

# Fundamental study on volume reduction of heavy metal-contaminated soil by magnetic separation

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## Abstract

Large-scale civil engineering works discharge a large amount of soil suspension contaminated with natural heavy metals. Most of the heavy metal ions due to industrial activities and minings are accumulated in the soils and the sediments of lakes and inner bays through the rivers. It is necessary to remove heavy metals from the soils and the sediments, because some of these heavy metals, such as arsenic and cadmium, have significant biological effects even in small amounts. This study proposes a new volume reduction method of the contaminated soils and sediments by superconducting magnetic separation. Our process can remove the specific minute minerals selectively, which adsorbs heavy metals depending on pH. As a fundamental study, the adsorption behaviors of arsenic and cadmium on minute minerals as a function of pH were investigated, and the adsorption mechanism was discussed based on the crystal structure and pH dependence of surface potential in each minute minerals.

*Keywords:* heavy metal, ion removal, clay minerals, adsorption behavior, zeta potential

## 1. INTRODUCTION

Large-scale civil engineering works such as roads and railways constructions discharge a large amount of surplus soil containing natural heavy metals [1]. It is also known that most heavy metal ions from industrial wastewater are adsorbed and accumulated on the sediments of lakes and inner bays [2].

Some of the soil and sediment are disposed and stored at the disposal site because they contain heavy metals such as arsenic and cadmium that are harmful to humans even in small amounts. A method to reduce the volume of contaminated soil is required, especially in Japan where the disposal site for contaminated soil is tight. One of the conventional methods for reducing the volume of contaminated soil is the classification method. The method classifies contaminated soil into sand gravel and minute minerals (silt and clay), based on the fact that the smaller soil particles with larger specific surface area can adsorb

more heavy metals than larger particles. This method, however, requires post-processing because the volume reduction rate is low. As one of the post-processings, iron powder adsorption method which removes heavy metals by adding iron powder as an adsorbent to contaminated soil is widely used. Although, this method requires a large amount of additives and has a problem of secondary waste.

Hence, this study proposes a novel method for purifying the contaminated soil without any adsorbents by superconducting magnetic separation. Fig. 1 shows the flow chart of the proposed volume reduction method. In the first process of soil purification, the contaminated soil is classified into sand gravel ( $> 75 \mu\text{m}$ ) and minute minerals (silt and clay,  $< 75 \mu\text{m}$ ). Then, the pH of the contaminated muddy water was adjusted to change the surface potentials of the minerals. Then, heavy metal ions can be adsorbed selectively to the specific paramagnetic or diamagnetic minerals.

After that, the contaminated soil is separated by using a

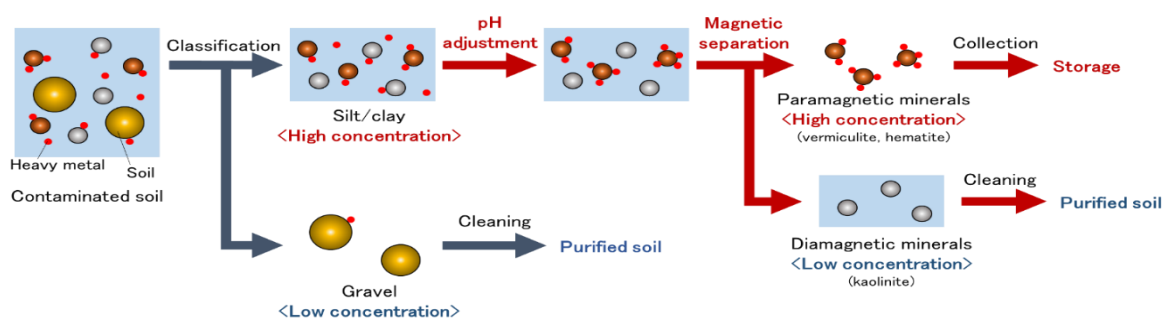


Fig. 1. Proposed method flow diagram for heavy metal contaminated soil.(When heavy metal ions are adsorbed on paramagnetic minerals.)

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superconducting magnet into the minerals that adsorb heavy metal ions and ones hardly adsorb them. This method utilizes the difference of the adsorption amount of heavy metal and the magnetic susceptibility depending on the type of minute minerals. Fig. 1 shows an example of a processing flow in case heavy metal ions are adsorbed on the paramagnetic minerals.

