Functionalization of Shirasu-balloons Surface for Removal of Cadmium Ions from Contaminated Soil

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Abstract

Microspheres of aluminosilicate glass from volcanic sediment, whose surface was modified with functional groups, Shirasu-balloons (SB) were investigated as an adsorbent to remove cadmium ion from the contaminated soil. The introduction of thiol group (-SH) on the surface of SB enabled to adsorb cadmium ion, meanwhile the introduction of an alkyl group (-ODS) made the surface of SB hydrophobic, consequently increased the mechanical strength of SB. Those adsorbents could float up on the water surface after adsorption process. The prepared adsorbent was characterized by FTIR spectrophotometer, elemental analysis and optical microscope for photographic images. The adsorption of cadmium ions on the adsorbent was investigated by comparing the results by a plain SB with those by thiol-functionalized SB. The adsorption maximum for cadmium ion was 3.75 mg/g for SH-SB and 2.62 mg/g for SH-ODS-SB, respectively. The adsorption of cadmium ions on the functionalized SH-SB and SH-ODS-SB was fitted well to the Langmuir isotherm equation. After shaking time for 24 hours, the recovering ratios of the absorbents from soil were 73 wt% for SH-SB and 98 wt% for SH-ODS-SB absorbents. In addition, the kinetic and adsorption-desorption properties of the adsorbent were also discussed.

Keywords: Shirasu-balloons, Surface modification, Cadmium ion, Adsorption, Remediation.
Introduction

Heavy metals have been still now released in the environment from many kinds of industrial activities such as electric battery\(^1\), metal plating\(^2\), and mining.\(^3\) These pollutions with heavy metals have become the public concerns because of the potential effects on the human health\(^4\) and ecosystem.\(^5\) Particularly, cadmium ions, one of most toxic metals, in paddy soil are accumulated to the plants such as rice and wheat in the growing season and many kinds of disease were caused by cadmium poisoning, for example, softening of bone and kidney failure.\(^6\) The high fatality rate among the patients was considered due to the reason that this disease had the chronic effect on the patient’s life span. The first disease caused with cadmium ions in Japan was the *Itai-itai disease* in the Jinzu River area of Toyama prefecture.\(^7\) The concentration of cadmium in the contaminated rice at Jinzu area, one of the most contaminated area in the past, was in the range between 0.02 – 1.06 mg/L.\(^8\) According to the standard value of cadmium ion in water of public area set by the basic law of environment, the concentration of cadmium should be less than 0.01 mg/L.\(^6\) Recently, Joint FAO/WHO Expert Committee on Food Additives (JECFA) have reported similar pollutions problems with cadmium in the world. Cadmium is readily taken up from contaminated soil by various crops, especially vegetables and rice which, together with other foodstuffs such as shellfish can contribute to excessively high levels of Cd intake.\(^9\) The influence of cadmium might be found out after several years because of the slow accumulation in the livings and human body.\(^10\)

Many kinds of adsorbents have been used to remove hazardous substances in water and soil, that is, activated carbon,\(^11\)-\(^13\) ion exchange resin,\(^14\),\(^15\) zeolite,\(^16\) bio-surfactants,\(^17\) clay-soils,\(^18\) etc. These materials are effective as an adsorbent for removal of cadmium ion. When the adsorbents are used in environment, the adsorbents adsorbing pollutants should be collected from the environment. If the adsorbent cannot be collected after the adsorption process, the pollutants
would diffuse into the environment again. Therefore, it is very important to develop the adsorbent that can be easily collected after the adsorption of pollutants. The ease collection of adsorbents is an essential feature for application of the adsorbent to the actual contaminated sites.\textsuperscript{19}

