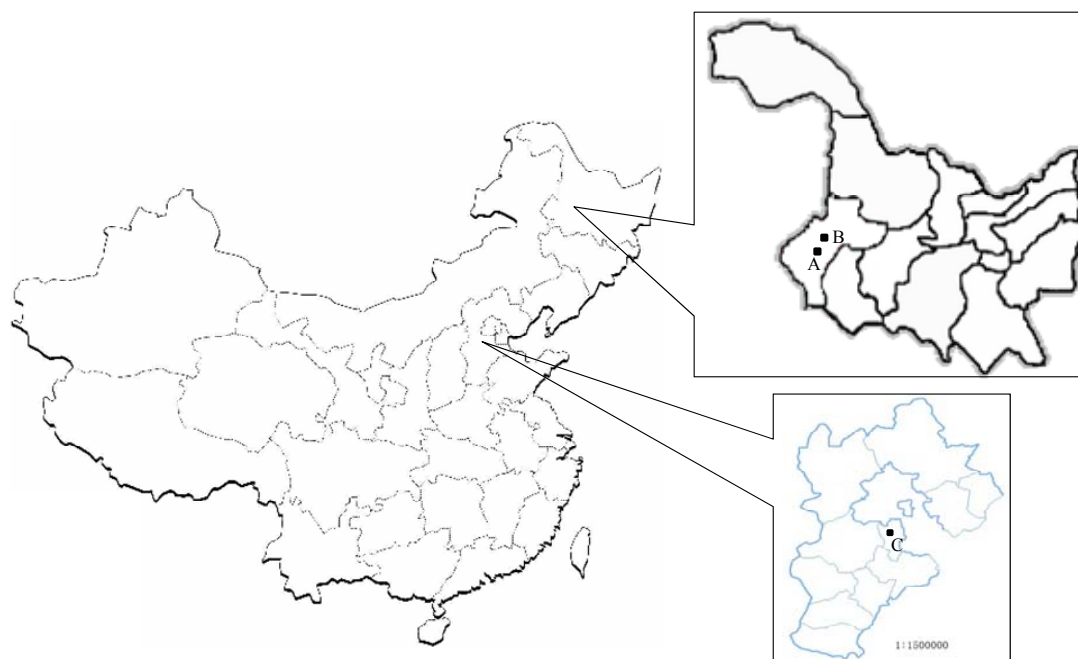
### *2.2 Samples*

Two kinds of sludge samples used in this work were collected from a domestic wastewater treatment plant in Qiqihar of Heilongjiang Province and from an electroplate factory in Langfang of Hebei Province, China (September 2011). For a reference, natural soil samples (i.e., no plow soil) were also collected from Chaoxian village, Qiqihar City (denoted as Natural soil A), China. Location of sampling points for soil and sludge is shown in Fig. 1 (A: Chaoxian village, Qiqihar City, Heilongjiang Province, China; B: The domestic wastewater treatment plant, Qiqihar City, Heilongjiang Province, China; C: The electroplate factory, Langfang City, Hebei Province, China). The sludge and soil samples were air-dried and removed coarse sand and stone, then ground and sieved through 120 mesh (0.125 mm).

The pH, EC (electric conductivity), moisture content and CEC (cation exchange capacity) in the air-dried sludge and soil samples were measured based on the same method used in our previous work [27]. For measuring organic matter content, 10 g air-dried sludge samples were heated for 2 h at 105 °C, then burned at 550 °C in a furnace for 6 h. Organic matter content was estimated from the weight differences of the sludge before and after burning divided by the sludge weight before burning. Permeability is an important physical parameter to determine the feasibility of the soil flushing process. Therefore, the permeability of the sludge was also determined using the Unfirmated Water Head Test [28].

### *2.3 Determination of Metallic Elements in Sludge*

For measuring total metal content, the sludge and



**Fig. 1** Location of sampling points for soil and sludge.

soil samples were digested with  $\text{HNO}_3$ -HF by using the microwave digestion method based on EPA3051A [29]. After digestion, the solution obtained was evaporated acid then was diluted to 100 mL using 3%  $\text{HNO}_3$  solution, and filtered through 0.45  $\mu\text{m}$  membrane for analysis.

For fractional metal content, all heavy metals including REEs, Th and U in sludge and soil samples were partitioned into six fractions with sequential extraction procedures [30, 31]. These six fractions: water soluble, exchangeable, bound to carbonates, bound to organic matter, bound to Fe-Mn oxides and residual were denoted as F1, F2, F3, F4, F5 and F6, respectively. For the initial step in this sequential extraction procedure, 7 g of dried sludge (or soil) sample in 100 mL polypropylene centrifuge tube was used. Following extraction in each step, the mixture of sludge (or soil) and each extraction reagent was centrifuged (3,000 rpm  $\times$  30 min) using a centrifugal separator (Kubota Co. 5200). This procedure is the same used in our previous work [27].

After these, the concentrations of metallic elements in each fraction were determined with ICP-AES or

ICP-MS as well as the total metal concentration.

#### 2.4 Batch Test and Column Test

Effect of the concentration and pH value of bio-surfactant solution on the removal of heavy metals in the electroplate sludge was investigated in batch experiments at room temperature (25  $^\circ\text{C}$ ). Each 0.5 g of the electro-plate sludge was weighed into a centrifuge tube, and 25 mL of bio-surfactant solution, varying initial concentrations from 5  $\text{g}\cdot\text{L}^{-1}$  to 50  $\text{g}\cdot\text{L}^{-1}$ , was added to each tube. The tubes were then shaken in a reciprocating shaker for 24 h to attain equilibrium. The suspension was centrifuged (3,000 rpm  $\times$  30 min) using a centrifugal separator (Kubota Co. 5200). The filtrate obtained were evaporated to near dryness on a hot plate, and redissolved with 3%  $\text{HNO}_3$  solution for analysis. Subsequently, the effect of pH value (varying from 2.5 to 6.5) was investigated with the same procedure as above- mentioned.