The classification method as the first process has already been established. Thus, the purpose of this study was to clarify the feasibility of our method that can remove specific minerals adsorbing heavy metal ions from the classified minute minerals. Firstly, the zeta potential of each minute mineral in the soil as a function of pH was measured to clarify the acid and basic properties of each minute mineral. Next, the adsorption amount of heavy metal ions to each minute mineral was evaluated. Thirdly, the mechanism of adsorption behavior of heavy metal ions was discussed based on the pH dependence of zeta potential in each mineral. Finally, a soil volume reduction process after classification was proposed based on the results.

## 2. OBJECTIVE HEAVY METAL IONS AND MINUTE MINERALS

### 2.1. Objective heavy metal ions

Heavy metals that may exceed the soil elution standard of the Soil Contamination Countermeasures Act due to natural factors in Japan are eight substances: cadmium, arsenic, hexavalent chromium, cyanide, mercury, lead, fluorine, and boron [3]. These heavy metals are mainly adsorbed on the soil particles as ions. In this study, cadmium and arsenic, which are naturally occurring heavy metals and have a significant biological effect even at low concentrations, were targeted.

Arsenic exists in the environment as trivalent or pentavalent. It is clear that trivalent arsenic is mainly present in the crust, while pentavalent arsenic is mainly present in soil and water. Thus, pentavalent arsenic was targeted in this study. Pentavalent arsenic exists as a salt of arsenic acid ( $H_3AsO_4$ ), and the types of ionic species depend on the pore water pH of the soil. As shown in Fig. 2, the arsenate species mainly exists as monovalent or divalent anions ( $H_2AsO_4^-$ ,  $HAsO_4^{2-}$ ) at pH is 3 to 9 [4]. On the other hand, cadmium is present in the soil as cations such as cadmium ions ( $Cd^{2+}$ ) and complexes with water molecules or chloride ions ( $Cd(H_2O)_4^{2+}$ ,  $CdCl^+$ ) [5]. Therefore, using arsenic and cadmium as targets, the behavior of these heavy metal ions can be the model systems of the existing ions in the muddy water each as anions and cations

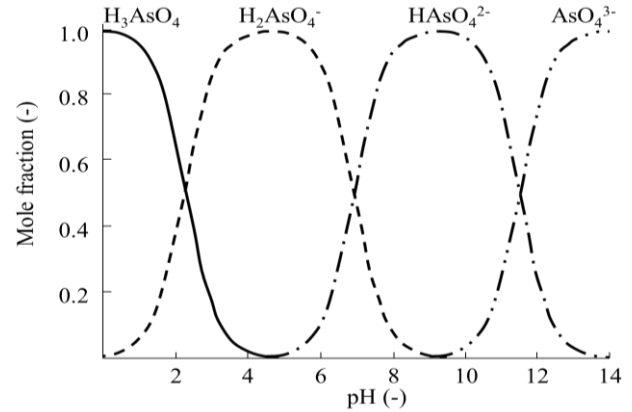


Fig. 2. the proportion of arsenate species as a function of pH.

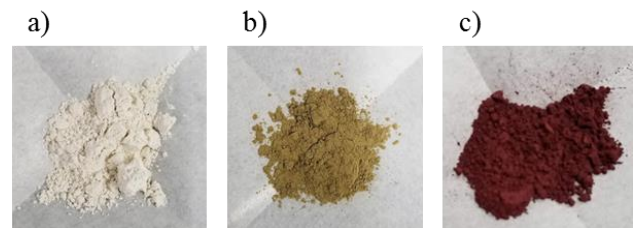


Fig. 3. Minute minerals used in this experiment. a) kaolinite, b) vermiculite, c) hematite

### 2.2. Objective minute minerals

As shown by red arrows in the flow chart in Fig. 1, this study aims to reduce the volume of minute minerals obtained by classification of the contaminated soil. TABLE I shows the types of major minerals in the soil and their magnetic properties. It is known that 1:1 clay minerals are diamagnetic, whereas 2:1 clay minerals, iron oxide, and iron hydroxide are paramagnetic minerals [6]. In this study, kaolinite, vermiculite, and hematite were respectively used as representative minerals of 1:1, 2:1 type clay, and iron oxide. Fig. 3 shows the appearance of the minute minerals used in this experiment.

## 3. ZETA POTENTIAL OF EACH MINUTE MINERAL IN THE SOIL

### 3.1. Experimental methods

Firstly, the pH dependence of zeta potential was investigated to clarify the change in surface potentials caused by the acid and basic properties of the three types of minute minerals in water.