“Shirasu” is fine-grained pumice and volcanic ash distributed as a thick stratum throughout southern Kyushu, Japan.\textsuperscript{20} Most of Shirasu are now disposed as solid waste to the landfill.\textsuperscript{21} In Japan, hollow glass microspheres named as Shirasu-balloons have been produced from vitric volcaniclastic materials named as Shirasu or Hakudo (a kind of the “perlite”).\textsuperscript{22} The application of the volcanic sediment as a raw material of adsorbent has some advantages in reducing the amount of solid waste and the cost for the treatment and also providing a low cost adsorbent for removal of cadmium ion. Shirasu-balloons (SB) composed mainly of hollow glassy microspheres are produced by heating the glassy volcanic material.\textsuperscript{23} The mean particle size of plain SB is several micrometer if they were prepared in a fluidized sand bed furnace by rapid heating of the pulverized Shirasu.\textsuperscript{24} The SB based on volcanic sediment have a high possibility as eco-materials widely used in industry for the treatment of waste water and soil treatment.\textsuperscript{24} Since the specific gravity of SB are lighter than water (the specific gravity was 0.5 at 25°C), we can collect them on the surface of water after separation from water and soil. However, the SB themselves are not so mechanically stable in water. The invasion of water into the cavity of the balloons led to the loss of the buoyancy. In order to solve these problems and develop SB as the excellent adsorbent, the modification of the surface of the balloon by introducing chelating and hydrophobic groups seems to be effective (Fig. 1). In this study, we expected that the modification with hydrophobic compound on the surface of SB could prevent water from entering into the inside of the balloon through the holes and cracks and we attempted the modification of SB with ODS groups. In addition, the modification with thiol groups on SB was conducted to increase in the cadmium adsorption capacity (Fig. 2).
The purpose of this study is to enhance the stability of the balloons in water and soil and to develop the novel adsorbent by the modification of the SB, which have the well adsorbing ability for heavy metal ions and can be collected from contaminated water or soil easily after adsorption of heavy metal ions on the basis of the difference in the specific gravity.

**Experimental**

*Plain SB*

Shirasu-balloons (SB-201 type) were obtained from Silax Co., Ltd. (Kagoshima prefecture, Japan). Shirasu-Balloon (SB) is a foamed hollow glass microspheres prepared from Shirasu (perlite), one of volcanic materials, by heating at about 1000°C.\(^2\) SB has an excellent thermal insulation ability because of including the air in the hollow structure. However, among the commercially available SB, there are some SBs whose hollow structure has broken and some SBs having a small hole or crack. The buoyancy of SB is lost when water comes into the inside of the balloon from the holes and the cracks. The commercially available SB include not only complete balloons but also broken balloons and some ashes. To get only the complete balloons whose specific gravity is less than that of water, the commercially available SB were put in distilled water for 24 h. The broken Shirasu balloons and some ashes sank in the bottom of water and only the complete balloons remained on the surface of water. The percentages of the sedimented fraction were 80 wt% and only 20 wt% remained on the surface of water. The SB on the surface of water were collected and dried at 50°C for 24 h.

*Preparation of SH-SB adsorbents*

The preparation of thiol group modified SB (SH-SB) was carried out according to the published procedure by using 3-Mercaptoethyltrimethoxysilane.\(^2\) The typical process was as
follows: Five gram of plain SB was added in 45 mL of ethanol solution containing 2.5 vol% ammonia and 0.3 mL of 3-Mercaptopropyl-trimethoxysilane (Tokyo Chemical Industry, Co LTD). The mixture was added in 100 mL beaker glass and then stirred in thermostatic water bath at 50°C for 3 h. The prepared SH-SBs were filtered by a filter paper (Whatman No. 1, the pore size: 11 µm) and then washed with 5 mL of ethanol twice, finally, dried at 85°C for one hour and cooled in a desiccator.

Preparation of functionalized ODS-SB material

The procedure similar to that described above was carried out for preparation of ODS-SB. Five gram of plain SB was added in 45 mL of toluene solution containing 0.55 g of n-Octadecyltrimethylchlorosilane (Tokyo Chemical Industry, Co LTD). The mixture was added in 100 mL beaker glass and then stirred in thermostatic water bath at 50°C for 3 h. The prepared ODS-SBs were filtered, washed and dried by the same procedure as the case of SH-SB.

