Adsorption Properties of As(III) and Cr(VI) in Water Environment by Calcined Gibbsite

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The adsorption properties of As(III) and Cr(VI) by gibbsite (GB) calcined at 200 to 1150 °C was investigated on basis of their specific surface area, number of hydroxyl groups, surface pH and adsorption isotherms. The amount of As(III) and Cr(VI) adsorbed on the calcined GB at 300 or 400 °C was the highest. In the case of the calcination temperature was more than 700 °C, the amount adsorbed decreased with the increasing calcination temperature. In a single solution system, the amount of As(III) adsorbed on calcined GB was higher than that of Cr(VI). The amount of As(III) and Cr(VI) adsorbed on calcined GB was higher in a binary solution system than those in a single solution system. The pH in solution after As(III) and Cr(VI) adsorption was greater than that before adsorption. These results indicated that the adsorption mechanism of As(III) and Cr(VI) was as followed: the hydroxyl groups on calcined GB were exchanged to As(III) and Cr(VI) and they adsorbed n the calcined GB surface. In the case of coexistence of As(III) and Cr(VI), they could be removed better by calcined GB because the pH in binary solution was lower than that in single solution. Both As(III) and Cr(VI) in water environment could be removed by the calcined GB simultaneously.

Key words   adsorption; water treatment; As(III); Cr(VI); calcination; gibbsite

Safety of the water supply is the most important for human health. Sometimes, heavy and toxic metals have been contained in drinking water. In industrial countries, drinking water has been treated with many kinds of technologies and has been supplied to the people. While in developing countries, heavy and toxic metals are contained in drinking water because the developing country does not have a system for water treatment. Heavy and toxic metals have been detected many times, their concentrations are over the standard values for drinking water at the World Health Organization (WHO). The developing countries need a policy as soon as possible.[1]

On the other hand, copper, chromium and arsenic (CCA) have been used as an antiseptic for wood around the world. For example, their consumption is approximately 350 thousands ton/year and 20 million ton/year in Japan and in India, respectively. The Waste Study Foundation reported the amount of CCA contained in waste woods in Japan to be 425, 1053 and 460 mg/kg, respectively. The problem concerning wastes has occurred not only Japan but also in many countries and is very important. Their metals are presented in the ash after burning of waste wood and flow from reclaimed ground into seawater. However, large amounts ingested cause adverse reactions such as acute toxicity, nausea, vomiting and diarrhea, and chronic toxic, dermatitis, pigmentation, myelopathy, peripheral neuropathy, jaundice and renal failure.[2] The toxicity of inorganic arsenic is higher than that of organic arsenic. Arsenic has been detected over the standard value in the wastewater of factories in Japan. Especially, in Bangladesh, Taiwan, northern China, Mexico, Chile, Argentina and the United States of America, these problems are serious. While activated carbon[3,4] and hydroxyl cerium[5] are famous as adsorbates to remove As(III). In 1993, the WHO decreased from 50 to 10 μg/l the standard value for arsenic concentration in drinking water. Cr(VI) shows a strongly oxidative action, causing inflammation of the throat and mucous membranes of the nose. A high concentration of Cr(VI) causes nasal septal perforation. The carcinogenicity of As(III) and Cr(VI) has been reported in many studies.[6—9] It is necessary that the technology for removal of heavy and toxic metals be low cost and easy to use.

Aluminum is a perfectly recyclable metal. Gibbsite (GB, Al(OH)$_3$) as well as boehmite (BE, AlOOH) is components of bauxite, and it is well known that GB is cheaper than BE. BE has a high As(III) adsorption ability,[10] the structure of GB changes to that of BE by calcination.[11] The adsorption mechanism of As(III) on GB based on model calculations was reported by Oliveira *et al.*[12] and the specific bonding of arsenate on GB was reported by Weerasooriya *et al.*[13] However, the adsorption ability of As(III) on GB in binary solution system (containing both As(III) and Cr(VI)) has never been reported.

In this study, calcined GB was used, and the adsorption ability and adsorption mechanism of both As(III) and Cr(VI) were studied. We estimated the application of their use as an adsorbent based on the results of the specific surface area, the number of hydroxyl groups, surface pH and the adsorption isotherm of As(III) and Cr(VI) on the calcined GB surface. The removal properties of As(III) and Cr(VI) from lake water were investigated.