Column tests were also conducted to remove heavy metals from the electroplate sludge at the optimum concentration and pH in the bio-surfactant solution obtained from the batch experiments. The operation method in detail was the same as shown in the paper [2].

### 2.5 Recovery of Heavy Metals and Reuse of Saponin from Sludge Leachates

The precipitation method was applied by using 3 mol·L<sup>-1</sup> NaOH (sodium hydroxide) solution [32]. The leachates from the electroplate sludge washed with 25 g·L<sup>-1</sup> and 30 g·L<sup>-1</sup> saponin solution (pH = 2.5) were used as Sample 1 and Sample 2. The pH value of the leachate was gradually increased to pH 11 so that heavy metals were precipitated as hydroxide. The suspension was allowed to stand for 24 h before being centrifuged, and after that, the concentrations of heavy metal and saponin were analyzed with ICP-AES and UV-Vis spectrophotometer (HITACHI, U-5100), respectively. All samples were diluted by 100 times for the measurement of saponin by UV-Vis ( $\lambda_{max} = 279.9$  nm). Thereafter, the saponin solution recovered was adjusted to pH 2.5 with 3 mol·L<sup>-1</sup> HNO<sub>3</sub> again, then batch experiment procedure with the recovered saponin was followed as shown in Section 2.4. The process above-mentioned was repeated for two times to confirm the effectiveness of recovered saponin.

## 3. Results and Discussion

### 3.1 Characterization of Sludge

Physical and chemical characteristics of sludge and soil were shown in Table 1. The electroplate sludge is alkaline judging from pH (H<sub>2</sub>O) and pH (KCl) values. EC values of the two kinds of sludge are higher than those of natural soil A. It indicates that there is a large amount of ionic substance in these sludge samples,

which is also confirmed from the high CEC values. On the other hand, organic matter content in the domestic sludge is much larger than that in the electroplate sludge or that in national soil A, which is coincide with the characteristics of the domestic sludge. It is known that soil flushing proves effective only for permeable soil ( $K > 1.0 \times 10^{-3}$  cm·s<sup>-1</sup>) [33]. The permeability of the electroplate sludge studied in this work ( $K \approx 6.16 \times 10^{-4}$  cm·s<sup>-1</sup>) is much lower than the value of permeable soil, so quartz sand was added into the sludge to improve its permeability in column washing experiments.

### 3.2 Concentrations and Distribution of Heavy Metals in Sludge

The concentrations of heavy metals (Zn, Pb, Cd, Ni, Cr, Cu, Co, Mn and Fe) in sludge and soil are listed in Table 2. The RSD (relative standard deviation) of the triplicate analyses of each sample was less than 5%. From Table 2, the metallic elements concentrations in the domestic sludge do not exceed the limit of the national standards about pollutants in sludge from agricultural use, China [34]. However, they are extremely high in the electroplate sludge, even as high as  $1.25 \times 10^4$  mg·kg<sup>-1</sup>,  $3.05 \times 10^4$  mg·kg<sup>-1</sup>,  $4.28 \times 10^4$  mg·kg<sup>-1</sup> and  $2.53 \times 10^3$  mg·kg<sup>-1</sup> for Zn, Ni, Cr and Cu, respectively. It suggests that the electroplate sludge has been severely polluted with heavy metals. It is also found that the concentrations of heavy metals in domestic sludge are higher than those in natural soil A. The reason may be that the domestic sludge was

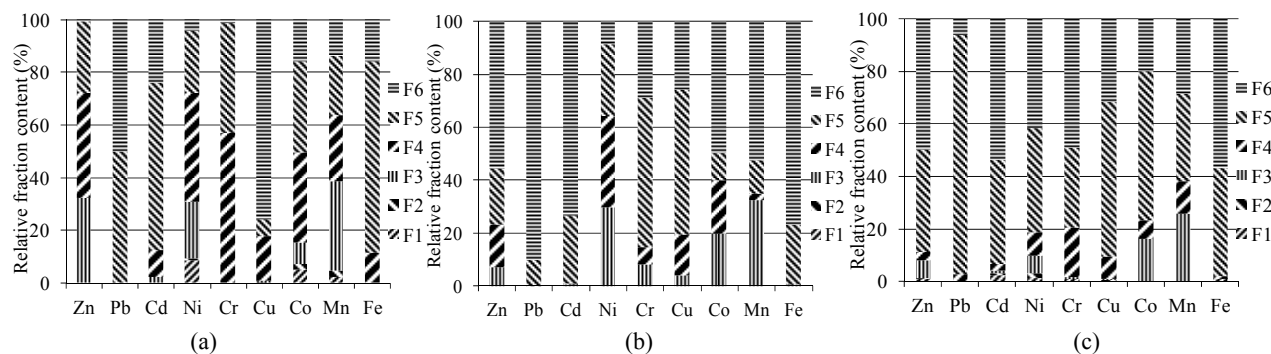
**Table 1 Physical and chemical characteristics of sludge and soil.**

Parameters	Domestic sludge	Electroplate sludge	Natural soil A
pH (H <sub>2</sub> O)	6.39	8.76	7.81
pH(KCl)	6.21	8.58	6.72
EC (μS·cm <sup>-1</sup> )	$9.94 \times 10^3$	$3.22 \times 10^4$	86.7
Moisture content (%)	7.85	14.75	1.54
Permeability (cm·s <sup>-1</sup> )	-	$6.16 \times 10^{-4}$	-
Organic matter content (%)	48.8	13.67	4.13
CEC (cation exchange capacity) (cmol·kg <sup>-1</sup> )	$1.07 \times 10^2$	$1.76 \times 10^2$	15.9

-: means the data was not determined or obtained.

