Adsorption of Arsenic(V) by Use of Aluminium-Loaded Shirasu-Zeolites

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A P_1 type Shirasu-zeolite (SZP_1) was treated with an aluminium sulfate solution, and thus an aluminium-loaded SZP_1 (Al-SZP_1) was prepared. By use of Al-SZP_1 as an adsorbent, the adsorption of As(V) was examined. The Al-SZP_1 was superior to an activated alumina and other aluminium-loaded zeolites in terms of the adsorption ability for As(V).

Arsenic is one of highly toxic elements and the arsenic level of water is regulated below 0.1 mg L^{-1} in wastewater by the Japanese Effluent Standard (Prime Minister's Office, 1993) and 0.01 mg L^{-1} in natural water by the Environmental Quality Standards for Water Pollution (Environmental Agency, 1993). However, according to a recent survey of the Environmental Agency for the arsenic concentration of well water, 2-3% out of ca. 3000 wells which spread all over Japan showed excess values over the new standard. Also, in West Bengal region in India, Inner Mongolia region in China, Thai, and Taiwan, serious arsenic pollutions are running through. Thus, it is urgently needed to develop adsorbents for arsenic which are good in terms of both efficiency and cost.

The most common arsenic removal method is precipitation with lime and iron(III) salts followed by adsorption onto the resulting iron(III) hydroxide flocs.[1] However, the flocs are usually quite fine and colloidal form, so that it is difficult to dewater the flocs. Therefore, a large volume of wet sludge is produced and secondary treatments are required.[2,3] Various adsorbents for arsenic, which are easy to remove from aqueous media after the adsorption of arsenic, have been developed. The adsorbents include activated alumina,[4,5] activated carbon,[6,7] metal-loaded activated carbon,[8,9] metal-loaded coral limestone,[10,11] lanthanum hydroxide or carbonate,[2,12,13] and a hydrous zirconium oxide.[3]

Various types of zeolite have so far been prepared from "Shirasu" which is a volcanic pile and present in southern Kyushu area in Japan in large quantities.[14] Some of such Shirasu-zeolites have an advantage of easy synthesis. Especially, P_1 type zeolite (SZP_1) is easily prepared by one-step reaction in which Shirasu is only treated with a sodium hydroxide solution at 105 °C for several hours. In the present work, we prepared an aluminium-loaded SZP_1 (Al-SZP_1) by treating SZP_1 with an aluminium sulfate solution, and found that Al-SZP_1 works as an excellent adsorbent for arsenate (As(V)).

A Shirasu-zeolite, SZP_1, and other Shirasu zeolites were donated from Sankei Kagaku Co., Ltd. (Kagoshima, Japan). The composition of SZP_1 was $Na_2O \cdot Al_2O_3 \cdot 3.3SiO_2 \cdot 4.3H_2O$ to $Na_2O \cdot Al_2O_3 \cdot 5.3SiO_2 \cdot 5.7H_2O$; while the average particle size was 35-45 μm, the effective pore size was 0.35 nm, and the specific surface area was ca. 0.1 $m^2\ g^{-1}$. Other aluminium-loaded Shirasu-zeolites, Al-SZP_2 and Al-SZA, were also prepared from P_2 type Shirasu-zeolite (SZP_2) and A type Shirasu-zeolite (SZA), respectively, in a similar manner.

The preparation of Al-SZP_1 was carried out as follows. To an aqueous solution (1 L) of 7 mmol L^{-1} aluminium sulfate was added 10 g of SZP_1, which had been washed with deionized water and with 0.1 mol L^{-1} sodium nitrate solution, and the mixture was agitated for 12 hours. Then the Al-SZP_1 thus obtained was washed with deionized water and dried. The Al-SZP_1 contained 7.3 wt% of aluminium loaded by the treatment.

The adsorption of As(V) by the aluminium-loaded Shirasu-zeolites was examined. An aqueous solution (20 mL) of 7.0 mg L^{-1} As(V) (added as $Na_2HAsO_4 \cdot 7H_2O$) was shaken with 0.1 g of the adsorbent at 24-25 °C for a definite period. After removal of the adsorbent, the concentration of arsenic remaining in the aqueous solution was determined by atomic absorption spectrophotometry using a Nippon Jarrel Ash AA-890 with a FLA-1000 flameless atomizer unit.

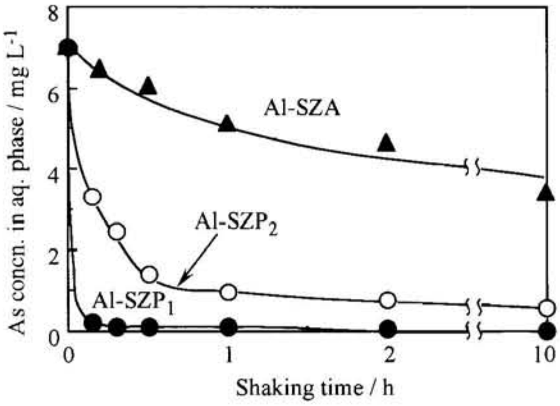

Figure 1. Adsorption of As(V) by aluminium-loaded Shirasu-zeolites.

