Adsorption of Zinc(II) and Copper(II) to Shirasu (Pyroclastic Flow)

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A fundamental study on the adsorption of metal elements on Shirasu, a pyroclastic flow deposit distributed in southern Kyushu, Japan, has been conducted. The adsorption experiment was carried out by a batch method, and by using Zn(II) and Cu(II) under several conditions; the effects of the initial concentration of metal ions, grain size, and pH were investigated. At smaller grain sizes, the amount of Zn(II) and Cu(II) adsorbed increased. At higher pH values, the amount of Zn(II) and Cu(II) adsorbed increased. Plots of the adsorption isotherm indicated that the adsorption of Zn(II) and Cu(II) on Shirasu followed the Langmuir isotherm model, and the Langmuir isotherm constants, W₀ and b, were obtained. W₀ at pH 5.0 was approximately two-times larger than that at pH 3.0. This may reflect an increase in the number of anionic binding sites on the surface of Shirasu with an increase in the pH. The b value for Zn hardly changed with an increase in the pH, and for Cu the value decreased with an increase in the pH. These observations suggest that anionic binding sites have a low stability constant, since the apparent stability constant, b, is obtained as the average of stability constant of all sites on the Shirasu surface.

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Introduction

In the South Kyushu region (especially, Kagoshima Prefecture) of Japan, a pyroclastic flow deposit, locally known as Shirasu, is the main geological characteristic of the region. Shirasu is a volcanic ash property of being sandy, which includes pumice, pumice fall, and these secondary sediments. Most of the secondary sediments originated from pyroclastic flow following an enormous eruption that occurred approximately 25000 years ago in the “Aira caldera,” which is located in Kagoshima Bay.1,2 Shirasu may have a significant effect on the behavior of trace elements in this region, since the adsorption of chemical substances in the environment can be closely related to the geological characteristics. Many studies on the adsorption of chemical substances on clay minerals,3 marine or river sediments,4–9 soil,10,11 etc. have been conducted. On the other hand, studies on Shirasu have mainly focused on disaster countermeasures and engineering utilization,12 and there have been no detailed basic reports on the adsorption of heavy-metal ions on Shirasu.

In a previous study, we investigated the adsorption behavior of Cu(II) ions on Shirasu.13 From this study, it could be clearly observed that the adsorption of Cu(II) depended on the grain size of Shirasu and the pH of the testing solutions, and that the adsorption behavior could be expressed by the Freundlich isotherm. It was also reported that the Freundlich isotherm can be applied to the adsorption phenomenon of porous adsorption mediums (active carbon, silica gel, etc.).14 Thus, this result indicated that the surface of Shirasu was porous. On the other hand, a physicochemical discussion could not be provided by using the Freundlich isotherm, since it is an empirical formula.14 Thus, in some studies6,7,10 a physicochemical consideration of the adsorption behavior was carried out by using the Langmuir isotherm.

In the present study, in order to obtain physicochemical information on the adsorption of metal ions on Shirasu, the adsorption behavior of not only Cu(II), but also Zn(II) was investigated, and the result of the adsorption experiment was examined by using the Langmuir isotherm. Bodergat et al. reported that the Zn(II) concentration in the seawater of Kagoshima Bay was high in some areas,15 and that this feature was concerned with geothermal activity, such as the occurrence of hot springs. Knowledge of the adsorption behavior of Zn(II) on Shirasu is important for estimating the behavior of heavy metals in this region.