100 mL of distilled water was added to 1.0 g each of

TABLE I  
MAIN MINUTE MINERAL TYPES AND MAGNETIC SUSCEPTIBILITY [6].

Types of minerals	Magnetic properties	Representative minerals	Magnetic susceptibility (-)
1:1 type clay mineral	Diamagnetic	Kaolinite	$-6.0 \times 10^{-5}$
2:1 type clay mineral	Paramagnetic	Vermiculite	$7.0 \times 10^{-4}$
Iron oxide/hydroxide	Paramagnetic	Hematite	$1.6 \times 10^{-4}$

kaolinite (Average particle size 6.6  $\mu\text{m}$ , Hayashi Kasei Co., Ltd., Japan), vermiculite (Average particle size 17.3  $\mu\text{m}$ , Tomoe Engineering Co., Ltd., Japan), and hematite (Average particle size 1.5  $\mu\text{m}$ , Toda Kogyo Corp., Japan), respectively. The pH of the suspension was adjusted using 1 mol/L nitric acid or 1 mol/L aqueous ammonia [7]. Here, nitric acid and aqueous ammonia were used for pH adjustment, because both are main acid and base contents existing in the soil pore water. Then, the suspension was shaken with a shaker (SHK-101B, Iwaki Co., Ltd., Japan) at 150 rpm for 24 hours, and the migration speeds of the minute mineral particles were measured using a microscope electrophoresis device (Model 502, Nihon Rufuto Co., Ltd., Japan). The migration speed was determined by averaging the measured values of the migration speeds of a total of 20 particles, while switching the polarity of the electrode, and taking the average.

### 3.2. Results

Fig. 4 shows the zeta potential of each minute mineral as a function of pH. It was confirmed that the zeta potential of all minerals decreased with increasing pH. It is also confirmed that the isoelectric point of kaolinite and vermiculite was around pH=2, while that of hematite was around pH=7.

### 3.3. Discussions

The cause of the decrease in the zeta potential as the increase in pH is that the minute mineral has surface hydroxyl groups, which acts as acid or a base, thereby exhibiting a buffering effect on the increase or decrease of pH. Si-OH and Al-OH groups are present on the surface of clay minerals, and Fe-OH groups on the surfaces of iron oxide and iron hydroxide. These hydroxyl groups are called surface hydroxyl groups, which cause an  $\text{H}^+$  addition or dissociation reaction depending on the surrounding pH. Equation (1) shows the addition reaction between the Si-OH groups and  $\text{H}^+$ . When the surrounding pH decreases, the surface hydroxyl groups become positively charged by adding  $\text{H}^+$ . In this case, a positive charge is generated on the surface of minute minerals.

On the other hand, Equation (2) shows the dissociation reaction of  $\text{H}^+$  from the Si-OH group. When the surrounding pH decreases, the surface hydroxyl groups dissociate  $\text{H}^+$  and become negatively charged [8-9]. In this case, a negative charge is generated on the surface of minute minerals. The surface charge that changes depending on the surrounding pH is called "variable charge". Due to this variable charge, the zeta potential of minute minerals is high at low pH, while low at high pH.

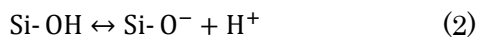
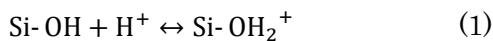


Fig. 4 indicates that the surface potential of the minute mineral is positive in the acidic solutions, which suggests that the adsorption of heavy metal anions with the opposite charge will increase. In contrast, in the basic solutions, the surface potential of the minute mineral becomes negative, which promotes the adsorption amount of heavy metal cations.

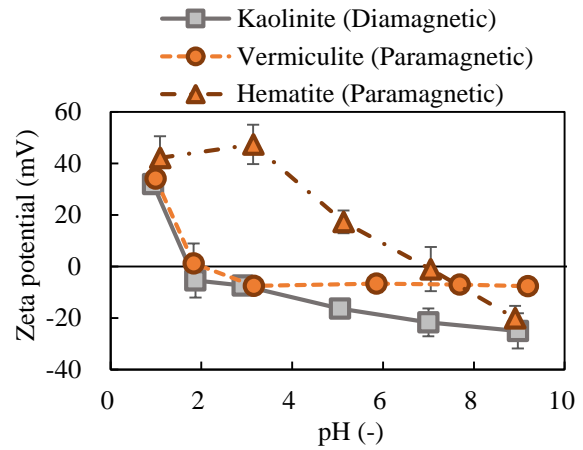


Fig. 4. Zeta potential of each minute mineral as a function of pH.