Experimental

Materials   As(III) and Cr(VI) were obtained as As$_2$O$_3$ and K$_2$Cr$_2$O$_7$ purchased from Wako Pure Chemical Ind., Japan. GB (GBH-42M) was purchased from Showa Denkou in Japan. The mean particle size, specific surface area, moisture adsorption capacity and the amount of surface hydroxyl groups were 1.1 μm, 5 m^2/g, 0.90% and 4.23 mmol/g, respectively. The specific surface area was measured using Flow SorbII 2300 (Micrometrix Co., U.S.A.) based on the nitrogen adsorption method. For X-ray diffractometry (XRD), we used RINTO2100V (RIGAKU, Japan), conditions are 40 kV, 20 mA, and Cu$K\alpha$. The amount of surface hydroxyl groups was calculated based on the amount of fluoride ion adsorbed.[14] Calcined GB was prepared by treating 20 g of virgin GB in a muffle furnace with the temperature of 200—1150 °C (GB200-GB1150) for 2 h. The surface pH of virgin GB was measured as follows: approximately 2.0 g of virgin or calcined GB was separately put into 100 ml of deionized water (pH 7.0) for 2 min, and the pH in

solution was measured with a digital pH meter (Horiba Ltd., Japan).

Adsorption of As(III) and Cr(VI) on GB The amount of As(III) and Cr(VI) adsorbed was measured by the following method: 50 mg of virgin or calcined GB is added to 50 ml of As(III) and/or Cr(VI) solution at a concentration of 500—1000 μg/l. The solution was shaken at 25 °C for 24 h and then was filtrated using a 0.45 μm membrane filter. The concentration of As(III) and Cr(VI) was measured using a inductively coupled plasma (ICP-7500, Shimadzu Co., Ltd., Japan). The amount of As(III) and Cr(VI) adsorbed on virgin or calcined GB was calculated according to Eq. 1 using the concentration before and after adsorption.

$$X = \frac{(C_0 - C)V}{1000M} \qquad (1)$$

where X is amount of As(III) and Cr(VI) adsorbed (μg/g), C_0 is the concentration before adsorption (μg/l), C is the concentration after adsorption (μg/l), V is the solvent volume (ml) and M is the weight of virgin or calcined GB (g).

Influence of pH on Adsorption The pH of the solution was adjusted from 2 to 7 by adding a suitable volume of 0.1 mol/l hydrochloric acid or 0.1 mol/l sodium hydroxide solution. Chloride ion did not adsorb on virgin or calcined GB.[15] The initial concentration of As(III) and Cr(VI) was 500 and 1000 μg/l, respectively. The solution was shaken at 25 °C for 24 h and then was filtrated using a 0.45 μm membrane filter. The concentration of As(III) and Cr(VI) was measured using a ICP-AES. The amount of As(III) and Cr(VI) adsorbed on GB400 was calculated according to Eq. 1 using the concentration before and after adsorption.

Removal of As(III) and Cr(VI) from Lake Water The lake water was obtained from Lake Biwa, the largest lake in Japan) in Shiga prefecture. The concentration of As(III) and Cr(VI) in the lake water were 0 μg/l. As(III) and Cr(VI) were added to the lake water, the concentration of As(III) and Cr(VI) after addition was 600 and 300 μg/l, respectively. The amount of As(III) and Cr(VI) adsorbed was measured by the following method: 50 mg of GB400 is added to 50 ml of the lake water, The solution was shaken at 25 °C for 24 h and then was filtrated using a 0.45 μm membrane filter. The concentration of As(III) and Cr(VI) was measured using a inductively coupled plasma (ICP-7500, Shimadzu Co., Ltd., Japan).