Experimental

Apparatus and reagents

For drying Shirasu, an automatic oven (Tokyo Rikakikai, EYELA NDO-400, Tokyo, Japan) was used. The Zn(II) and Cu(II) concentrations were measured by atomic absorption spectrometry (AAS) (Shimadzu, AA-6200, Kyoto, Japan; C₂H₂-air flame). The pH of the solutions was measured with a pH meter (DKK HPH-130, Tokyo, Japan). The chemical composition of Shirasu was analyzed by ICP-AES (Perkin-Elmer, Optima 4300DV). The mineral composition of Shirasu was analyzed by XRD (Rigaku, RAD-C, Tokyo, Japan). A multishaker (Tokyo Rikakikai, EYELA MMS-3010) and a constant-temperature chamber (Tokyo Rikakikai, EYELA FMC-1000) were used for a experiment employing a batch method. Zn(II) and Cu(II) solutions (0.50 - 3.50 mg dm⁻³) were prepared by diluting the standard solution for atomic-absorption spectrometry (1000 ppm, Zn(NO₃)₂ in 0.1 mol dm⁻³ HNO₃; 1000 ppm, CuCl₂ in 0.1 mol dm⁻³ HCl, Nacalai Tesque, Kyoto, Japan) with water. The pH of the Zn(II) and Cu(II) solutions was adjusted by adding a 2.0 × 10⁻³ mol dm⁻³ NaOH solution. Ultrapure water prepared by Water Purification Systems (Nihon Millipore, Elix 5 UV and Mill-Q SP, Tokyo, Japan) was used throughout the study.

Samples

Shirasu samples were collected from outcrops in Kagoshima
City, Makizono town, and Tarumizu City in Kagoshima Prefecture, Japan (Fig. 1). The sample of site A was collected in our previous study. After excluding the surface part (approximately 10 cm in thickness) of the outcrop, Shirasu samples were taken in a polyethylene bag using chucks. The samples were brought back to the laboratory and dried in an automatic oven at 45˚C for three days. Subsequently, they were fractionated into grain sizes of <74, 74–105, 105–150, 150–250, 250–500, and >500 μm using a sieve. The sieved, samples having grain sizes from <74 to 250–500 μm were used for the experiment.

Adsorption experiment

An amount of 0.125 g of the sample and 25 ml of the Zn(II) and Cu(II) solutions, having concentrations of 0.50, 1.00, 1.50, 2.00, 2.50, and 3.50 mg dm⁻³, were poured into a 100-ml Erlenmeyer flask with a ground-glass stopper. The content was shaken using a multishaker under a constant temperature of 25˚C. After shaking for 1 h, the contents of the flask were filtered with a 0.45-μm cellulose acetate syringe filter (Advantec), and the filtrate was analyzed for the equilibrium concentration of Zn(II) and Cu(II) ions by AAS.

The amount of Zn(II) and Cu(II) adsorbed was calculated using the following equation:

\[
W (\text{mg g}^{-1}) = \frac{(C_0 - C_e) (\text{mg l}^{-1}) \times 0.025 \text{ (l)}}{0.125 \text{ (g)}},
\]

where \(C_0\) is the initial concentration of Zn(II) and Cu(II), \(C_e\) the equilibrium concentration of Zn(II) and Cu(II), and \(W\) the amount of Zn(II) and Cu(II) adsorbed on a Shirasu particle.

Results and Discussion

Grain sizes and chemical composition of Shirasu

From the result of a blank test, it was observed that the concentration of Zn and Cu on Shirasu was under the detection limit of AAS. Hence, it was considered that the concentration of metal ions in the water phase was only little influenced by elusion from Shirasu in this experiment. Table 1 gives the grain size distribution of Shirasu. In the sample obtained from the site A, grains with sizes of less than 74 μm were the dominant fraction, while in the samples taken from B and C, grain sizes of less than 74 μm and those in the range of 250–500 μm were the dominant fractions.

The results of chemical analyses of the three samples are given in Table 2. The major component of the samples was SiO₂ and its content was approximately 70%. It has been reported that Shirasu mainly comprises volcanic glass and that 65–73% of the volcanic glass is SiO₂. As shown in Fig. 2, peaks of quartz and plagioclase in Shirasu can be clearly observed in the X-ray diffraction measurements.

No significant difference was observed among the samples for the chemical components presented in Table 2 and Fig. 2. The sample taken from the site A was used for a following experiment.