Preparation of SH-ODS-SB

A procedure similar to that described above was carried out for preparation of SH-ODS-SB, Five gram of plain SB was added in 45 mL of ethanol solution containing 2.5 vol% ammonia, and 10 mL of toluene solution containing 0.3 mL of 3-Mercaptopropyl-trimethoxysilane and 0.55 g of n-Octadecyltrimethylchlorosilane (Tokyo Chemical Industry, Co LTD) were added. The prepared SH-ODS-SBs were filtered, washed and dried by the same procedure as the case of SH-SB. The functional groups containing in the samples were identified by FT-IR spectrophotometer (FT/IR-4100, Jasco, Japan), meanwhile the composition of carbon, hydrogen, sulfur were determined by using the elemental analyzer (Micro Corder JM 10, Yanaco, Japan).
Adsorption test

A batch technique was applied to determine the metal binding ability of the prepared adsorbents. 0.5 g of adsorbents were equilibrated with 50 mL of a 10 mg/L cadmium solution containing 0.1 mol/L citric acid/NaOH to adjust pH of the solution at 1-7. The solution was shaken at 150 rpm (Eyela cute mixer CM-1000, Eyela, Japan) for 24 h. After standing the solution for more than an hour, the SBs floating on the water surface were collected by filtration with a Whatman No. 1 filter paper. After separation of the SB from the solution, the concentration of Cadmium remaining in the solution was measured by Flame-Atomic Adsorption Spectrophotometry (Hitachi A-2000, Hitachi, Japan). Cadmium standard solution used in quantitative analysis was purchased from Wako Pure Chemical Co., Osaka, Japan.

Collection of cadmium ion in soil with SB

The soil sample collected from paddy field (Hachinohe city, Aomori Prefecture) was classified by a sieve mesh to be < 2 mm of the size. Cadmium ions were added to the 100 g of the soil to be 10 mg/kg of cadmium concentration. Cadmium ion contaminated soil is dried at room temperature. Ten gram of the cadmium contaminated soil were added into 100 mL of the leaching solution and further 0.5 g of the SB were added. After mixing them at 150 rpm of the agitation rate, the SB was separated from the soil by the difference in the specific gravities. The leaching parameters of cadmium ion in soil were investigated by the following steps; (1) measuring the concentrations of cadmium in the leaching solution by AAS after mixing 10 g soil with 100 mL of the leaching solution (0.1 mol/L citric acid/ NaOH buffer solution) at 150 rpm of the agitation rate (the soil/solution w% ratio was 1/10), and; (2) changing the agitation time (0.5, 1.0, 2.0, 3.0 and 6.0 hours), and measuring the concentrations of cadmium; (3) changing the separation time (6 hours, 24 hours and one week) after stopping the agitation, and measuring the weight of SB to evaluate the stability of SB in water; and (4) investigating the
distribution of cadmium in SB/solution/soil systems at pH1-7 as well as the total recovery of cadmium ion. In this way, the optimum condition for the leaching parameters for cadmium ion from soil was determined. The microscopy images of the morphology on the SB surface after one week are shown by Olympus Ck-2, Japan.

