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Removal of arsenious ion by calcined aluminum oxyhydroxide (boehmite)

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Abstract

Aluminum oxyhydroxide (boehmite, BE) shows adsorption ability of arsenious ion. In this study, we calcined BE in the temperature range 200–1150 °C, and examined the amount of arsenious ion adsorbed and adsorption mechanism. As a result, the adsorption amount of arsenious ion by BE calcined at 400 °C showed the highest value as compared with those by BE calcined at other temperatures. On the other hand, the amounts of arsenious ion adsorbed onto BE showed lower values at 200, 600, and >1000 °C than that by BE before calcination. The amount of surface hydroxyl group of calcined BE showed the highest value at the calcination temperature of 400 °C. As a result of X-ray analysis, BE showed boehmite structure at less than the calcination temperature of 300 °C, while BE was converted to the transitional state of aluminum oxide at more than 400 °C. From the result of the amount of arsenious ion adsorbed and FT-IR, it turned out that calcined BE dissociated water molecule when suspended in the water, hydroxyl group was generated on the surface, and the amount of arsenious ion adsorbed was increased because of the ion exchange of these hydroxyl groups with arsenious ions. It was clarified that an adsorbent with high adsorption ability of arsenious ion was obtained by calcination of BE.

Keywords: Arsenious ion; Adsorption mechanism; Boehmite; Calcinations

1. Introduction

Bauxite was imported in large quantities for the purification of aluminum of which recycling is completely possible. Bauxite consists of gibbsite and BE. This material is known to be cheap, easily processable, and useful for recycling. It is well known that BE, which is the molecular formula of $(\mathrm{AlOOH})_n$, is colorless, insolubility in water, acid or base residence, thermal residence. That has used to make a catalyst, an abrasive or a filler.

On the other hand, arsenic is an essential element for the human body. However, large amount of ingestion causes adverse actions such as acute symptoms (nausea, vomiting, diarrhea) and chronic symptoms (dermatitis, pigmentation, myelopathy, peripheral neuropathy, jaundice, renal failure) [1]. In 1993, the World Health Organization (WHO) lowered standard value of arsenic concentration in drinking water from 50 to 10 μg/L. According to the standard value of WHO, many countries lowered the value to 10 μg/L. On the other hand, not a few developing countries maintain the standard value of 50 μg/L, because it is impossible to measure lower concentration for lack of appropriate facilities [2]. Pollution of ground water at the arsenic concentration of more than 50 μg/L is discovered all over the world. Arsenic concentrations are beyond several thousands times as much as standard value in several areas. Especially, in Bangladesh, Taiwan, northern China, Mexico, Chile, Argentina, and the United States of America they are serious [2]. In Japan high concentration of arsenic, exceeding the standard value, is detected in soil and ground water from the site of the factories [3].

With respect to adsorption/desorption of arsenious ion, many methods including activated carbon [4], aluminum oxide [5], activated alumina [6,7], ion-exchange resin, and their modifiers have been reported until now. However, at present, there is no report about relationship between calcination temperature of calcined BE and adsorption ability of arsenious ion.

In this study, we evaluated BE calcined at 200–1150 °C as adsorbent of arsenious ion based on the results of FT-IR, specific surface area, and the amount of surface hydroxyl group of BE and adsorption isotherm of arsenious ion.

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2. Materials and methods

2.1. Materials

AD220NS (Tomita Pharmaceutical, Japan) was used as BE. For the BE, we placed noncrystalline aluminum hydroxide in an aqueous media, and after heat treatment for 1–3 h at 90–100 °C, spray-dried the obtained aluminum oxyhydroxide. The compositions of BE are shown in Table 1.

2.2. Characteristics of BE

For the Fourier transform infrared spectrometry, we used AVATAR360 (Thermo Nicolet Corp., Japan). For the X-ray diffractometry, we used RINT2100V (RIGAKU, Japan), conditions are 40 kV, 20 mA, and Cu$K\alpha$. For the measurement of specific surface area, we used Flow Sorb 2300 (Micrometorix, USA). Amount of surface hydroxyl group was calculated based on amount of fluoride ion adsorbed [8]. Samples (0.05 g) were added to 50 mL of 0.01 mol/L sodium fluoride solution of which pH was adjusted to 4.6 with 0.2 mol/L acetic acid, 0.2 mol/L sodium acetate buffer, and shaken at 25 °C for 20 h. Then, fluoride concentration in the supernatant was measured using DR4000U (HACH, USA) and amount adsorbed was estimated based on the difference from the initial concentration [9].

