

Preparation of a Solid Adsorbent Derived from Concrete Sludge and its Boron Removal Performance

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ABSTRACT: We prepared a solid adsorbent for boron removal using real concrete sludge. The sludge was diluted with water at dilution ratios from 1 to 15. The diluted concrete sludge was then filtered and dried. Two types of drying methods were examined: natural drying under atmospheric conditions and forced drying in an oven at 105 °C. The boron removal performance was examined using a boric acid solution containing 100 mg_B/L. All of the adsorbents prepared showed boron removal capacity. The adsorbent prepared with dilution ratio 10 and forced drying exhibited the highest boron removal capacity; the boron concentration after 24 h was just 3.33 mg/L, which is below the Japanese standard for industrial effluent (10 mg/L), and the maximum adsorption capacity for boron was 50 mg_{boron/gadsorbent}. The drying method had a significant effect on both the rate and capacity of boron removal. With natural drying under atmospheric conditions, the adsorption initially proceeded quickly, but the final amount adsorbed was lower than that for the force-dried adsorbents. The boron removal can be attributed to ion exchange and uptake of boron in the ettringite phase. These results indicate that boron adsorbents prepared from concrete sludge can be applied for the removal of boron from effluents.

1. INTRODUCTION

Boron is an essential micronutrient for plants and humans and is widely distributed throughout the environment. Boron is an important material in industries such as glass, ceramic, semiconductor, and detergent manufacturing. A high concentration of boron in irrigation water sources has a toxic effect on most plants.¹ Long-term intake of excess amounts of boron through drinking water is potentially toxic to humans and animals.² The World Health Organization (WHO) recommends that the maximum boron level in drinking water be 0.5 mg/L.³ To prevent health and environmental effects caused by high concentrations of boron in drinking and irrigation waters, the anthropogenic discharge of boron into the environment must be controlled. For these reasons, boron removal from industrial wastewaters has received much attention in recent years. In Japan, the permitted boron concentrations in industrial wastewater discharged into the environment are set at 10 and 230 mg/L for nonsea and sea environments, respectively.^{4,5} A number of physicochemical methods have been proposed for boron removal from industrial wastewaters,⁶ such as coagulation, sedimentation, adsorption and ion exchange, and membrane separation. Adsorption and ion exchange with solid adsorbents could be advantageous over other methods in terms of the overall simplicity and cost of the process. Some adsorbents and ion-exchange resins show excellent boron removal performance; however, most adsorbents and resins are rather expensive for the treatment of large amounts of effluent. Lower-cost adsorbents for boron removal need to be developed to reduce the overall costs of treating boron-containing wastewater. Agents containing calcium, such as lime,⁷ fly ash,⁸ and ettringite,⁹ have been examined for the removal of boron. Ettringite [Ca₆Al₂(SO₄)₃(OH)₁₂·26H₂O] is a

crystalline compound formed in cement. The SO₄²⁻ ions in ettringite can be exchanged with other oxyanions such as B(OH)₄⁻, CrO₄²⁻, SeO₃²⁻¹⁰⁻¹² and F⁻.¹³ Hiraga and Shigemoto⁹ demonstrated that this ion-exchange ability can be used to remove boron. Ettringite is formed during the hydration of Portland cement;¹⁴ here, we focus on the ettringite contained in concrete sludge as an adsorbent for boron removal.

Concrete sludge is fresh waste concrete in the form of a slurry of hydrated cement and aggregate in water. About 1–2% of fresh concrete prepared for construction use is discarded as concrete sludge because it is necessary to prepare an excess amount of concrete to avoid shortages at construction sites and because the quality of the prepared concrete is sometimes below that required. Concrete sludge is used as a landfill material after solid/liquid separation followed by neutralization with an acid such as sulfuric acid. This treatment process is costly (estimated cost of about USD 60 per metric ton). An effective and low-cost recycling or reuse process for concrete sludge is needed. By using the ettringite in waste concrete for boron removal, a simultaneous process of waste management and wastewater treatment can be realized. In this study, we have investigated the boron removal behavior of an adsorbent prepared from waste concrete sludge.