**Results and Discussion**

**Characteristic of SB**

According to the report by Sodeyama et al, the main components of the SB are SiO$_2$, Al$_2$O$_3$, K$_2$O, Na$_2$O, CaO, Fe$_2$O$_3$ and the percentages of them are 69.7, 12.6, 3.36, 2.89, 1.59, and 1.56, respectively. It was confirmed that the SB particle has an average particle size of 15-25 µm by optical microscopy observation, and the density of 0.5 g/cm$^3$ was determined by pycnometry. In Table 1, the results of the elemental analysis for C, H and S in some kinds of SB were summarized. Carbon and sulfur were not found on the plain SB. When the SB was modified with the 3-Mercaptopropyl-trimethoxysilanes, the sulfur content was 11.36 wt% for the SH-SB and 5.12 wt% for the SH-ODS-SB. The presence of sulfur was clearly confirmed on the functionalized SB by the elemental analysis. FTIR spectra of SB before and after the modification with n-Octadecyltrichlorosilane and (3-Mercaptopropyl)-trimethoxysilane were measured in the range of 600-4000 cm$^{-1}$. The broad peak around 3000-4000 cm$^{-1}$ might be due to the OH stretching vibrations of silanol groups on the modified SB (Fig. 3a). The new peak which appeared at 2900-3000 cm$^{-1}$ (Fig. 3b) was assigned to the CH stretching vibrations of alkyl groups introduced by the modification and a small peak at 2540-2560 cm$^{-1}$ (Fig. 3c and d) was assigned to the SH stretching vibrations of thiol groups. These results implied that both of alkyl chains and thiol groups were successfully introduced to the surface of SB by the modification process. The intensity of the peak derived from the CH stretching vibration
seemed to be in the order of SH-SB < ODS-SB < SH-ODS-SB depending on the C content of the elemental analysis value. However, the peaks of the CH stretching spectra were not in the order, and it needs more detail investigation in future. The modification of the surface of SB with n-Octadecyldimethylchlorosilane converted the surface from hydrophilic to hydrophobic. Consequently, almost 100 wt% of the modified SB remained on the surface of water even after one week. Thus, it was confirmed that the buoyancy of SB could be retained for a long time by the surface modification using organo-functional silane coupling agents.

**Removal of cadmium ion with SB**

The adsorption efficiency of the modified SBs for cadmium ion was investigated. When 0.5 g plain SB, SH-SB or SH-ODS-SB were injected into 50 mL of 10 mg/L cadmium ion solution and the mixture was shaken gently for six hours at the room temperature as shown in Fig. 4. Cadmium ion did not adsorb on the plain SB because the SB contained slightly silanol groups, and neither thiol groups or other binding sites (Fig. 4a). Moreover, ODS-SB did not have the ability to adsorb cadmium ions. However, SH-SB and SH-ODS-SB could adsorb cadmium ion within two hours due to the strong interaction between cadmium ions and the SH groups modified on the SB (Fig. 4b and c). As increasing pH of the solutions, the adsorption capacity of cadmium ion onto SH-SB was increased (Fig. 5). The binding of cadmium ion with the surface functional groups strongly depended on the pH of soil and water.

Cadmium ion could be adsorbed on SH-ODS-SB when the pH of solution was higher than 3.0. The removal ratio of cadmium ion increased with increasing pH of the solution. The adequate pH for the adsorption with SH-ODS-SB was in the range of 3 to 7. The adsorption equilibrium constant ($K$) and the saturation adsorption amount ($Q_{\text{max}}$) of SH-SB (a) and SH-ODS-SB (b) for cadmium ion were evaluated at pH 3.0 by using a Langmuir adsorption equilibrium model as shown in Fig. 6. The $Q_{\text{max}}$ value of SH-SB obtained from Langmuir
adsorption isotherm was larger than that of SH-ODS-SB as shown in Table 2. It seemed to depend on the modified amounts of thiol group on SB, which was suggested from the sulfur contents on the modified SB (Table 1). SH-SB and SH-ODS-SB have the potential for removing a variety of pollutants from contaminated soils at weakly acidic solution. In this study, the elution of cadmium from soil with citrate buffer was investigated at various pH. As a result, under the condition of pH 3, the elution efficiency of cadmium ion was the maximum of 84.5%. Therefore, the experiments of the adsorption kinetics for SH-SB and SH-ODS-SB at pH 3 were carried out at pH 3.

**Kinetics of adsorption**

Adsorption kinetics of cadmium ion on SH-SB and SH-ODS-SB were investigated under the condition of 10 mg/L cadmium ion as the initial concentration at pH 3.0. We conducted the experiments for adsorption kinetic by using the same amount of SB, because it was thought that the difference in the removal amount of cadmium ion by the modified SBs would not significantly affect the kinetic discussion.

