Removal of Borate Ions from Wastewater Using an Adsorbent Prepared from Waste Concrete (PAdeCS)

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ABSTRACT: The removal of boron from model wastewater using PAdeCS, a material derived from waste concrete, was studied. Three different types of boron removal methods were examined: adsorption with untreated PAdeCS, adsorption with heat-treated ettringite-enriched PAdeCS, and coagulation–sedimentation method by mixing untreated PAdeCS as a calcium source and aluminum sulfate as an aluminum and sulfate ion source for the formation of ettringite. The highest boron removal performance was observed for the coagulation–sedimentation method, where the boron concentration in the model wastewater decreased rapidly from 100 mg/L to the level below the Japanese effluent standard at 10 mg/L when the weight ratio of PAdeCS addition into water is 4.0% with aluminum sulfate, of which the added amount corresponds to the stoichiometric condition for the formation of ettringite (Ca:Al:SO$_4$$_2$ = 6:2:3). The heat-treated ettringite-enriched PAdeCS also showed higher boron removal performances compared with untreated PAdeCS. The dependency of the boron removal capacity on the aqueous boron concentration can be expressed by the Langmuir equation for all the cases. The maximum capacity ($q_m$) values were 1.83, 3.39, and 3.02 mg/g-solid for adsorption with untreated PAdeCS, adsorption with heat-treated ettringite-enriched PAdeCS, and coagulation–sedimentation, respectively. These capacities were higher or comparable with the ones reported in the literature.

1. INTRODUCTION

Boron is an essential micronutrient for living organisms, although excess intake causes poisoning symptoms. The chemical form of boron in water is dependent on the pH, existing as undissociated boric acid (B(OH)$_3$) under acidic conditions and borate ions (B(OH)$_4$$^-$) under alkaline conditions. The concentration of boron in seawater is about 4.5 mg/L; river water contains approximately 0.2–1.2 mg/L.$^{1,2}$ Boron and its compounds are widely used as raw materials for heat insulators, semiconductors, ceramics, porcelains, reinforced plastic, glass fibers, and cosmetics. Wastewaters from these industrial production processes contain boron compounds.$^3$ Boron is also present in scrubber wastewaters of waste incineration plants and coal-fired power plants and wastewaters from landfill disposal. To protect human health, effluent and water quality standards limit the concentration of harmful elements for discharged wastewater and drinking water. Boron concentrations in drinking water are set below 0.5 mg/L by the World Health Organization.$^5$ Japanese effluent standards stipulate that the concentration of boron in wastewater should be 10 mg/L or lower.$^5$

Many studies have been published so far on the removal of boron from wastewater. A variety of adsorbents have been tested for boron removal such as chelating resins,$^{6–10}$ activated carbons,$^{11–13}$ double-layered hydroxides,$^{14–16}$ oxides or hydroxides,$^{17,18}$ and adsorbents derived from industrial wastes.$^{19–21}$ The coagulation–sedimentation method is also effective for the removal of boron in water.$^{22–25}$ The disadvantage of the coagulation–sedimentation method is the treatment of waste sludge after removal.

In this study, we examined the boron removal ability of PAdeCS (phosphorous absorbent derived from concrete sludge). PAdeCS is obtained by filtration of fresh waste concrete after addition of excess water to prevent hardening. The main component of PAdeCS is hydrated cement, which is strongly alkaline (pH ∼12) and rich in calcium (∼28.9 wt %). PAdeCS was originally prepared for recovering phosphorus from wastewater to form hydroxyapatite (HAP) as a calcium and alkaline source. PAdeCS also contains a small amount of ettringite (Ca$_6$Al$_2$(SO$_4$)$_3$(OH)$_{12}·26$H$_2$O), a product of cement hydration, which is known for having an ion exchange ability by replacing sulfate ions with other anions. The removal of boron with ettringite has been reported by several authors,$^{26–29}$ and the boron removal ability can be enhanced
by heat treatment; dehydration of ettringite by heat treatment would destroy the crystal structure to convert meta-ettringite, an amorphous phase, which can enhance the accessibility of ion exchange.\(^{28,30,31}\) In this study, we use PAdCS as a calcium source for the removal of boron in water. First, we prepared an ettringite-enriched PAdCS by reacting calcium in PAdCS with an aluminum source and a sulfate source and heat-treated ettringite-enriched PAdCS by the heat treatment. The heat-treated ettringite-enriched PAdCS was then applied to the removal of boron in model wastewater as an adsorbent. Second, we examined the boron removal ability of the sedimentation–coagulation method by using PAdCS as a calcium source mixed with an aluminum source and a sulfate source to form and capture boric ions through in situ formation of ettringite.

2. MATERIALS AND METHODS

2.1. Preparation of Heat-Treated Ettringite-Enriched PAdCS. PAdCS (SP-00, 15–30 μm in diameter) was provided by Nippon Concrete Industries Co., Ltd., Japan. The specific surface area is 107 m\(^2\)/g by the nitrogen adsorption method (Belsorp mini, Bel Japan Inc., Tokyo, Japan). The calcium composition in PAdCS is 28.9% based on the measurement with X-ray fluorescence (XRF, Rigaku ZSX Primus II).