Effect of grain size of Shirasu on adsorption

The effect of the grain size of Shirasu on the adsorption of Zn(II) and Cu(II) was examined. The pH of the metal solutions

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Table 1 Grain size distribution of Shirasu

<table>
<thead>
<tr>
<th>Grain size/μm</th>
<th>Weight, %a</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>A</td>
</tr>
<tr>
<td>&lt; 74</td>
<td>34.0</td>
</tr>
<tr>
<td>74–105</td>
<td>18.3</td>
</tr>
<tr>
<td>105–150</td>
<td>18.8</td>
</tr>
<tr>
<td>150–250</td>
<td>17.9</td>
</tr>
<tr>
<td>250–500</td>
<td>11.0</td>
</tr>
<tr>
<td>&gt;500</td>
<td></td>
</tr>
</tbody>
</table>

a. >500 μm fraction was excluded (the data for A site were obtained from Ref. 13).

Table 2 Components (%) of Shirasu

<table>
<thead>
<tr>
<th>Component</th>
<th>Weight, %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>A</td>
</tr>
<tr>
<td>SiO₂</td>
<td>70.6</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>9.52</td>
</tr>
<tr>
<td>Na₂O</td>
<td>4.10</td>
</tr>
<tr>
<td>K₂O</td>
<td>3.22</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>2.67</td>
</tr>
<tr>
<td>CaO</td>
<td>1.40</td>
</tr>
<tr>
<td>MgO</td>
<td>0.51</td>
</tr>
<tr>
<td>MnO</td>
<td>0.06</td>
</tr>
<tr>
<td>P₂O₅</td>
<td>0.02</td>
</tr>
<tr>
<td>Ignition loss</td>
<td>2.70</td>
</tr>
</tbody>
</table>

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Fig. 1 Sampling points.

Fig. 2 XRD of Shirasu (sample A).
was adjusted to 3.0. The results are given in Fig. 3. The initial concentrations of the Zn(II) and Cu(II) solutions varied from 0.50 to 3.50 mg dm\(^{-3}\). In every case, the highest values for the adsorption of Zn(II) and Cu(II) were observed for the smallest fractionation (< 74 \(\mu\)m); the larger was the grain size, the smaller was the adsorbed amount.

**Effect of the pH on the adsorption of metal ions**

The fraction with grain sizes of less than 74 \(\mu\)m was used as the adsorbent for the experiment. The pH for 25 ml of Zn(II) and Cu(II) solutions (0.50–3.50 mg dm\(^{-3}\)) was varied from 1.0 to 5.0. The results are given in Fig. 4. The amount of Zn(II) and Cu(II) adsorbed increased with the increase in the pH. Many studies have reported that the higher is the pH, the higher is the adsorption ability of soil for metallic ions.\(^{6-8,17}\) It was reported that H\(^+\) is released from the oxide surface of an adsorbent for high values of the pH, which causes a change in the electric charge of the oxide surface.\(^{18}\) As a result, the adsorption ability of soil increases for positive ions. The increase in the amount of Zn(II) and Cu(II) adsorbed observed in the current study may have been caused by an increase in the negative charge on the Shirasu surface with an increase in the pH.
A plot of the equilibrium concentration vs. adsorbed amount is shown in Fig. 5. The slope of the adsorption isotherm observed at pH 5.0 is larger than that at pH 3.0, reflecting the increase in the amount of Zn(II) and Cu(II) adsorbed with the pH. Langmuir isotherm

The Langmuir isotherm is represented by the following equation:

$$W = \frac{W_0 C_e}{1 + b C_e},$$

where $W$ is the adsorbed amount (mg g$^{-1}$) at equilibrium and $C_e$ is the equilibrium concentration of the adsorbate ions (mg dm$^{-3}$). $W_0$ and $b$ are the Langmuir constants; $W_0$ indicates the maximum capacity, while $b$ is the stability constant, which reflects the adsorption energy. It is known that the Langmuir isotherm can provide information about the process of chemisorption.