The adsorption of cadmium ion on SH-SB and SH-ODS-SB reached the equilibrium within two hours. To clarify the characteristics of adsorption kinetics of cadmium ion on the modified SB, the adsorbing processes were described by both the pseudo first-order and pseudo second-order kinetics.\(^{29}\) The Lagergren equation often used for the pseudo first-order kinetics is represented as Eq. (1),

\[
\ln(Q_e - Q_t) = \ln Q_e - k_t t
\]

Eq. (1)

Where, \(Q_e\) (mg/g) is the amount of cadmium ion adsorbed at the equilibrium, \(Q_t\) (mg/g) is the
amount of cadmium ion adsorbed at the time of \( t \), and \( k_1 \) (1/min) is the pseudo first-order constant. The pseudo second-order kinetics can be described by the following equations: \(^{30}\)

\[
\frac{t}{Q_t} = \frac{1}{h} + \frac{1}{Q_e} t \tag{2}
\]

\[
h = k_2 Q_e \tag{3}
\]

\[
t_{1/2} = \frac{1}{k_2 Q_e} \tag{4}
\]

Where, \( k_2 \) (1/min) is the pseudo second-order constant as Eq. (2). The parameters of \( Q_e \) and \( k_2 \) were obtained from the intercept and the slope of the plot \( t/Q_t \) against the time \( t \). The initial rate of adsorption, \( h \) (mg \( \cdot \) g\(^{-1} \) \( \cdot \) min\(^{-1} \)), can be obtained by using \( k_2 \) and \( Q_e \) at the initial adsorption time as Eq. (3). The half time \( t_{1/2} \) (min), which is the time required for 1/2 \( Q_e \) of cadmium ion to be adsorbed, is calculated from Eq. (4). The pseudo second-order model fitted with the kinetics data better than the pseudo first-order model. The parameters describing the adsorption process on SH-SB and SH-ODS-SB are summarized in Table 3. The pseudo rate constants of SH-SB were higher than those of SH-ODS-SB. The half time of SH-SB was shorter than that of SH-ODS-SB at pH 3.0 condition. This was likely due to the easiness in the contact of cadmium ion with the binding site of SH-SB. In the cases of the SH-ODS-SB, the binding sites of thiol groups might be sandwiched between the long alkyl groups, whose property is hydrophobic, and therefore, it might take longer time for cadmium ion to approach to the binding sites of thiol groups.

**Separation of SB from soil**

The separation of the SB from the treated soil after adsorbing cadmium ion for one week was
demonstrated as shown in Fig. 7. The separation efficiency of the plain SB and SH-SB collectable on the water surface after around 24 h shaking time were 11 wt% and 73 wt%, respectively. On the other hand, the separation efficiency of ODS-SB and SH-ODS-SB were 103 wt% and 98 wt%, respectively. Fig. 8 shows the photograph of those SBs by an optical microscope. Fig. 8 (a) shows the surface morphology of SB beads prior to the recovery of cadmium ion from the soil. After one week, the surface of a plain SB seems to be damaged and the penetration of water into the cavity of the SB was observed in Fig. 8 (b). The microscopy images indicated that the recovered SH-SB homogeneously maintained the initial morphology without the holes and cracks on the surface of the SH-SB as shown in Fig. 8 (c). The modification with alkyl chains and thiol groups on the surface of SB seems to prevent the balloons from the physical deterioration and damage and the penetration of water into the cavity of the SB in Fig. 8 (b). The separation time is an important factor for the considerations of the application of the adsorbent to the treatment of actual wastewater and soil. The high assembling property based on hydrophobic interaction shown in the case of SH-ODS-SB is essential for the high recovery of the SB as shown in Fig. 8 (d).