The ettringite-enriched PAdCS was prepared by the following method. A water slurry (the ratio of water to PAdCS at 60.2 g/g, optimal conditions determined from previous experiments) was mixed with the water solutions of aluminum acetate (Al\(_4\)O(CH\(_2\)_4COO)\(_4\)·nH\(_2\)O; purchased from Wako Pure Chemical Industries Ltd., Osaka, Japan, purity > 85.0%) as an aluminum source and sodium sulfate (Na\(_2\)SO\(_4\); purchased from Wako Pure Chemical Industries Ltd., Osaka, Japan, purity of 99.0%). The amount of each compound after mixing was adjusted to match the stoichiometric ratio of Ca:Al:SO\(_4\)\(_2\) to 6:2:3 in ettringite (Ca\(_6\)Al\(_2\)(SO\(_4\))\(_3\)(OH)\(_{12}\)·26H\(_2\)O). The mixture was then stirred at 400 rpm at 80 °C for 24 h. Then, the mixture was vacuum-filtered through a nitrocellulose filter paper (pore size: 0.1 μm). The solid residues were washed with distilled water and dried at 25 °C for 24 h. The dried solid so prepared is referred to as ettringite-enriched PAdCS.

The ettringite-enriched PAdCS was then heat-treated in a constant-temperature oven at 100 °C to prepare heat-treated ettringite-enriched PAdCS. The crystal phases of the solid samples were determined by X-ray diffraction (XRD; Rigaku, Ultima IV, Japan; Cu K\(\beta\) (\(\lambda = 1.3847\) Å); the voltage and current for X-ray generation were 40 kV and 40 mA, respectively) to identify the crystalline phases.

2.2. Boron Removal by Coagulation–Sedimentation. Untreated PAdCS and aluminum sulfate (Al\(_2\)(SO\(_4\))\(_3\)), a source for aluminum and sulfate, were mixed in the model wastewater. The mass fraction of PAdCS was changed in the range of 2.0–8.0%, and that of aluminum sulfate was fixed at 0.82%. The stoichiometric condition for ettringite corresponds to the mass ratio of PAdCS at 2.0%, indicating that all other conditions are excess calcium conditions. The mixture was stirred with a magnetic stirrer at 400 rpm for 24 h.

3. RESULTS AND DISCUSSION

3.1. Preparation of Ettringite-Enriched PAdCS and Its Heat Treatment. Figure 1 shows XRD patterns of untreated PAdCS, ettringite-enriched PAdCS, and heat-treated ettringite-enriched PAdCS.

Figure 1. X-ray diffraction patterns of untreated PAdCS, ettringite-enriched PAdCS, and heat-treated ettringite-enriched PAdCS.
3.2. Boron Removal Performance of Untreated PAdeCS. Figure 2 shows the time change of the boron concentration for the removal experiment with untreated PAdeCS. The concentration decreased sharply during the initial 10 min and then gradually decreased to 24 h. The boron removal ratio increased with increasing dose of PAdeCS. The lowest boron concentration at 7.0 mg/L was observed for the case of 8.0% dose after 24 h, which is below the Japanese effluent standard at 10 mg-B/L. Other conditions did not achieve the Japanese effluent standard. The pH increased to approximately 12 immediately after mixing untreated PAdeCS with the model wastewater and remained almost constant after that. This pH value at 12 corresponds to that of saturated calcium hydroxide solution, suggesting that calcium hydroxide, a product of cement hydration reactions of PAdeCS, was dissolved into water and saturated.

Figure 3 shows the XRD patterns of untreated PAdeCS before and after the boron removal experiments. No remarkable change before and after boron removal was observed; no peak assigned to compounds containing boron was detected. The removal of boron should be attributed to the ion exchange of borate ions with sulfate ions in ettringite, and ettringite could be converted to charlesite, a crystalline mineral with an ettringite-like structure in which boric ions are incorporated instead of sulfate ions. However, due to the small amount of ettringite in untreated PAdeCS and the small extent of ion exchange, no peak assigned to charlesite was observed for the present case. The peak assigned to calcium hydroxide was undetected after removal for the case with 1.0% dose, which can be attributed to the dissolution of calcium hydroxide into water from untreated PAdeCS.

Table 1 summarizes the results of boron removal using ettringite-enriched PAdeCS. A higher dose (8.0%) and longer dose time (24 h) are necessary to achieve the Japanese effluent standard at 10 mg/L. The boron removal efficiency, however, should be improved for the practical applications.

3.3. Boron Removal Performance of Heat-Treated Ettringite-Enriched PAdeCS. Figure 4 shows the time change of boron concentration for adsorption with the heat-treated ettringite-enriched PAdeCS (hereafter referred to as heat-treated PAdeCS). The boron concentration rapidly decreased with time and reached 7.32 and 3.61 mg/L after 10 min for the doses of 6.0 and 8.0%, respectively, achieving the Japanese effluent standard at 10 mg/L. The boron removal performance was significantly improved compared to the cases for untreated PAdeCS.