Results and Discussion

Characteristics of GB The specific surface area, the number of hydroxyl groups and the surface pH of GB are shown in Table 1. This result indicates that the structure of GB200 is similar to that of virgin GB and the structure of GB was changed at the calcination temperature of more than 300 °C. It is evident that specific surface area becomes maximum when the calcination temperature is 400 °C. There is a report that specific surface area becomes maximum when the calcination temperature is 300 °C,[16] but in this study the calcination temperature of about 400 °C gave the maximum value of specific surface area. Garcia *et al.* and we used the bayer hydrate and the gibbsite, respectively. Both are aluminum compounds, but the specific surface area of them was different. And it is recognized that the specific surface area decreased as the calcination temperature is raised in the range over 400 °C. It is reported that specific surface area of pseudo-boehmite by calcining GB at 500 °C is 265 m²/g,[17] and in the calcining experiment of GB in this study, the specific surface area at the calcination temperature of 500 °C was 227 m²/g. The two values are very close with each other.

The relationship between the specific surface area and the number of hydroxyl groups is shown in Fig. 1. The number of hydroxyl groups increased with the increasing specific surface area; the correlation coefficient is 0.969. The specific surface area and the number of hydroxyl groups of GB400 were the largest. When the calcination temperature was from 400 to 900 °C, the structure of GB changed to the amorphous aluminum oxide. The specific surface area and the number of

Table 1. Specific Surface Area and the Number of Hydroxyl Group of GB Calcined at Different Temperatures

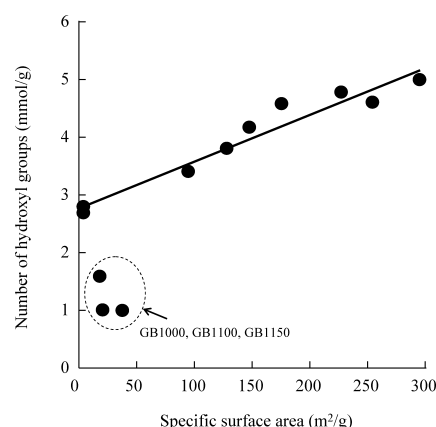| Samples	Specific surface area (m²/g)	Number of hydroxyl group (mmol/g)	Surface pH
Virgin GB	4.2	2.7	8.7
GB200	4.6	2.8	9.3
GB300	253.9	4.6	9.7
GB400	295.3	5.0	9.8
GB500	227.3	4.8	9.3
GB600	176.1	4.6	9.4
GB700	147.7	4.2	9.6
GB800	128.1	3.8	9.6
GB900	95.4	3.4	9.7
GB1000	36.8	1.0	10.0
GB1100	20.8	1.0	10.3
GB1150	17.7	1.6	10.2

Fig. 1. Relationship between the Specific Surface Area and the Number of Hydroxyl Groups
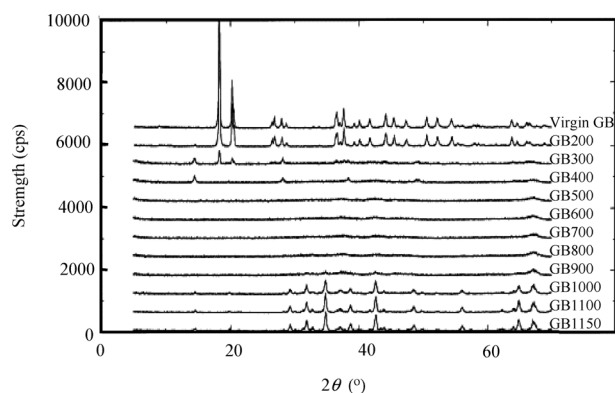

Fig. 2. Results of the X-Ray Diffractometry of Virgin and Calcined GB

hydroxyl groups decreased with the increasing calcination temperature. The calcined GB at more than 1000 °C might become aluminum oxide, a stabler crystal structure. The structural conversion of GB by calcination has been reported; the structure of GB is changed to that of BE[18] or γ-type GB.[19] The structural transformation of calcined GB at more than 1150 °C has been reported.[20]

Results of X-ray diffractometry(XRD) for virgin or calcined GB were reported[15] (in Fig. 2). Then, it became evident that when the calcination temperature is 200 °C, the structure of GB for calcined GB at 200 °C is the same as that

of virgin GB, but when the calcination temperature was higher than 300 °C, structure of GB was destroyed, and when the calcination temperature was 400 °C, BE structure appeared and amorphous aluminum oxide was produced. There is a report[18] that the structure of the substance changes from GB structure to boehmite structure, and in this study, it is reconfirmed that similar structural change happens when the substance is calcined at around 400 °C. Furthermore, it must be pointed out that when the calcination temperature is higher than 1000 °C, GB became aluminum oxide with crystal structure which is a very stable substance.[11]