TABLE II  
AMOUNT OF THE MINUTE MINERAL ADDED IN THIS EXPERIMENT.

	As aqueous solution	Cd aqueous solution
kaolinite	1.0 g	1.0 g
vermiculite	1.0 g	0.1 g
hematite	1.0 g	1.0 g

Since the isoelectric points of kaolinite and vermiculite are around pH=2, the pH range where the mineral surfaces are negatively charged is wide. In contrast, since the isoelectric point of hematite is pH=7, the mineral surface is positively and negatively charged across the neutral pH. This indicates that each clay mineral can selectively adsorb the different heavy metal ions by changing the solution pH.

## 4. ADSORPTION AMOUNT OF HEAVY METAL TO MINUTE MINERALS

### 4.1. Experimental methods

Next, pentavalent arsenic and cadmium ions were adsorbed on each minute mineral in different pH solutions, and the adsorption amount was investigated.

$\text{Na}_2\text{HAsO}_4 \cdot 7\text{H}_2\text{O}$  (Nacalai tesque Inc., Japan) was dissolved in distilled water to prepare 100 mL of 10 ppm As aqueous solution. In the same way,  $\text{CdCl}_2 \cdot 2.5\text{H}_2\text{O}$  (Nacalai tesque Inc., Japan) was dissolved in distilled water to prepare 100 mL of 10 ppm Cd aqueous solution. Then, 1 mol/L nitric acid or 1 mol/L ammonia aqueous solution was added to adjust pH to 3, 5, 7 and 9 using a pH meter (HM-30G, DKK-TOA Corporation, Japan). Kaolinite, vermiculite or hematite were added to these suspensions. TABLE II shows the amount of the minute mineral added in this experiment. When 1.0 g of vermiculite was added to the Cd aqueous solution, all the Cd in the solution was adsorbed and the saturated adsorption amount of vermiculite could not be measured, thus the amount added was 0.10 g. The suspension was shaken at 150 rpm for 24 hours, filtered under reduced pressure through membrane filters (pore size 0.45  $\mu\text{m}$ , HAWP04700, Merck Millipore Ltd.), and then the Cd and As concentrations in the filtrate were measured with an ICP (inductively coupled plasma) emission spectrometer (ACPE-9820, Shimadzu Corporation, Japan).

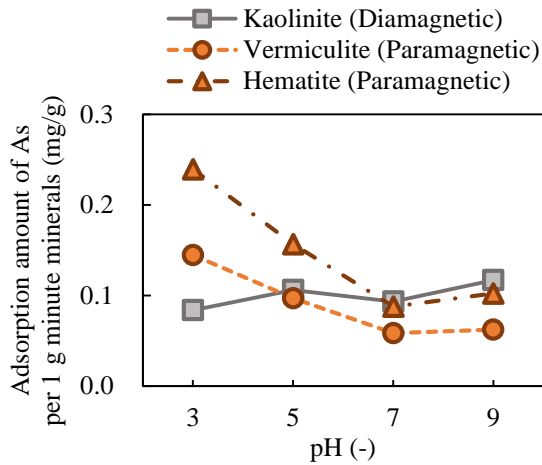


Fig. 5. Adsorption amount of As as a function of pH.

#### 4.2. Adsorption amount of As on minute minerals

Fig. 5 shows the adsorption amount of As per unit mass of each minute mineral as a function of pH. It was confirmed that hematite adsorbed arsenic the most below pH=7. This may be because hematite has a higher positive zeta potential than any other minerals in the acidic solution. Fig. 4 indicates that only the zeta potential of hematite was positive at pH=3 to 7, where other minerals were negative. It is considered that the anionic arsenate ion was easily adsorbed to hematite in acid solution. As a result, hematite, which is originally contained in soil, effectively acts as an adsorbent for heavy metal anions under acidic conditions.

#### 4.3. Adsorption amount of Cd on minute minerals

Fig. 6 shows the adsorption amount of Cd per unit mass of each minute mineral as a function of pH. The adsorption amount (mg/g) shown in Fig.6 are the saturated adsorption amounts in the conditions in Table II, so we cannot compare the results of vermiculite with 0.10g directly with those of different weights of minerals. But as a relative and obvious trend, the adsorption amount of Cd to vermiculite was significantly high among three minerals.