**Table 2** The concentrations of heavy metals in sludge and soil ( $\text{mg}\cdot\text{kg}^{-1}$ ).

Sample	Zn	Pb	Cd	Ni	Cr	Cu	Co	Mn	Fe
Domestic sludge	691	46.2	10.0	26.9	121	108	6.42	509	$4.30 \times 10^4$
Natural soil A	44.7	11.6	3.78	11.0	20.6	6.51	5.00	351	$1.58 \times 10^4$
Electroplate sludge	$1.25 \times 10^4$	352	49.6	$3.05 \times 10^4$	$4.28 \times 10^4$	$2.53 \times 10^3$	35.1	$1.36 \times 10^3$	$3.38 \times 10^5$



**Fig. 2** The relative fraction of heavy metals in (a) domestic sludge, (b) electroplate sludge and (c) natural soil A.

mainly produced accompanying with wastewater from many kinds of paths such as small chemical factories, hospitals, municipal water for public, sanitary sewage and so on. Among these metallic elements investigated, the concentrations of Zn and Cu in domestic sludge were about 15 and 16 times of those in natural soil A. Zn and Cu are necessary for plant and/or soil microbe to some extent, so they are beneficial in a certain concentration range, and are toxic at elevated concentration. Pb, Cd and Cr (as the three elements of the most toxic five metallic elements (As, Pb, Hg, Cd and Cr)) are never essential. Their concentrations in domestic sludge were about 2.5-6.0 times of those in Natural soil A. Pb is easily adsorbed to soil clay as carbonate or phosphate, and not migrated. Generally, the risk of lead poisoning through the food chain increases as the lead level in soil rises above 300 ppm [35]. Cd is very easily absorbed by plant, especially for rice, and produces toxicity to animal and human through the food chain. Cr may transfer between Cr (VI) (i.e., toxic, soluble species) and Cr (III) (i.e., less-toxic, less-soluble species) affected by the organic matter contents (such as humic substances) in soil [25], and the mobility and the absorption of Cr by crops are varied. In addition, the concentrations of Ni and Co in domestic sludge

were 2.4 times and 1.3 times of those in Natural soil A. These results suggest that heavy metals in domestic sludge may tend to accumulate in agricultural soil if the sludge is used repeatedly as fertilizers or soil modifier.

It is well known that the influence of heavy metal in soil on environment and plant mainly depends on the mobile fraction or available fractions rather than the total content. Then, the relative distribution of heavy metals in sludge and natural soil A is investigated and is shown in Fig. 2. It suggests that the relative distribution characteristics of heavy metals in two sludge samples are obviously different from those in Natural soil A. In domestic sludge, Pb almost completely exists as the residual fraction (F6) and Fe-Mn oxide fraction (F5), and Cu mainly exists as organic fraction (F4) following the residual fraction (F6). In case of Cd and Fe, F5 fraction is primary except F6. Carbonate fraction (F3) is the greatest proportion among six fractions for Mn, whereas F5 and F4 are main proportion for other heavy metals. Furthermore, F3 and F1 for Ni, F3 for Zn, and F3 and F1 for Co exist as a certain proportion. On the other hand, Pb, Cd, Cr and Cu mainly exist as Fe-Mn oxides fraction (F5) in addition to the residual fraction (F6) in electroplate sludge. Mn exists as F3 following F6.

However, Zn, Ni and Co mainly exist as nearly equally proportion of F5, F4 and F3. From above-mentioned results, it is noted that F3 proportion of metallic elements is mostly large in these sludge. Therefore, the authors should treat and dispose these elements with caution because F3 are apt to be released into water environment and soil environment.

Comparing Fig. 2a and Fig. 2c, the proportion of residual fraction (F6) in natural soil A is relatively larger than that in domestic sludge. In contrast, it can be observed that the proportions of organic fraction (F4), carbonate fraction (F3) and water soluble (F1) in domestic sludge are larger than those in natural soil A. From these results, it is found that heavy metals in domestic sludge usually exist in a more unstable state than those in natural soil. It indicates that heavy metals in domestic sludge are easy to permeate into groundwater or to be absorbed by crops. On the other hand, the high proportion of organic fraction and carbonate fraction in sludge may be due to large contents of organic matter and anaerobic environment in sludge.

In brief, the concentrations of heavy metals in sludge are larger than those in natural soil. In addition, the relative distribution of residual fraction in sludge is lower than that in natural soil, whereas the proportion of organic fraction and carbonate fraction in sludge is higher than that in natural soil.