Adsorption Isotherms of As(III) and Cr(VI)   The adsorption isotherms of As(III) on virgin or calcined GB are shown in Fig. 3a. The As(III) did not adsorb on the virgin GB and GB200. The amount of As(III) adsorbed on GB300 or GB400 was the greatest and decreased with the increasing calcination temperature. That of As(III) adsorbed on GB depends on the specific surface area and the number of hydroxyl groups of GB because of the largest specific surface area and number of hydroxyl groups of GB. In contrast, that on GB increased up to 400 °C calcination temperature and decreased with increasing calcination temperature. The hydroxyl groups in the GB appear due to a hydration reaction between GB and water. Many hydroxyl groups may exist on the surface of the calcined GB, and the amount of As(III) adsorbed on GB300 or GB400 was the greatest.

The adsorption of heavy metals on adsorbents depends on the pH in solution. The pH in solution before and after As(III) adsorption is shown in Fig. 3b. The pH in solution after adsorption was greater than that before adsorption because the hydroxyl groups on the GB surface would exchange with As(III). Moreover, it is considered that As(III) was adsorbed to the surface of GB because of the increasing specific surface area.

The amount of Cr(VI) adsorbed on virgin or calcined GB is shown in Fig. 4a. The amount of Cr(VI) adsorbed on calcined GB was smaller than that of As(III), and that on GB300 or GB400 was the largest. The amount of Cr(VI) adsorbed on calcined GB decreased with increasing calcination temperature. The adsorption behavior of Cr(VI) on calcined GB is similar to that of As(III). GB could adsorb both As(III) and Cr(VI) and could be utilized for the treatment of water containing As(III) and Cr(VI).

The pH in solution before and after Cr(VI) adsorption is shown in Fig. 4b. In spite of the fact that Cr(VI) hardly adsorbs on virgin GB, GB200, GB1000, GB1100 and GB1150 the pH in solution after adsorption increased was compared with that before adsorption. This result indicates that the surface pH of calcined GB was alkaline, that is, when calcined GB is added to water, the pH in solution increases. The pH in solution after adsorption by GB300—GB900 is greater than that before adsorption because of the ion exchange between the Cr(VI) and the hydroxyl groups. Moreover, Cr(VI) was adsorbed to the surface of calcined GB. The amount of As(III) and Cr(VI) adsorbed on calcined GB depends upon both the specific surface area and the number of hydroxyl groups present. The adsorption mechanism of both heavy metal ions on GB involves ion exchange between the As(III) and Cr(VI) and the hydroxyl groups. Moreover the As(III) and Cr(VI) would adsorb on calcined GB surface.

There are many kinds of heavy metals in water. The adsorption mechanism of As(III) and Cr(VI) on calcined GB in
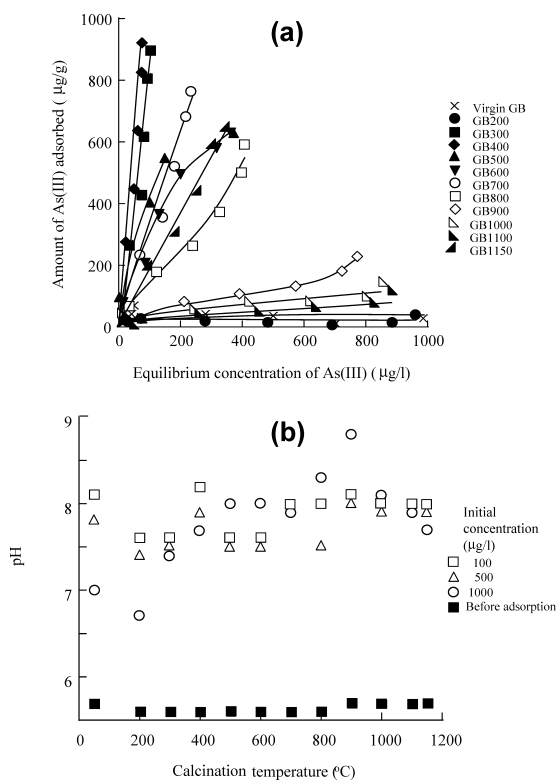