This is because 2:1 clay minerals such as vermiculite have negative charge called “permanent charge”, in addition to “variable charge”.

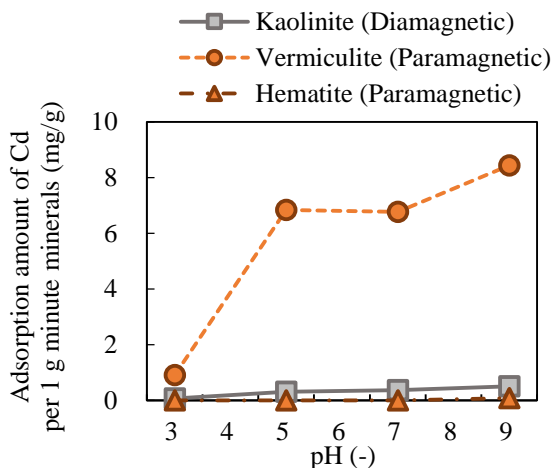


Fig. 6. Adsorption amount of Cd as a function of pH.

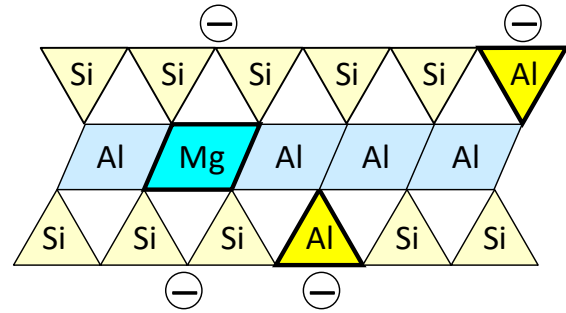


Fig. 7. Mechanism of developing permanent charge.

Clay minerals consist of two of sheets: tetrahedral sheet and octahedral sheet. The former consists of two-dimensionally arrayed Si-O tetrahedra, and the latter consists two-dimensionally arrayed Al-O octahedra. In the 2:1 type clay mineral, a unit layer is composed of an octahedral sheet sandwiched by two tetrahedral sheets. In case the cation in the tetrahedral sheet is only  $\text{Si}^{4+}$  and that in the octahedral sheet is only  $\text{Al}^{3+}$ , the mineral is electrically neutral and has no charge. In many 2:1 clay minerals including vermiculite, however, the cations of tetrahedral and octahedral sheets are replaced by other low-valent cations ( $\text{Si}^{4+} \rightarrow \text{Al}^{3+}$ ,  $\text{Al}^{3+} \rightarrow \text{Mg}^{2+}$ , etc.) as shown in Fig. 7, which is called isomorphic substitution. For this reason, the 2:1 type clay mineral has negative permanent charge between the unit layers [10]. In vermiculite, the permanent charge between the layers that is not affected by pH largely promotes the adsorption of cadmium ions ( $\text{Cd}^{2+}$ ). Therefore, vermiculite originally contained in the soil is an effective adsorbent for heavy metal cations.

Fig. 6 also suggests that the adsorption amount of Cd on vermiculite was significantly reduced at pH=3. This suggests that the amount of heavy metal cations adsorbed by the permanent charge depends on the hydrogen ion concentration in the solution. As described in section 4.1, the Cd concentration in this experiment is about  $10^{-4}$  mol/L (=10 ppm). At pH=3, the hydrogen ion concentration was higher than the cadmium ion concentration, which made the adsorption of hydrogen ions dominant. Therefore, it is assumed that the adsorption amount of Cd was reduced by the exchange reaction of hydrogen ions ( $\text{H}^+$ ) with cadmium ions ( $\text{Cd}^{2+}$ ). On the other hand, at pH=5 or more, the cadmium ion concentration was higher, which suggests that the adsorption amount of Cd increased by a decrease in the concentration of hydrogen ions.

Fig. 8 shows the adsorption amount of Cd per unit mass of kaolinite and hematite as a function of pH (enlarged view of Fig.6). It was shown that the adsorption amount of Cd increased with increasing pH. This is considered because the absolute value of the zeta potential of each minute mineral increases with increasing pH, as shown in Fig. 4.

From above results, 1 g of vermiculite adsorbs about 7 mg of Cd at pH=5. Even if the minute minerals in the soil contains only 10% 2:1 type clay mineral, it can be applied to Cd contaminated soil with 4 times the standard value of 150 mg/g. But as for arsenic, the adsorption capacity of hematite is relatively low, and further consideration is needed.