### 3.3 Concentrations and Distribution of REEs, Th and U in Sludge

REEs, Th and U were also extracted from the sludge along with heavy metals, and determined with ICP-MS. The concentrations of these elements are shown in Table 3. The RSD (relative standard deviation) of the triplicate analyses of each sample was less than 10%. From Table 3, the concentrations of REEs, Th and U are variable depending on the kinds of sludge. They are much lower than those in natural soil A. However, REEs pattern in domestic sludge is similar to that in natural soil A due to the

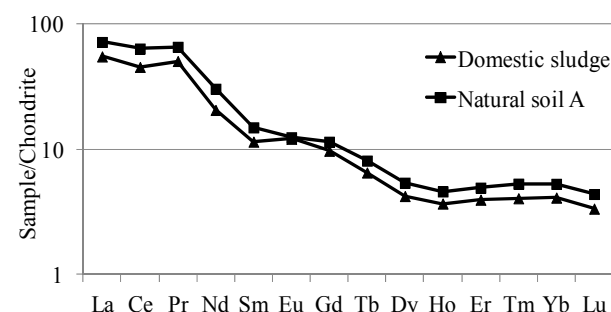
same sampling place (Fig. 3).

On the other hand, the concentrations of REEs, Th and U in electroplate sludge are much lower than those in natural soil A. One possible reason is that REEs, Th and U can be hardly transferred into water and settled in the sludge at pH > 8 [36-38].

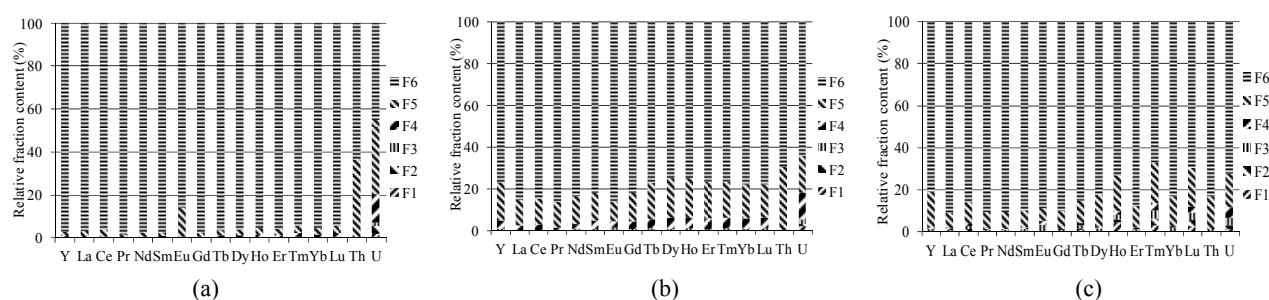
The relative distribution of REEs, Th and U is shown in Fig. 4. Comparing Fig. 4a and Fig. 4b, it can be found that the residual (F6) of REEs in domestic sludge is higher than that in Natural soil A, whereas the proportions of F5 and F4 are lower than those in natural soil A. In addition, it is noticeable that the exchangeable proportion (F2) of U is remarkably higher in domestic sludge than that in natural soil A, because exchangeable fraction of metals is generally

**Table 3 The concentrations of REEs, Th and U in sludge and soil (mg·kg<sup>-1</sup>).**

Metallic elements	Domestic sludge	Natural soil A	Electroplate sludge
La	20.7	27.0	2.79
Ce	44.1	61.8	2.51
Pr	6.95	9.03	0.527
Nd	14.7	21.7	1.96
Sm	2.64	3.43	8.96 × 10 <sup>-2</sup>
Eu	1.04	1.07	0.145
Gd	3.02	3.57	0.722
Tb	0.37	0.46	2.48 × 10 <sup>-2</sup>
Dy	1.65	2.11	9.10 × 10 <sup>-2</sup>
Ho	0.32	0.4	1.57 × 10 <sup>-2</sup>
Er	1.01	1.26	6.61 × 10 <sup>-2</sup>
Tm	0.13	0.17	7.07 × 10 <sup>-3</sup>
Yb	0.9	1.16	4.73 × 10 <sup>-2</sup>
Lu	0.13	0.17	7.24 × 10 <sup>-3</sup>
Th	5.39	11.2	0.158
U	1.86	2.08	0.136



**Fig. 3 REEs patterns of domestic sludge and natural soil A.**



**Fig. 4** The relative fraction of REEs, Th and U in (a) domestic sludge (b) natural soil A and (c) electroplate sludge.

considered as the directly available content in crops. For the electroplate sludge, the distribution characteristics of REEs, Th and U are generally similar to those of Natural soil A. However, F1 to F4 proportion of HREE and U can be obviously observed because of their low concentrations.

As mentioned above, the concentrations of REEs, Th and U in the sludge are lower than those in Natural soil, and REEs and Th in the sludge exist as relative stable fraction. These results are contrastive to the characteristics of heavy metals in the sludge mentioned in Section 3.2.

### 3.4 Removal of Heavy Metals in Electroplate Sludge

The removal of several heavy metals (Zn, Ni, Cr, Cu, Mn and Fe) in electroplate sludge was investigated with elution technology by using bio-surfactants (sophorolipid and saponin). To investigate the factors influencing the removal efficiency of bio-surfactant, the effects of the concentration and pH value of the bio-surfactant solution in batch experiments, and the washing volume of the bio-surfactant solution in column experiments were tested in this work.