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Table 1. Elemental Composition of the Concrete Sludge

element	composition (wt %)
Ca	12.3
Si	1.5
Al	0.3
Fe	1.3
other	85.6

Table 2. Preparation Conditions for Adsorbents

adsorbent	dilution ratio [(kg of diluted sludge)/(kg of sludge)]	hydration time (min)	drying method
N-UT	no dilution	—	natural
N-5	5	60	natural
N-10	10	60	natural
N-15	15	60	natural
F-UT	no dilution	—	oven
F-5	5	60	oven
F-10	10	60	oven
F-15	15	60	oven

2. EXPERIMENTAL SECTION

2.1. Preparation and Characterization of the Adsorbent. Real concrete sludge sampled at the Kawashima-Daini Plant of East Nippon Concrete Company Ltd., Chikusei, Japan, was used for the preparation of the adsorbent. The specific gravity of the concrete sludge was 1.3×10^3 kg/m³. The chemical composition of the concrete sludge was determined with an X-ray fluorescence analyzer (Rigaku ZSX Primus II). The calcium content was 12.3 wt % (Table 1).

The concrete sludge was diluted with distilled water and stirred at 1000 rpm with a magnetic stirrer for 60 min. During this treatment, hydration of cement components in the concrete sludge will proceed, and water-soluble components such as calcium ions will be partially dissolved into the water. Both the rate and products of the hydration process are expected to depend on the ratio of water to concrete sludge. The weight ratio of diluted concrete sludge to concrete sludge was changed from 1 (no dilution) to 15 to clarify the effects of the hydration. The concrete sludge was then dehydrated with a filter press apparatus (Nihon Rokasuchi Co. Ltd.) under a pressure of 0.5 MPa. The air permeability of the canvas filter used was $420 \text{ mL} \cdot \text{cm}^{-2} \cdot \text{min}^{-1}$. The dehydrated concrete sludge was then dried overnight either in an oven at 105 °C (forced

drying) or under atmospheric conditions (natural drying). Dried concrete sludge was crushed and sieved with a 106-μm sieve; particles smaller than 106 μm were used for boron removal experiments. Table 2 summarizes the adsorbents prepared under different conditions.

2.2. Boron Removal Experiments Using Concrete-Sludge-Derived Adsorbent. An aqueous solution of boric acid (100 mg_B/L) was prepared from ion-exchange water and reagent-grade boric acid (Wako Pure Chemical Industries, Osaka, Japan). This initial concentration matches that in wastewater from typical hot springs in Japan, which is a main target of the present study. In addition, no buffering agent was added to the system to evaluate the boron removal capacity under practical conditions. The adsorbent was added to the boron solution in a plastic beaker, and the solution was stirred for 24 h with a magnetic stirrer at 350 rpm. The weight ratio of adsorbent to the solution was fixed at 3.0–100 g. The pH was measured intermittently with a pH meter (DKK-TOA HM-25R, Analyticon, Springfield, NJ). The solutions were sampled intermittently through a 0.20-μm cellulose filter, and the concentrations of boron and calcium in the aliquots were determined by inductively coupled plasma atomic emission spectroscopy (ICPS-7500, Shimadzu, Kyoto, Japan). At the end of the adsorption experiment, the solution was filtered through a 0.075-μm cellulose filter, and the filtered solid was dried under atmospheric conditions. The dried samples were analyzed by X-ray diffraction (XRD; Ultima IV, Rigaku, Tokyo, Japan) and a nitrogen-adsorption analysis (BELSORP II mini, BEL Japan, Toyonaka, Japan). All runs were performed at 25 °C.