Collection of cadmium ion in soil with SH-ODS-SB

The removal of cadmium ion deliberately added in paddy soil was investigated by using SH-ODS-SB at various pH. The pH of the solution was adjusted to 1-6, with nitric acid, citrate buffer solution and pure water. The efficiency of cadmium ion leached from soil and the adsorption of cadmium ion SH-ODS-SB are summarized in Table 4. When the pH of the leaching solution was 3, 84.5% of cadmium ion in soil was removed from soil and 84.2% of cadmium ion was collected on SH-ODS-SB within six hours. However, when the pH of the leaching solution was in the higher range of 4 to 6, the leaching efficiency of cadmium ion decreased remarkably. The elution of cadmium ions adsorbed on soil components is achieved by
ion-exchanging the bound cadmium ions with proton. The decrease in the proton concentration leads to the decrease in the leaching efficiency due to the reduction of the ion-exchange ability. Therefore, the lower pH is suitable to elute cadmium ions from soil. On the other hand, for the binding of cadmium ion with SH group, the acid dissociation of SH group is necessary, and the higher pH is suitable to this condition. The pH which can satisfy the two conditions was around pH 3 and under this condition the maximum values were obtained in the elution of cadmium ion from soil and the collection of cadmium ion with SH-ODS-SB.

**Conclusions**

A new type of adsorbents was developed for the treatment of the contaminated soil and wastewater through the functionalization with thiol groups and alkyl groups on the surface of the SB. This adsorbent is lighter than water and then can be collected on the surface of water easily after adsorption of pollutants. The adsorption capacity of cadmium ion was estimated 3.75 mg/g for SH-SB and 2.62 mg/g for SH-ODS-SB. It was confirmed that that the presence of thiol groups onto the SB contributed to the adsorption of cadmium ion. On the other hand, the modified alkyl groups on SH-ODS-SB did not largely hinder the adsorption of cadmium ion. The 84.5 % amounts of cadmium ions in soil was eluted from the soil and adsorbed in the SH-ODS-SB at the pH 3. The separation of SB on the water surface was achieved after around 24 h shaking time. The separation efficiency became 73 wt% for SH-SB and 98 wt% for SH-ODS-SB. The higher assembling property based on the hydrophobic surface on the SB by the modification of alkyl groups has a large advantage in the high recovery of the SB. Consequently, the higher recovery of the SB after the adsorption process will lead to the enhancement of the higher removal of cadmium ions from soil. We successfully developed a low cost adsorbent which can achieve the elution of cadmium ion from soil and the adsorption at one-step, just by injecting it to the contaminated site without using a column and can collect.
easily.

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Table 1  Elemental composition of SB

| Sample       | C (wt%) | H (wt%) | S (wt%) |
|--------------|---------|---------|---------|
| Plain SB     | 0.00    | 0.00    | 0.00    |
| ODS-SB       | 14.83   | 2.69    | 0.00    |
| SH-SB        | 9.49    | 2.78    | 11.36   |
| SH-ODS-SB    | 27.35   | 4.90    | 5.12    |
Table 2  Langmuir’s parameters for Cadmium ion adsorption by SH-SB and SH-ODS-SB

| Sample       | pH | $K$   | $Q_{\text{max}}$ | $R^2$  |
|--------------|----|-------|------------------|--------|
| SH-SB        | 3.0| 0.955 | 3.75             | 0.9997 |
| SH-ODS-SB    | 3.0| 1.335 | 2.62             | 0.9994 |

Adsorption equilibrium constant ($K$), Saturation adsorption amount ($Q_{\text{max}}$).
Table 3  Pseudo-first-order and pseudo-second-order model constants for the adsorption of Cadmium ion at pH 3.0.

|               | Pseudo-first-order | Pseudo-second-order |
|---------------|--------------------|---------------------|
|               | $k_1$ (min$^{-1}$) | Q$_e$ (mg g$^{-1}$) | R$^2$ | $k_2$ (g mg$^{-1}$ min$^{-1}$) | t$_{1/2}$ (min) | h (mg g$^{-1}$ min$^{-1}$) | Q$_e$ (mg g$^{-1}$) | R$^2$ |
| SH-SB         | 5.91×10$^{-2}$     | 1.11                | 0.9746 | 1.41×10$^{-1}$ | 2                  | 1.79                | 3.57                | 0.9999 |
| SH-ODS-SB     | 4.20×10$^{-2}$     | 1.73                | 0.9332 | 9.20×10$^{-2}$ | 5                  | 0.47                | 2.27                | 0.9998 |