Fig. 3.   Adsorption Isotherm and pH in Solution before and after Adsorption of As(III) in a Single Solution System

(a) Adsorption isotherm, (b) pH in solution after adsorption.
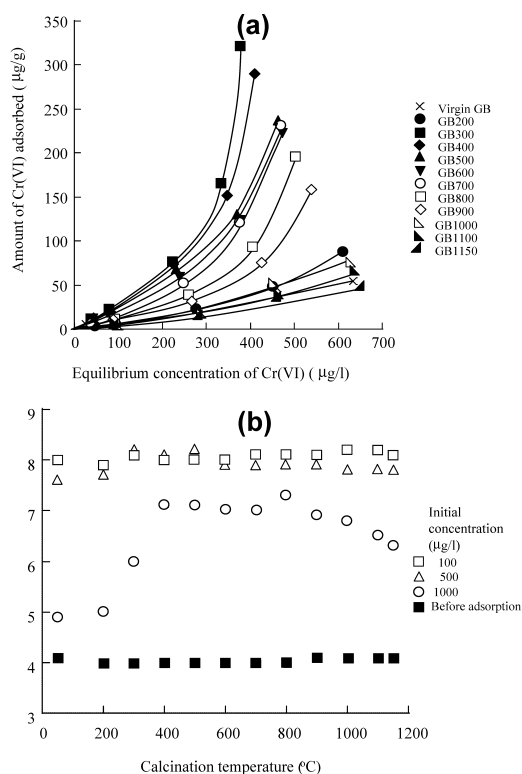

Fig. 4.   Adsorption Isotherm and pH in Solution before and after Adsorption of Cr(VI) in a Single Solution System

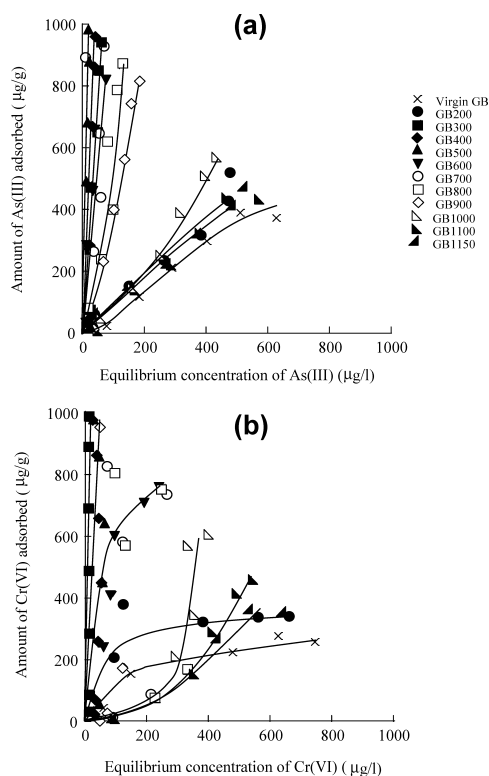(a) Adsorption isotherm, (b) pH in solution after adsorption.

Fig. 5. Adsorption Isotherm of As(III) and Cr(VI) in a Binary Solution System

(a) Adsorption of As(III), (b) adsorption of Cr(VI).
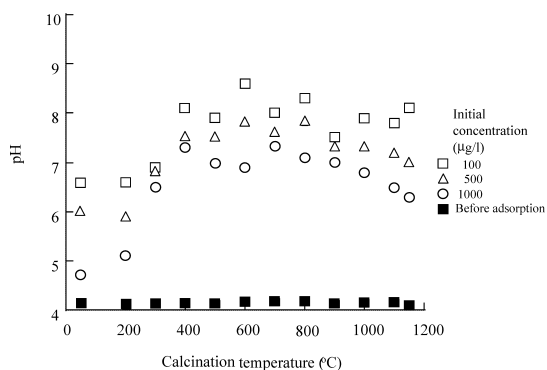

Fig. 6. pH in Solution after Adsorption of As(III) and Cr(VI) in a Binary Solution System

Fig. 7. Amount of As(III) and Cr(VI) Adsorbed on GB400 in Different pH Solutions

binary solution system is important for the evaluation of removal efficiency. The amount of As(III) and Cr(VI) adsorbed on GB is shown in Figs. 5a and 5b, respectively. The amounts of As(III) and Cr(VI) adsorbed on GB300, GB400 and GB500 are higher than on the calcined GB at other temperatures. GB had a higher adsorption ability for As(III) and Cr(VI) in a binary solution system compared with that in a single solution system. Hence, As(III) and Cr(VI) easily could adsorb on GB surface. Especially, the amount of Cr(VI) adsorbed on GB increased compared with As(III). If both As(III) and Cr(VI) are contained in contaminated water, calcined GB can remove those ions with high efficiency.