3. RESULTS AND DISCUSSION

In Figure 1, SEM images of both the naturally dried and force-dried adsorbents are shown. No obvious differences in the surface appearance were noted; both samples were aggregates of small particles (with diameters of several microns). As shown in Figures 2 and 3, the boron concentration decreased with time for all of the adsorbents tested. Table 3 summarizes the final boron concentrations and amounts of boron adsorbed after 24 h. For the naturally dried adsorbents, the boron concentration decreased rapidly over the initial 30 min and decreased gradually after that. The boron concentration was highest for N-5 adsorbent and lowest for N-10 and N-UT at 30 min. After 24 h, the lowest boron concentration was observed

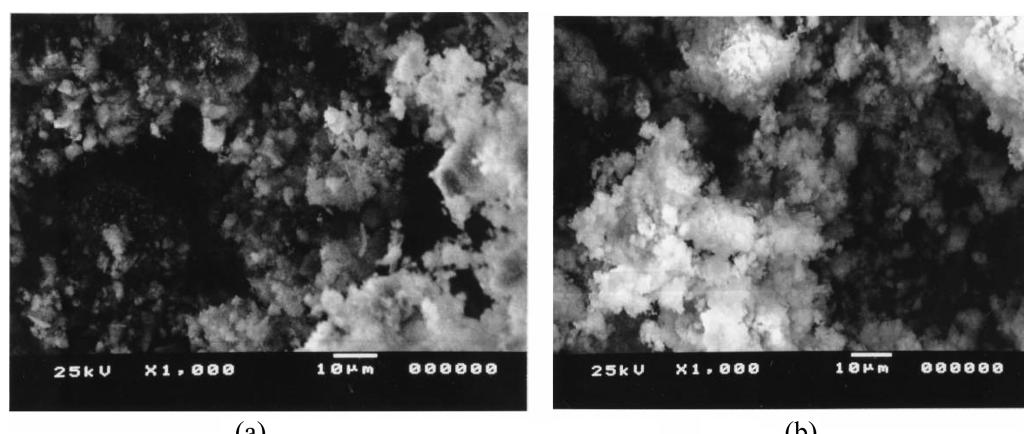


Figure 1. SEM images of the adsorbents derived from concrete sludge: (a) adsorbent F-10, (b) adsorbent N-10.

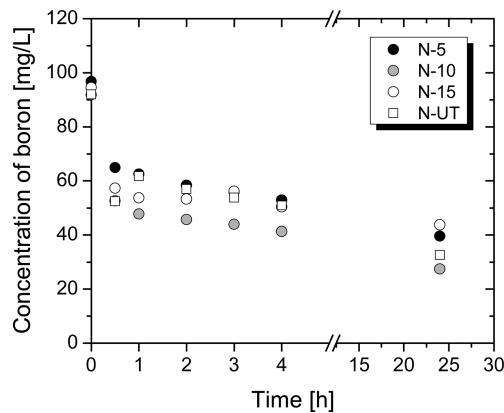


Figure 2. Time variation of boron concentration in water after addition of naturally dried concrete-sludge-derived adsorbents.

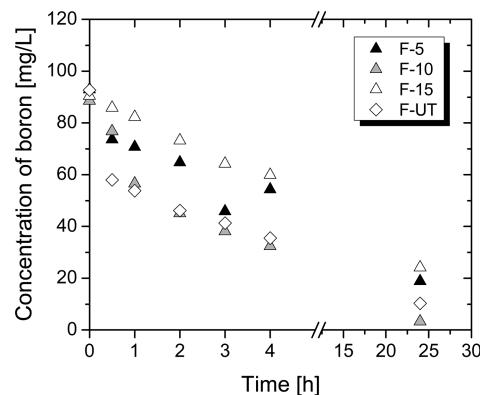


Figure 3. Time variation of boron concentration in water after addition of force-dried concrete-sludge-derived adsorbents.