2.3. Calcination of BE

For the calcination treatment, 20 g of BE was placed in a porcelain crucible. Then, the temperature was raised to 200–1150 °C during 2 h and kept for 2 h using a Muffle.

2.4. Adsorption isotherm of arsenious ion

For the adsorption isotherm of arsenious ion, 50 mg of calcined BE was added to 50 ml of arsenic trioxide solution having different concentrations (50, 100, 300, 500, 700, 900, and 1000 µg/L), the mixture was shaken at 25 °C for 20–24 h, and concentration of arsenious ion in the filtrate was measured after filtration using a 0.45-µm membrane filter. Concentration of arsenious ion was measured using a plasma emission spectrometer (ICP-7500, Shimadzu, Japan). The amount of arsenious ion adsorbed by BE was calculated according to Eq. (1) using an initial concentration and an equilibrium concentration.

$$q = V(C_0 - C_e)/W_s, \tag{1}$$

where q is amount of arsenious ion adsorbed (µg/g), W_s is amount of BE (g), C_0 is initial concentration (µg/L), C_e is equilibrium concentration (µg/L), and V is sample volume (L).

Table 1
Composition of BE

Loss on drying	7.8%
Cl^-	>0.1%
SO_4^{2-}	>0.8%
pH	pH 8.2
Particle size	av. 100 µm
Pore volume	0.402 ml/g
Al_2O_3	69.5%

3. Results and discussion

3.1. Characteristics of calcined BE

Results of XRD from calcined BE are shown in Fig. 1. As a result, BE calcined at the temperature range 200–300 °C showed boehmite structure, whereas boehmite structure was destroyed in BE calcined at the temperature of >400 °C and aluminum oxide was generated. It has been clarified that most structural water is lost by heat dehydration at the temperature of >417.9 °C from the result of differential thermo-analysis of BE [10] as in the case of this study. When calcination temperature was increased, aluminum oxide passed through transitional states (β-form → η-form → γ-form → δ-form → θ-form), finally becoming stable α-form. These changes in crystal system were almost the same as the result generally observed in the calcination of aluminum oxide [11].

The principal phases, the specific surface area and the amount of hydroxyl groups are shown in Table 2. As a result, specific surface area of BE was decreased with increase of calcination temperature. It has been reported that decrease of specific surface area caused by of noncrystalline aluminum oxide is attributed to formation of thermodynamically stable

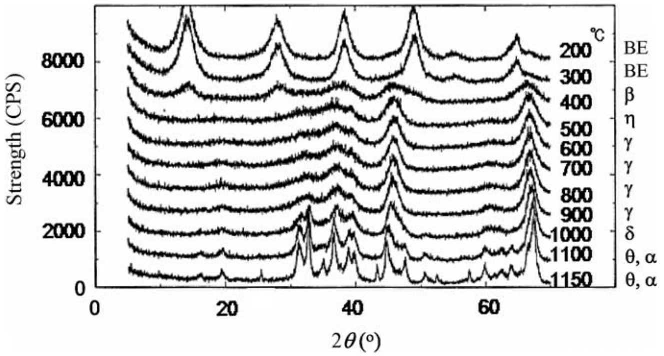

Fig. 1. XRD of calcined BE at different temperatures.

Table 2
Principal phase, specific surface area, and amount of hydroxyl group of BE calcined at different temperatures

Calcination temperature (°C)	Principal phase	Specific surface area (m^2/g)	Amount of hydroxyl group (mmol/g)
BE	BE	297	3.95
200	BE	224	4.47
300	BE	218	4.53
400	β	217	8.42
500	η	197	3.95
600	γ	175	4.16
700	γ	164	4.00
800	γ	160	3.95
900	γ	146	3.63
1000	δ	123	3.84
1100	θ, α	87	2.68
1150	θ, α	64	2.32