Equation (2) is transformed into

$$\frac{C_e}{W} = \frac{C_e}{W_0} + \frac{1}{b W_0}.$$  

In this study, a linear relation was obtained for both Zn(II) and Cu(II) on Shirasu in a plot of $C_e/W$ against $C_e$, along with a high correlation coefficient (Fig. 6). This fact suggests that the adsorption behaviors of Zn(II) and Cu(II) followed the Langmuir isotherm. The correlation coefficient of the $C_e$ vs $C_e/W$ plots for Zn(II) for a pH 3.0 was lower than that for Cu(II). This may be due to the lower affinity of Zn(II) to Shirasu, as compared to that of Cu(II). For a high pH, the correlation coefficient of Zn(II) increased and approached that of Cu(II). The $W_0$ and $b$ values could be obtained from the slope of the line and the intercept on the ordinate, respectively. The values are listed in Table 3. $W_0$ at pH 5.0 was approximately two-times larger than that at pH 3.0. This may reflect an increase in the number of anionic binding sites on the surface of Shirasu with the pH. As shown in Fig. 5, the amount of Zn(II) and Cu(II) adsorbed approached the $W_0$ values along with an increase in the equilibrium concentration. Although the $W_0$ values listed in Table 3 seem to be independent of the particle size, the highest values are observed for the smallest fraction (< 74 μm).

With regard to the adsorption of metal ions on Shirasu, an equilibrium can be represented by the following equation:

$$k_1 [A][B] = k_2 [A – B],$$

where $[A]$ is the metal ion concentration and $[B]$ is the density of adsorption sites on Shirasu. When metal ions bind with the sites electrostatically, H$^+$ ions may compete with the metal ions for binding with the sites. Thus, the equilibrium between H$^+$ ions and the binding sites has to be considered to explain the effect of the pH on the adsorption of metal ions. The equilibrium constant of the reaction can be represented as the dissociation constant of [H – B]:

$$K_a = \frac{[H^+][B]}{[H – B]} \quad (H – B \rightleftharpoons H^+ + B),$$

$$[H – B] = \frac{[H^+][B]}{K_a},$$

where $K_a$ is the dissociation constant of [H – B].

The total density of the sites that do not bind with metal ions on Shirasu, $[D_a]$, equals the sum of [H – B] and [B]. [B] is the
density of the sites that adsorb neither H+ ions nor metal ions.

\[ [D_a] = [B] + [H - B] \]
\[ = \frac{K_a[B] + [B][H^+]}{K_a} \]
\[ = [B] \left( \frac{K_a + [H^+]}{K_a} \right) \]

The ratio of \([B]\) to \([D_a]\) is

\[ \frac{[B]}{[D_a]} = \frac{K_a}{K_a + [H^+]} = \alpha \]

When \([B] = \alpha[D_a]\) is substituted in Eq. (4b), we obtain

\[ K_a = \frac{[A - B]}{[A][D_a]} = b. \]

Here, \(b\) is calculated by using the Langmuir isotherm. From the equations, it is apparent that \(b\) should increase with a decrease in \([H^+]\), since \(\alpha\) increases with a decrease in \([H^+]\).

However, for the Zn solution, the \(b\) value for Zn hardly changed with an increase in the pH, and for Cu the value of \(b\) decreased with an increase in the pH. These observations suggested that binding sites with different \(b\) values exist on the Shirasu surface. In other words, by increasing the pH, binding sites with lower \(b\) values newly appeared due to the dissociation of H+; these sites cause an increase in the \(W_0\) values, but the \(b\) values may either decrease or remain fairly constant. Hence, the apparent stability constant is obtained as the average of the stability constants of all the sites appearing on Shirasu.

The variation in the \(b\) value resulting from a change in the pH was different for Zn(II) and Cu(II), which suggested that the adsorption mechanism on Shirasu differed for each of them. It was also inferred that Cu(II) is adsorbed on Shirasu more easily as compared to Zn(II).

In some studies, the \(W_0\) values of Zn(II) and Cu(II) were reported for sediments\(^6,18\) and peats\(^7,19\). When compared with those values, the \(W_0\) value for Shirasu obtained in this study was similar or smaller. However, Shirasu covers a large area, and thus the adsorption on Shirasu may be an important factor for elucidating the environmental behavior of metal ions in the study area.

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References