Table 3. Boron Concentrations, Amounts Adsorbed after 24 h, and Surface Areas for Various Adsorbents

adsorbent	drying method	final concentration of boron at 24 h (mg/L)	amount of boron adsorbed at 24 h (mg _B /g _{adsorbent})	BET surface area (m ² ·g ⁻¹)
N-UT	natural	32.6	1.98	16
N-5	natural	39.6	1.91	—
N-10	natural	27.4	2.15	23
N-15	natural	43.8	1.70	—
F-UT	oven	10.3	2.75	11
F-5	oven	18.9	2.46	17
F-10	oven	3.33	2.84	27
F-15	oven	24.2	2.21	17

for adsorbent N-10. The final boron concentration was 27 mg/L, which is above the effluent standard in Japan (10 mg/L). For the force-dried adsorbents, the boron concentration decreased almost linearly with time. Although the rate of decrease was less than the initial rate for the naturally dried adsorbents, the final boron concentrations after 24 h for the force-dried adsorbents were much lower than for the corresponding naturally dried adsorbents. The lowest boron concentration after 24 h was obtained for adsorbent F-10, with a final boron concentration of 3.33 mg/L. This value is below the effluent standard in Japan. Although the effect of dilution ratio was unclear, the highest boron adsorption performances were observed at a dilution ratio of 10 for both drying methods. One possible explanation might be that the ratio of ettringite phase and the

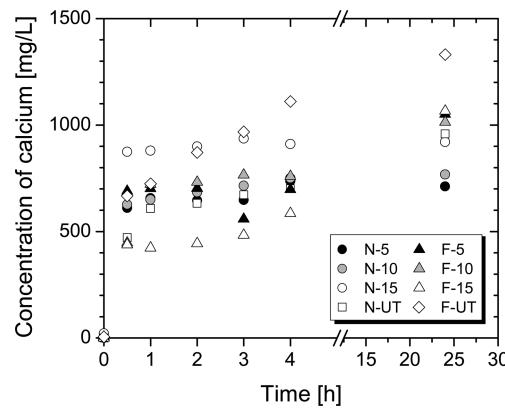


Figure 4. Changes in calcium concentration during the adsorption experiments.

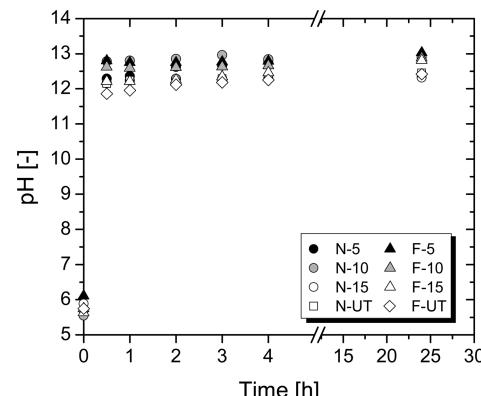


Figure 5. Changes in pH during the adsorption experiments.

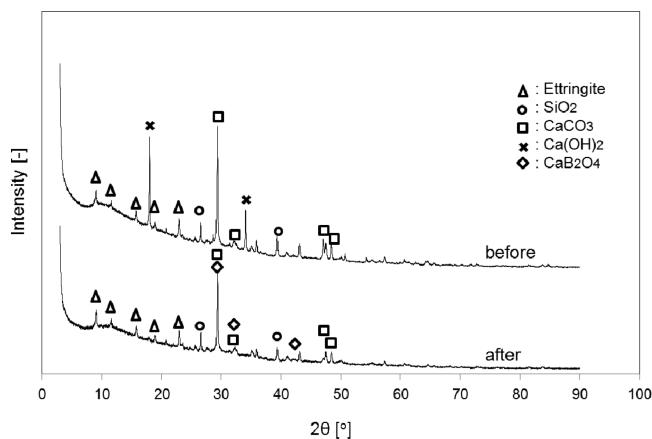


Figure 6. XRD patterns of adsorbent N-10, before and after the boron adsorption experiments.

effective surface area of the adsorbent might be maximized when the dilution ratio is 10. The BET (Brunauer–Emmett–Teller) surface area was the highest for adsorbent F-10, which partially explains its highest boron adsorption capacity. The amounts of boron adsorbed varied from 1.70 to 2.84 mg_B/g_{adsorbent}.