Pseudo first-order constant ($k_1$), Amount of cadmium ion adsorbed at the equilibrium (Q$_e$), Pseudo second-order constant ($k_2$), The half time, which is the time required for 1/2 Q$_e$ of cadmium ion to be adsorbed (t$_{1/2}$), Initial rate of adsorption (h).
Table 4  The rates of Cadmium ion desorption from soil and Cadmium ion adsorption on SH-ODS-SB

| Eluants (100 mL) | Soil pH | Desorbed (%) | Adsorbed (%) |
|-----------------|---------|---------------|--------------|
|                 | Finial  | Cadmium ion / Soil (0.01 mg/10 g) | SH-ODS-SB (0.25 g) | SH-ODS-SB (0.5 g) | SH-ODS-SB (1.0 g) |
| Nitric acid     | 1.13    | 99.8          | 0.0          | 1.2               | 1.2               |
| Ctric acid/NaOH | 2.23    | 93.0          | 35.0         | 45.1              | 60.1              |
| Ctric acid/NaOH | 3.28    | 84.5          | 70.4         | 84.2              | 84.2              |
| Ctric acid/NaOH | 4.49    | 48.0          | 40.0         | 48.0              | 48.0              |
| Ctric acid/NaOH | 5.39    | 15.0          | 15.0         | 15.0              | 15.0              |
| Ctric acid/NaOH | 6.09    | 6.0           | 6.0          | 6.0               | 6.0               |
| Pure water      | 6.59    | 2.2           | 2.2          | 2.1               | 2.1               |
**Figure Captions**

Fig. 1 Conceptual process for functionalized SB.

Fig. 2 Conceptual image of the removal of cadmium ion from soil and water using the SB.

Fig. 3 FTIR spectra of SB. a, plain SB; b, ODS-SB; c, SH-SB; d, SH-ODS-SB.

Fig. 4 Adsorption of cadmium ion on SB. pH 3.0; Temperature, 25°C; Concentration of the Cadmium ion, 10 mg/L; a, plain SB; b, SH-SB; c, SH-ODS-SB.

Fig. 5 Effects of pH on the adsorption efficiency (%). Amount of Adsorbents, 0.5 g of SH-SB (blue), SH-ODS-SB (pink); Concentration of Cadmium ion, 10 mg/L; pH condition, 0.1 mol/L citric acid/NaOH to adjust pH of the solution at 1–7; Temperature, 25°C; Agitation rate, 150 rpm; Agitation time, 24 h.

Fig. 6 Langmuir’s plot for cadmium adsorption. pH 3.0; a, SH-SB; b, SH-ODS-SB.

Fig. 7 Recovery of the SB from soil. Meanwhile, n=5; Condition for SB and Soil mixture separation, Dosage of Shirasu balloons, 0.5 g; Dosage of Soil, 10 g; Leaching solution, 100 mL of Ctric acid/NaOH buffer solution at pH 3.0; Agitation rate, 150 rpm.

Fig. 8 Photograph of adsorbent in solution with Optical microscope.; a, plain SB; b, plain SB after one week; c, SH-SB after one week; d, SH-ODS-SB after one week.
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Graphical Index

Shinnow-Rikoon (SB) Hollow glass Ø5-15 μm

Dehydration condensation

n-Octadecyldimethylchlorosilane (ODS)

Hydrophobilization

3-Mercaptopropyl-trimethoxysilane (MPTS)

Hybridizations

SH/ODS

Metal-Sulfur bonds Increase adsorption of cadmium and SB

SH-SB

SB surface

SH-ODS-SB

SB surface