#### 3.4.1 Batch Experiments

Effect of the concentrations and pH value of the bio-surfactants solution on the removal efficiency of heavy metals are shown in Figs. 5 and 6. The concentrations are ranged from  $5 \text{ g}\cdot\text{L}^{-1}$  to  $50 \text{ g}\cdot\text{L}^{-1}$ , and pH varied from 2.5 to 6.5. The removal efficiency of heavy metals generally ascended with the increase of the concentration and the decrease of pH value for

both bio-surfactants, although the concentration ( $20.0 \text{ g}\cdot\text{L}^{-1}$ ) and pH value (4.5) are optimal for most of heavy metals in electroplate sludge with sophorolipid solution. However, it is clearly observed that the removal efficiency of heavy metals is much higher with saponin solution than with soporolipid solution under the same conditions. In other words, saponin is more efficient than sophorolipid for the removal of heavy metals in this experiment. Although both bio-surfactants are nonionic, saponin used in this work contained the carboxyl group in sapogenin moiety [39]. For this reason, saponin reacts more easily with metallic elements, and to make metallic elements departed from the sludge surface into the soil solution. Thus, only the results using saponin are discussed in the following. The removal efficiency of each metal is greatest when the concentration of saponin solution (i.e.,  $50 \text{ g}\cdot\text{L}^{-1}$ ) is the highest (Fig. 5b). There are two processes for the removal of heavy metals in sludge by bio-surfactant washing. The first is though the complexation of the free metal in residing solution by bio-surfactant, which decreases the activity of the metal in solution, therefore, promotes desorption of the metal from sludge. The second is sorption of the bio-surfactant on the sludge particle surface, complexation with the sorbed metal on the surface; detachment of the complex of bio-surfactant and metal from the sludge surface into the sludge solution, and incorporation of the metal into bio-surfactant micelles by ion exchange, precipitation-dissolution, counterion association and so on [40, 41]. Generally, bio-surfactants are required to have minimal sorption



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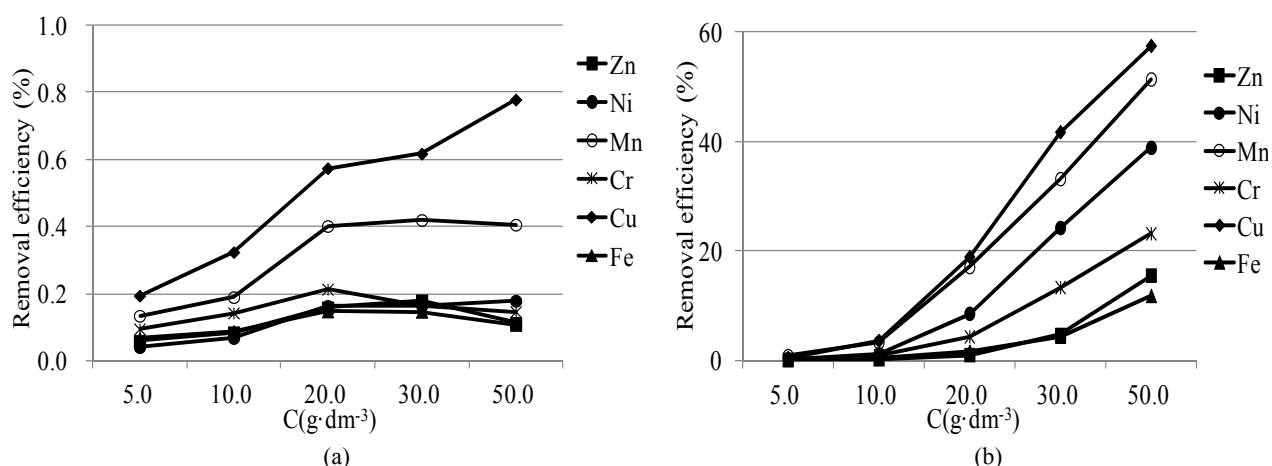


Fig. 5 Effect of (a) sophorolipid and (b) saponin concentrations on removal of heavy metals in electroplate sludge.

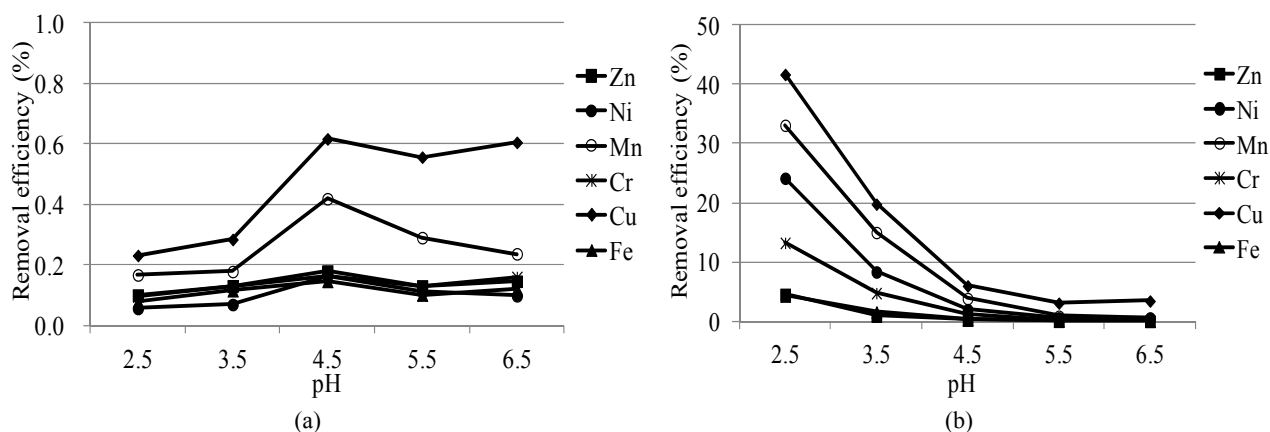


Fig. 6 Effect of pH value of (a) sophorolipid and (b) saponin solution on removal of heavy metals in electroplate sludge.