To evaluate the maximum capacity of boron adsorption of adsorbent F-10, a 24-h adsorption experiment was conducted with an initial concentration of 3000 mg/L, which was high enough for the adsorption sites to be fully occupied. As a result, the maximum adsorption capacity was found to be 50 mg_B/

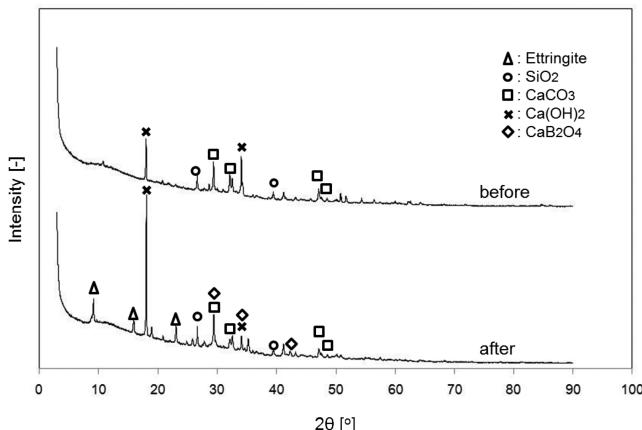


Figure 7. XRD patterns of adsorbent F-10, before and after the boron adsorption experiments.

$g_{\text{adsorbent}}$. This capacity is higher than previously reported values for calcium-based adsorbents: $13.0 \text{ mg}_B/g_{\text{adsorbent}}$ ($\text{pH } 11, 90^\circ\text{C}$)⁷ and $20.9 \text{ mg}_B/g_{\text{adsorbent}}$ ($\text{pH } 2.0, \text{ room temperature}$).⁸

Figure 4 shows the change in the calcium content of the solution during the adsorption experiments. The calcium concentration increased with time, indicating that calcium was dissolved from the cement components in the concrete sludge. The pH also increased with time, as shown in Figure 5. Both the pH and the calcium concentration rapidly increased during the initial 30 min for all adsorbents, irrespective of their drying methods. This trend is in contrast to the change in boron concentration with time, where the drying method affected behavior. According to the dissociation equilibrium of boric acid in the aqueous phase, the dominant form of boron under the pH conditions of this study was boric ions $[\text{B}(\text{OH})_4^-]$; hence, boron in the solution was adsorbed in this form.

Figure 6 shows the XRD patterns of adsorbent N-10 before and after the boron adsorption experiments. Peaks assigned to ettringite and to silica (SiO_2) and calcium carbonate (CaCO_3) were observed before the boron adsorption experiment. The peak at 18° is assigned to calcium hydroxide $[\text{Ca}(\text{OH})_2]$. The peaks at about 29° , 34° , and 50° are assigned to calcite. Ettringite, $\text{Ca}_6\text{Al}_2(\text{SO}_4)_2(\text{OH})_{12}\cdot26\text{H}_2\text{O}$, is a hydrated compound formed by the hydration of cement components. After boron adsorption, no noticeable change in the XRD pattern was observed, except for the appearance of very weak peaks

attributed to calcium borate, CaB_2O_4 . The content of ettringite in the adsorbent was estimated to be about 10% based on the standard addition method. This result suggests that boric ions $[\text{B}(\text{OH})_4^-]$ were taken up into the ettringite by ion exchange with sulfate ions (SO_4^{2-}) in ettringite. Boron might be partially removed by the precipitation of calcium borate. However, the amount of precipitant was low, indicating that this contribution is very limited. In addition, if the contribution of precipitation were high, the change in calcium concentration (Figure 4) should be closely related to boron removal (Figure 2). However, no noticeable correlation was found, suggesting another mechanism, ion exchange, should be dominant for the present system. It is also hard to explain the observed effect of the heat treatment of the adsorbent preparation process on the boron removal performance by the precipitation mechanism alone.