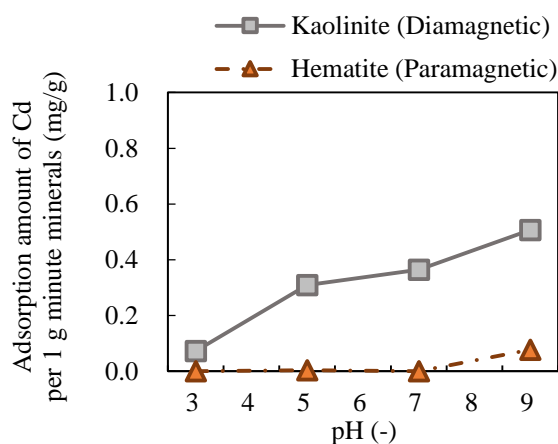


Fig. 8. Adsorption amount of Cd as a function of pH in kaolinite and hematite (enlarged view of Fig.6).

## 5. EXAMINATION OF SEPARATION METHOD OF HEAVY METAL IONS

From the above results, it was concluded that hematite was effective as an adsorbent for heavy metal anions and vermiculite was effective as an adsorbent for heavy metal cations, among the minute minerals originally contained in soil. TABLE I shows that hematite and vermiculite are both paramagnetic minerals, indicating the possibility of volume reduction of heavy metals-contaminated soil by selective separation of paramagnetic minerals using superconducting magnet.

In our previous research [11-12], we have already proposed a high gradient magnetic separation (HGMS) method, which can be used for the volume reduction of radioactive Cs contaminated soil discharged by the decontamination works in Fukushima. In the study, vermiculite that strongly adsorbs radioactive cesium between the layers was selectively separated from the contaminated soil using a strong magnetic field of 5-6 T and a magnetic filter with a wire diameter of 0.1-0.2 mm. Our works so far have been a lab-scale study, and the practical capture capacity and processing speed have not been achieved with the current system. Hence, it is considered that by using this method and designing an apparatus for mass treatment, it can be used for volume reduction of soil contaminated with heavy metals. Because heavy metal cations have a different ionic radius and hydrated ion radius from cesium ions, they may not be fixed as strongly as cesium between the layers of vermiculite, so it is necessary to verify in the future with a view to storage after separation.

Regarding pH adjustment as a pretreatment before performing magnetic separation, it is appropriate to adjust the pH to 3 for heavy metal anions for selective adsorption on hematite from Fig. 5, and to adjust the pH to 5 or more for heavy metal cations for selective adsorption on vermiculite from Fig. 6. Nevertheless, many heavy metal anions and cations are coexisting in the actual soil, so there is the possibility that the coexistence of multiple ions may affect the appropriate pH for separation. So it is necessary to study for the coexistence system.

## 6. CONCLUSION

This study proposed a novel method for volume reduction of heavy metal-contaminated soil without any adsorbents only by pH adjustment and superconducting magnetic separation. In order to realize this method, the zeta potential and the adsorption amount of Cd and As on each minute mineral in the soil as a function of pH was investigated as a fundamental study. The results of the zeta potential showed that the adsorption of anionic arsenate ion was promoted in the acidic solution, while the adsorption of cationic cadmium ion was promoted in the basic solutions. Heavy metal adsorption experiments showed that arsenate ions were adsorbed the most on hematite at pH=3, while cadmium ions were adsorbed the most on vermiculite above pH=5. These results suggest that it is the most effective to separate and remove hematite and vermiculite, respectively for arsenic for cadmium, after adjusting the pH of the mineral suspensions showing highest adsorption amounts for each set of heavy metals and adsorbent. Since both hematite and vermiculite are paramagnetic minerals, it was shown that it is effective to separate paramagnetic minerals in contaminated soil using a strong magnetic field of a high gradient superconducting magnetic separation.

However, the adsorption reaction of cadmium is also affected by other factors than zeta potential such as co-existing ions and other characteristics of the adsorbents. In the future, we will consider various effects such as the equilibrium reaction with coexisting ions and ionic radius of heavy metals. In particular, we will examine for the heavy metal adsorption on the minerals under coexistence of heavy metal anions and cations, in the presence of cations other than heavy metals included in general wastewater, such as  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Mg}^{2+}$ , and  $\text{Ca}^{2+}$ , changing the pH conditions.

## ACKNOWLEDGMENT

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