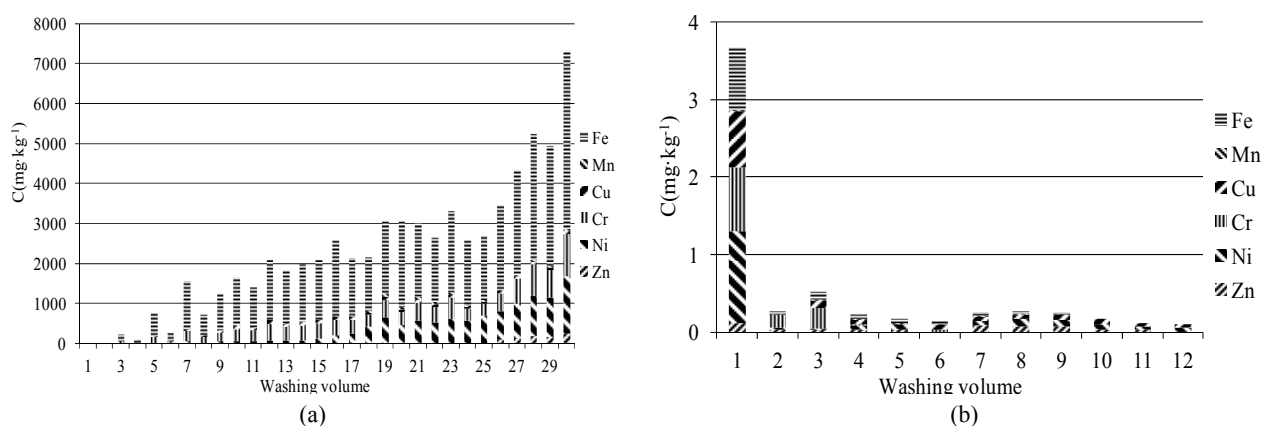
to the sludge to remain enough bio-surfactants in the aqueous phase for both processes. However, the sorption of bio-surfactants in sludge is inevitable, so high saponin concentration is required for the effective removal of metal. Then  $50 \text{ g}\cdot\text{L}^{-1}$  saponin solution was selected for the following column experiments.

From Fig. 6b, it is shown that the removal efficiency of metals is dependent on pH. When the pH value of saponin solution is higher than its  $\text{pK}_a$  (4.6), the removal efficiency is low. It may be considered, that sodium ions, which increased by adding NaOH to adjust pH of saponin solution, competes with heavy metals for saponin. In contrast, when the pH value was lower than its  $\text{pK}_a$ , the removal efficiency abruptly increased. On the other hand, the surface/intersurface tension of bio-surfactants depends on the solution pH as

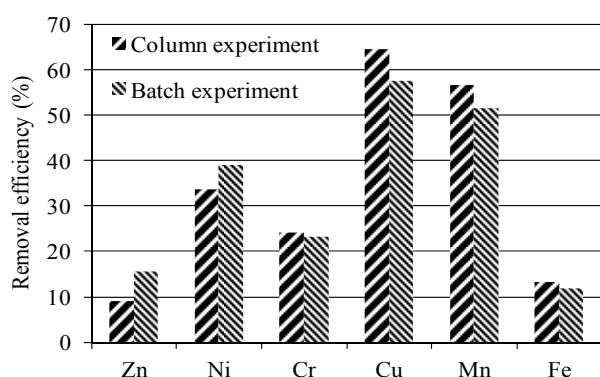
well as the type and size of aggregate (bilayers, vesicles and micelles) formed by bio-surfactant monomers [42]. These all factors indirectly affect the removal efficiency of the metals in sludge with varying pH values. The results show that the removal efficiency of metallic elements in the electroplate sludge is highest when the pH value is 2.5, which is not different in the case of the artificially polluted sludge [2]. The electrostatic attraction between saponin and sludge surface does not play a decisive role at low pH because of large quantity of metallic elements in the electroplate sludge. Therefore, pH 2.5 saponin solution was collected for the following column experiments.

#### 3.4.2 Column Experiments

The concentrations of heavy metals removed from the electroplate sludge with washing volume through column are illustrated in Fig. 7. In addition to saponin



**Fig. 7** Effect of washing volume on removal of heavy metals in the electroplate sludge (a) saponin (b) ultrapure water (1 w.v. (washing volume) = 6.2 mL).



**Fig. 8** Removal efficiency of heavy metals in the electroplate sludge by batch experiment and column experiment. Batch experiment: 0.5 g sludge, pH 2.5, 5% saponin solution, 25 mL. Column experiment: mass ratio of sludge and quartz sand = 1:4, pH 2.5, 5% saponin solution, 30 volumes (1 w.v. = 6.2 mL).

solution, ultrapure water was also performed as the control.

As seen in Fig. 7a, any metals hardly detected with leachate at initial stage of washing, which may be attributable to the fact that heavy metals in electroplate sludge exist mainly as relatively stable state throughout long-term contamination. Therefore, long contact time is needed to make metals divorced from the sludge surface into leachate. The removal of most metals (i.e., Zn, Ni, Cr and Fe) has been increasing with the increase of washing volume. The concentrations of Cu and Mn in electroplate sludge are low ( $2.528 \text{ g}\cdot\text{kg}^{-1}$  and  $1.355 \text{ g}\cdot\text{kg}^{-1}$ , respectively), so the removal of the two elements shows a peak through 30 washing volumes.  $1.127 \text{ g}\cdot\text{kg}^{-1}$  of Zn,  $10.23 \text{ g}\cdot\text{kg}^{-1}$