Figure 7 shows the XRD patterns of adsorbent F-10 before and after the boron adsorption experiments. Before the adsorption experiments, only peaks assigned to SiO_2 , CaCO_3 , and $\text{Ca}(\text{OH})_2$ were observed, with no ettringite peaks present. This is because of the dehydration of the ettringite in the adsorbent during forced drying at 105°C , which converts the crystalline structure into amorphous ettringite (meta-ettringite).^{15,16} On the other hand, peaks attributed to ettringite appeared after the boron adsorption experiments. This is because of the rehydration of meta-ettringite through the immersion of the adsorbent in water. At the same time, boric ions in water could be taken up into the ettringite structure during rehydration. This rehydration would be a rather slow process, which is the reason for the gradual decrease in the boron concentration for the case of force-dried adsorbents. The higher boron adsorption capacities of the force-dried adsorbent can be explained by the fact that boric acid could penetrate more easily into the amorphous ettringite than the crystalline ettringite. It has been reported that boron can be taken up into the ettringite phase through crystallization of ettringite and ion exchange when crystalline ettringite is synthesized in water containing boron.⁹ In the present case, the same mechanism for boron uptake might be occurring. As shown in Figure 8, the SEM images do not show any marked changes in the appearance of the adsorbent after the boron removal experiments.

4. CONCLUSIONS

Adsorbents prepared from concrete sludge exhibited boron removal capacities. The adsorbent prepared with a dilution ratio

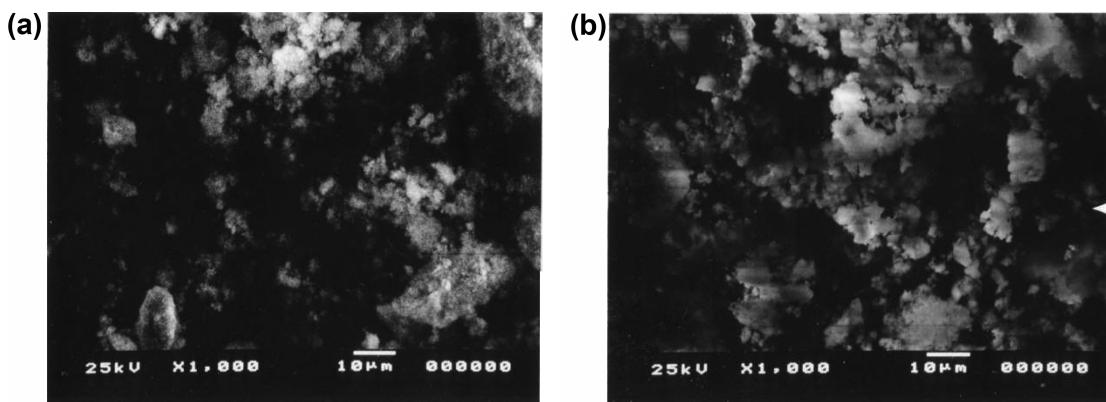


Figure 8. SEM images of adsorbents derived from concrete sludge after boron removal experiments: (a) sample F-10, (b) sample N-10.

10 and with forced drying showed the highest boron adsorption capacity at 24 h, where the final boron concentration was 3.33 mg/L for an initial boron concentration of 100 mg/L. The maximum capacity of boron removal by this adsorbent was 50 mg_B/g_{adsorbent}, which is higher than the capacities reported in the literature. The boron removal behavior was different depending on the drying method, namely, natural drying under atmospheric conditions or forced drying at 105 °C. For the naturally dried adsorbents, the boron would be taken up through ion exchange of boric ions with sulfate ions in the ettringite phase (a hydrated product of the cement components) in the concrete sludge. This process is rather quick, but the sulfate ions available for ion exchange are limited. On the other hand, the force-dried adsorbents can take up boric acid through the rehydration process of meta-ettringite to ettringite and ion exchange. This process is rather slow, but more sulfate ions would be used for ion exchange than in the crystalline ettringite. These results indicate that boron adsorbents prepared from concrete sludge can be applied for the removal of boron from wastewater effluents.

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Notes

The authors declare no competing financial interest.

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