As seen in Figure 1, when Al-SZP_1 was used for the adsorbent, the concentration of arsenic in the aqueous phase decreased to 0.2 mg L^{-1} after 10 min, resulting in less than 0.01 mg L^{-1} after 2 h. When Al-SZP_2 was used, the adsorption rate considerably decreased, and the arsenic concentration was 0.55 mg L^{-1} even after 10 h. SZP_1 is a cubic system while SZP_2 is a tetragonal system, which may relate to the difference in the adsorption ability. Details about the difference due to the structure of Shirasu-zeolite is now under study. The adsorption ability of Al-SZA was much inferior to those of Al-SZP_1 and Al-SZP_2. When unloaded SZP_1 was used, almost no decrease in the arsenic concentration was observed.

By use of those aluminium-loaded Shirasu-zeolites, the adsorption isotherm was examined. An aqueous solution of 400 mg L^{-1} As(V) was shaken with 0.05-2.0 g of the adsorbent at 24-25 °C for 15 h. After removal of the adsorbent, the arsenic concentration in the aqueous solution was determined. Figure 2 shows the adsorption isotherms of Al-SZP_1, Al-SZP_2 and Al-

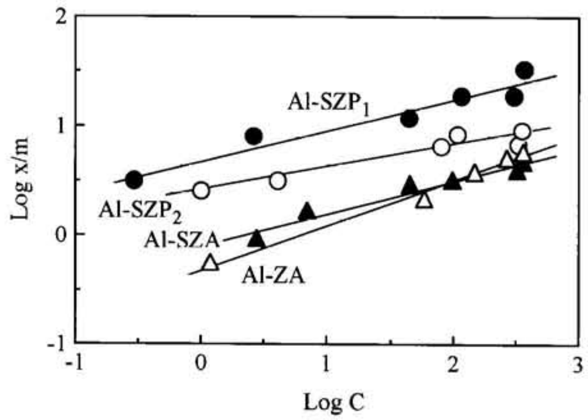

Figure 2. Adsorption isotherms of As(V) by use of various aluminium-loaded zeolites.
C: Equilibrium concn. of As in the aqueous phase (mg L^{-1}).
x/m: Amount of As adsorbed on the adsorbent (mg g^{-1}).

SZA, for which the Freundlich's constants 1/n are 0.27, 0.21, and 0.29, respectively; while the log K values are 0.69, 0.40, and -0.09, respectively. A commercially available synthetic zeolite (A type), which was purchased from Wako Pure Chemical Industries, Ltd., was treated with an aluminium sulfate solution in a similar manner and the resulting aluminium-loaded zeolite (Al-ZA) provided an adsorption ability similar to that for Al-SZA, as seen in Figure 2. Activated alumina has been often used as an adsorbent for As(V).[4,5] As shown in Figure 3, the absorption ability of Al-SZP$_1$ was better than that of an activated alumina (300 mesh; Wako Pure Chemical Industries).

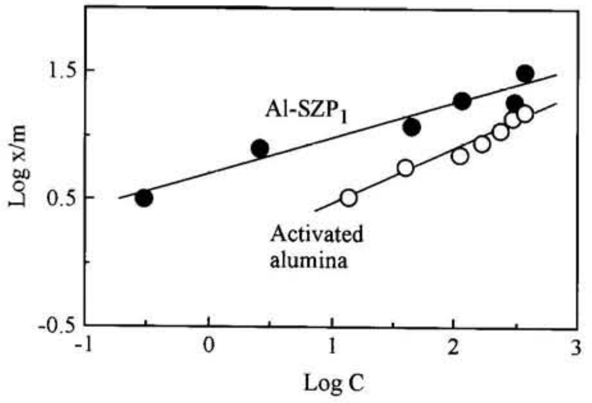

Figure 3. Adsorption isotherms of As(V) by use of Al-SZP$_1$ and activated alumina.
Symbols C and x/m are the same as those in Figure 2.

In conclusion, it is proved that by treating a Shirasu-zeolite, SZP$_1$, with an aluminum sulfate solution, an excellent adsorbent for As(V) can be prepared. It is proposed that the adsorption of As(V) proceeds through the formation of aluminium hydroxide on the surface and/or in the cavity of Shirasu-zeolite, followed by the replacement of the hydroxide anion by the arsenate anion in aqueous media. Similar mechanisms have been reported in the adsorption of phosphate by an aluminium-loaded alumina[15] and that of As(V) by a lanthanum-loaded silica gel.[12] Shirasu is abundantly present but currently useless resource in southern Kyushu area. The synthesis of SZP$_1$ is quite easy compared to other synthetic zeolites. Thus, the use of Al-SZP$_1$ as a practical adsorbent for hazardous anions, such as As(V), is certainly feasible and deserves further exploration.

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