of Ni,  $10.34 \text{ g}\cdot\text{kg}^{-1}$  of Cr,  $1.632 \text{ g}\cdot\text{kg}^{-1}$  of Cu,  $0.7696 \text{ g}\cdot\text{kg}^{-1}$  of Mn and  $44.29 \text{ g}\cdot\text{kg}^{-1}$  of Fe were removed overall from total loaded concentration respectively, and almost the same removal efficiency was obtained as in the case of batch experiment when using  $50 \text{ g}\cdot\text{L}^{-1}$  pH 2.5 saponin solution (Fig. 8). The total removal efficiency of Zn, Ni, Cr, Cu, Mn and Fe were reached 8.99%, 33.6%, 24.2%, 64.5%, 56.4% and 13.1% after 30 washing volumes, respectively. The results indicate that saponin is effective for removing the heavy metals from the actual electroplate sludge, and that saponin facilitates mobilization of metals selectively, and that the leaching behavior of bio-surfactant is dependent on the characteristics of the metals and of the sludge. This may be due to the specificity of bio-surfactant for each metal and the co-existence of metals in the sludge. Hong et al. [32] reported that 36%-62% of Cu and 85%-98% of Zn were removed from soils by saponin treatment. The maximum removal rate of Cr, that is 24.2%, was obtained from tannery sludge by washing with saponin solution based on the research by Kilic et al. [18]. By contrast, the removal efficiencies of Cu and Cr in this work are similar to those reported, although the removal efficiency for Zn is very low. These results may be attributed to the coexistence of many kinds and high concentration of heavy metals in the electroplate sludge investigated. In other words, these results are produced by the differences of the media investigated

### Concentration and Chemical Speciation of Heavy Metals in Sludge and Removal of Metals by Bio-surfactants Application

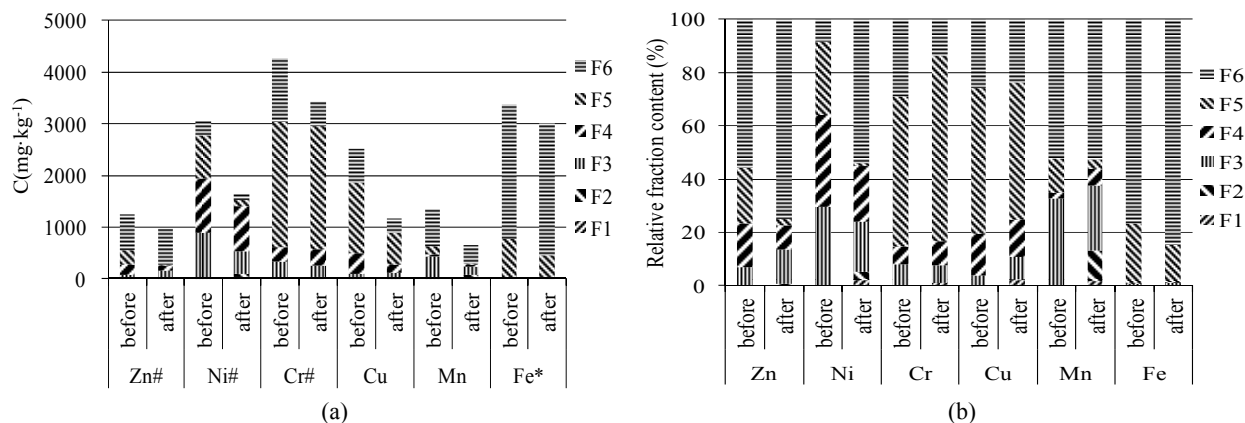
and by the differences of the concentrations of coexisting-metals. Although the removal efficiency of each metal is relative low, the removal amount is extremely large. Thus, this method can be a promising method for the recovery of metals from the electroplate sludge. Fig. 7b shows that hardly any metals were removed by ultrapure water with the same pH value except the removal of a small quantity of metals ( $< 4 \text{ mg}\cdot\text{kg}^{-1}$ ) existed mainly as water soluble state. The results indicate that saponin has high potential for the removal of heavy metals from the sludge compared to ultrapure water. From these results, column washing method is more effective for the sludge which suffers small-scale pollution (i.e., fewer kinds and low concentration of heavy metal) and short-term pollution than that for the sludge with large-scale pollution (i.e., many kinds and high concentration of heavy metal) and long-term pollution. Then, in order to improve the removal efficiency and to save the time, more detailed studies need to be conducted on the elucidation of mechanisms of bio-surfactants for the removal of heavy metals.

#### 3.4.3 Confirmation of Fraction Removed by Saponin Solution

Sequential extraction was conducted after column washing to confirm the fractions of heavy metals removed with saponin treatment. The concentrations and the relative distribution of heavy metals in the electroplate sludge before and after column washing

are shown in Fig. 9. A remarkable decrease of total concentration was found for each heavy metal as shown in Fig. 9a, and the concentration in each fraction was all changed regardless of the kind of metals. The concentrations of F1 and F2 for all metals, and F3 for Zn and Fe increased due to the residual saponin after column washing. For example, the total distribution ratio of F1 and F2 for Ni increased from nearly zero to 5%, and that for Mn increased up to 12%. The concentrations of F5 and F6 for all elements decreased after the column experiment (e.g., F5 of Zn reduced by 90%), and the concentrations of Ni, Cr, Cu and Mn in F3 also declined. It indicates that saponin can be effective to remove the metallic elements in residual fraction (F6) as well as those existed in carbonate fraction (F3) and oxide fraction (F5). In addition, it is noteworthy that F5 of Zn, Ni and Mn seem to react preferentially with saponin than F3 because of small F5 distribution proportion as shown in Fig. 9b. In addition, it is found that the proportion of the relative stable fraction of heavy metals becomes higher after column washing, and that the relative distribution characteristics of heavy metals are closer to those in natural soil.