The pH in a binary solution system is shown in Fig. 6. This result is similar to that in a single solution system. The pH before adsorption on GB was about 4 but increased after adsorption. This result indicated that one of the adsorption mechanism of As(III) and Cr(VI) involves ion exchange between heavy metal ions and hydroxyl groups and adsorption on surface.

Influence of pH on Adsorption In general, ion adsorption is affected by pH, and it is important to evaluate heavy metal ion adsorption behavior in different pH solutions. The amount of As(III) and Cr(VI) adsorbed on GB400 in different pH solutions is shown in Fig. 7. In the results, the amount of Cr(VI) adsorbed exhibited the highest in acid solution (pH around 3 or 4), and decreased with the increasing pH in solution. This is thought to occur because the hydroxyl groups in GB can exchange to Cr(VI) under acidic conditions. The Cr(VI)-contaminated water must have been treated with the calcined GB under acidic condition. After adsorption of Cr(VI), the calcined GB could recycle by alkali treatment.

The amount of phosphate adsorbed on BE at pH 4 was the greatest and decreased with increasing pH.[21] The adsorption mechanism of Cr(VI) on GB may be similar to that of phosphate on BE. While the amount of arsenic adsorbed did not change in the pH range of 4 to 8. As(III) can remove from As(III)-contaminated water without adjusting pH.

Removal of As(III) and Cr(VI) from Lake Water The concentration of metal ions in lake water is Mg (3 mg/l), Ca (18 mg/l), Mn (7 μg/l), Fe (68 μg/l), Zn (2 μg/l), Ba (34 μg/l), and Pb (1 μg/l). The As(III) and Cr(VI) were not detected form this lake water. Therefore, As(III) and Cr(VI) were added to the lake water. The amount of As(III) and Cr(VI) onto GB400 from lake water is shown in Table 2. That of As(III) onto GB400 was larger than that of Cr(VI). That of As(III) and Cr(VI) in a binary solution system was larger than that in a single solution system. These results indicated that GB400 would be used for the removal of As(III) and Cr(VI) from the water environmental.

Conclusions

GB was calcined at 200—1150 °C for 2 h. The number of hydroxyl groups on GB increased with the increasing calcination temperature up to 900 °C, and the relationship between the specific surface area and the number of hydroxyl groups was correlated. The amount of As(III) adsorbed on calcined GB was larger than that on virgin GB because of the greater number of hydroxyl groups produced by hydration of the calcined GB. The calcined GB at 300—900 °C could ad-

Table 2. Amount of As(III) and Cr(VI) Adsorbed on GB400 from Lake Water

Samples	Solution system	Equilibrium concentration (mg/l)	Amount adsorbed (mg/g)	Adsorption degree (%)
As(III)	As(III)[a]	160	460	74.2
	As(III)+Cr(VI)[a]	134	479	77.9
Cr(VI)	Cr(VI)[a]	332	18	5.1
	Cr(VI)+As(III)[a]	318	46	12.6

a) The concentration of As(III) and Cr(VI) after addition in lake water was 600 μg/l and 350 μg/l, respectively. The concentrations of As(III) and Cr(VI) in lake water, was obtained from Lake Biwa in Shiga prefecture, were 0 μg/l.

sorb both As(III) and Cr(VI). The one of the adsorption mechanism of As(III) and Cr(VI) on GB involves ion exchange between the hydroxyl groups and heavy metal ions. The amount of As(III) and Cr(VI) in a binary solution system was larger than that in a single solution system. In the case of coexistence of As(III) and Cr(VI), they could be removed better by calcined GB. As(III) and Cr(VI) in lake water would be removed by GB400.

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