From the above-mentioned, saponin is efficient for the removal of heavy metals from the electroplate sludge in this work. Removal efficiency of heavy metals by saponin depends on the species and existing forms of metals in sludge.



**Fig. 9** Variation of heavy metals in electroplate sludge before and after the column experiment: (a) concentrations (# and \* means 1/10 and 1/100 of the actual concentration), (b) relative fraction.

### 3.5 Recovery of Heavy Metals and Reuse of Saponin from Sludge Leachates

The precipitation method was applied for the recovery of heavy metals and the reuse of saponin solution from the sludge leachates. The leachates from the electroplate sludge washed with 25 g·L<sup>-1</sup> and 30 g·L<sup>-1</sup> saponin solution (pH 2.5) were used, and denoted as Sample 1 and Sample 2, respectively. The recovery efficiencies of heavy metals from the leachates at pH 11 are shown in Table 4. The concentrations and recovery efficiencies of saponin in the leachates are listed in Table 5.

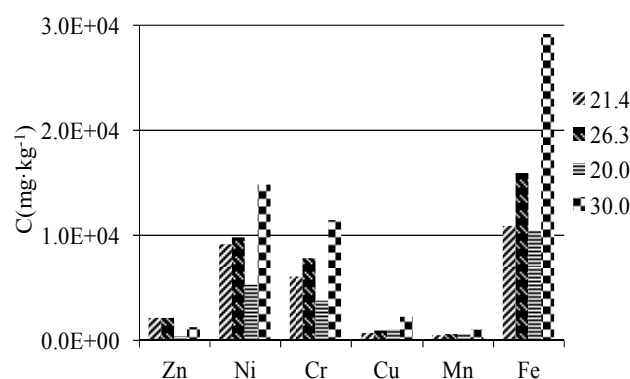
From Table 4, the recovery efficiency of each metallic element is varied between Sample 1 and Sample 2 because of the different original concentration of each metal in two leachates. However, it is found that the higher the concentration of metallic elements is, the higher the recovery efficiency is. The recovery efficiencies of the metallic elements are almost more than 90%, although the recovery efficiency of Cr is 88% in Sample 1 because the hydroxide compound of Cr is amphoteric and redissolved partly at pH 11.

From Table 5, the concentration of saponin in leachates decreases from initial concentration of 25 g·L<sup>-1</sup> to 24.7 g·L<sup>-1</sup> (or 30 g·L<sup>-1</sup> to 28.1 g·L<sup>-1</sup>) due to the sludge adsorption. The recovery efficiencies of saponin at first time are 86.6% for Sample 1 and 93.6% for Sample 2. The recovery efficiencies of saponin after reusing are 62.3% and 75.4%, respectively. It is obvious that the recovery efficiency

at the second time becomes lower with increasing the recycling times. From these results, it is found that alkaline precipitation is an effective method to separate saponin and heavy metals in the leachates. Furthermore, losing a part of saponin may be attributed to the adsorption on sludge surface and/or hydroxide compounds surface.

The concentrations of several metals removed with saponin solution recovered at first time were compared with those from the batch experiment shown in Fig. 10. It is found that the recovered saponin remains the satisfactory ability of removing heavy metals from the sludge. It suggests that saponin should be able to withstand the repeated use, and hence it can be a promising material for saving the cost.

Although some metallic elements in the electroplate sludge were removed with saponin, the residual



**Fig. 10** Removal of heavy metals in the electroplate sludge with the recovered saponin: (1) 21.4 and 26.3 are the concentrations of saponin in solution the first time recovered from Sample 1 and Sample 2; (2) 20.0 and 30.0 are the concentrations of saponin in solution used in batch experiment.

**Table 4** The recovery efficiency of heavy metals from the sludge leachates (%).

Metallic elements	Zn	Ni	Cr	Cu	Mn	Fe
Sample 1	97	94	88	98	96	92
Sample 2	78	70	62	57	74	64

**Table 5** Recovery and reuse of saponin.

Sample	$C_{saponin}$ (g·L <sup>-1</sup> )			Recovery efficiency (%)	
	C0	C1	C2	1st time	2nd time
1	24.7	21.4	15.4	86.6	62.3
2	28.1	26.3	21.2	93.6	75.4

concentrations are still high. Nevertheless, this work has quantitatively shown that saponin could be an efficient sorbent for the removal of heavy metals from sludge to some extent. However, further investigations are needed to improve the efficiency of removal process by saponin.

#### 4. Conclusions

The behavior and distribution characteristics of heavy metals including REEs, Th and U were investigated in the sludge from a domestic wastewater treatment plant and an electroplate plant. In addition, the characteristics in the domestic sludge were compared with that in the natural soil from the same sampling places. Furthermore, the removal/recovery process of heavy metals in the electroplate sludge was studied with bio-surfactant elution by batch and column experiments. Finally, the recovery and the reuse of saponin were performed. Consequently, the following matters have been obtained.

- The concentrations of heavy metals in sludge are larger than those in natural soil. Moreover, in case of sludge, the relative distribution of unstable fraction is larger than that in natural soil.

- Nonionic saponin is more efficient than sophorolipid for the removal of heavy metals from the actual electroplate sludge. Saponin has selectivity for the mobilization of heavy metals, and mainly reacts with F3 and F5 fractions of heavy metals.

- The recovery efficiency of heavy metals (Zn, Ni, Cr, Cu, Mn and Fe) in leachates from the electroplate sludge was attained 88%-97%.

- Saponin can be reused, and hence it can be a promising and cost-effective material.

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