Immediately after mixing of the heat-treated PAdeCS with the model wastewater, the pH increased and then remained constant at approximately 10. The final pH was lower than the case with the heat-treated PAdeCS; a lower pH value compared to the case of untreated PAdeCS (pH 12) would be due to the consumption of calcium hydroxide in PAdeCS by the ettringite-enrichment process.

Figure 5 shows XRD patterns of the heat-treated PAdeCS before and after boron removal. After the boron removal experiment, the peaks assigned to ettringite were observed, indicating that meta-ettringite was recrystallized to ettringite by the hydration reaction in water. This result suggested that the meta-ettringite generated from heat-treated PAdeCS can improve the boron removal performance. The improvement of
the boron removal performances with heat treatment could be due to the enhancement of the accessibility of boric ions into the crystalline structure of ettringite during the recrystallization.

In Table 2, the boron removal performance of the heat-treated PAdeCS is summarized. The removal ratio was as high as 96.6% for 8.0% dose with the boron concentration of 3.61 mg/L.

| dose (mass %) | initial concentration (mg/L) | concentration after 24 h (mg/L) | removal ratio (%) |
|--------------|-------------------------------|--------------------------------|------------------|
| 1.0          | 107.1                         | 75.51                          | 29.5             |
| 2.0          | 106.4                         | 50.98                          | 52.1             |
| 4.0          | 107.0                         | 17.90                          | 83.3             |
| 6.0          | 105.3                         | 7.32                           | 93.0             |
| 8.0          | 106.2                         | 3.61                           | 96.6             |

3.4. Coagulation–Sedimentation with Preparation of Ettringite in Boron Wastewater. Figure 6 shows the time change of boron concentration during coagulation–sedimentation. Boron removal performance was significantly improved compared with the cases with heat-treated PAdeCS. The boron concentration decreased rapidly at the initial stage of the treatment and leveled off. The boron concentration dropped dramatically for a given dose time with an increase in the dose of PAdeCS up to 5.0%. However, for the cases with a dose higher than 6.0%, the boron concentration was higher than the case with 5.0% dose. The concentration after 24 h was 0.41 mg/L for the case with 5.0% dose, which is slightly lower than the case with 6.0% dose (0.48 mg/L) and much lower than the case with 8.0% dose (1.2 mg/L) as shown in Table 3. The Japanese effluent standard can be achieved within 1 h for the cases with a dose higher than 4.0%.

| mass ratio of PAdeCS added (%) | initial concentration (mg/L) | concentration after 24 h (mg/L) | removal ratio (%) |
|-------------------------------|-------------------------------|--------------------------------|------------------|
| 2.0                           | 100.7                         | 41.01                          | 59.3             |
| 3.0                           | 103.3                         | 5.46                           | 94.7             |
| 4.0                           | 103.8                         | 2.13                           | 97.9             |
| 5.0                           | 104.0                         | 0.41                           | 99.6             |
| 6.0                           | 103.8                         | 0.48                           | 99.5             |
| 8.0                           | 102.7                         | 1.2                            | 98.8             |

Figure 7 shows the time changes of pH during coagulation–sedimentation. The pH was almost unchanged during the coagulation–sedimentation for each case of dose. With increasing dose, the pH was elevated from about 10 (2.0% dose) to 12 (8.0% dose). The higher dose of PAdeCS, of which the major component is calcium hydroxide, a strong alkali, resulted in the higher pH.

Figure 8 shows the XRD patterns of the solids before and after coagulation–sedimentation. The peak assigned to ettringite was detected for the cases with a dose higher than 3.0%. The peak strengths for ettringite were higher for the
cases with 3.0 and 4.0% PAdeCS doses than the cases with a dose higher than 5.0%. The stoichiometric condition for ettringite formation is achieved for the 2.0% dose of PAdeCS with a fixed mass ratio of 0.82% of aluminum sulfate in water based on the calcium content in PAdeCS at 28.9%. However, no XRD peak assigned to ettringite was observed for 2.0% dose, where the detected calcium-containing compound was gypsum (CaSO₄), and the XRD peaks assigned to ettringite were observed for a dose of PAdeCS higher than 3.0%. This result suggests that all the calcium contained in PAdeCS may not be used for the formation of ettringite, and excess dose of calcium in PAdeCS is required to meet the stoichiometric condition for ettringite formation. However, the further excess amount of calcium such as 8.0% dose would induce the formation of calcite instead of ettringite. This should be the reason for the decrease of boron removal performance with higher doses of PAdeCS like 5.0% and more. From the results obtained in this study, the highest boron performances were obtained by the coagulation–sedimentation method, where ettringite is in situ formed by calcium from PAdeCS and aluminum sulfate.

Boric acid is dissociated according to pH conditions,

\[ \text{B(OH)}_3 + \text{H}_2\text{O} \rightarrow \text{H}^+ + \text{B(OH)}_4^- , \quad \text{pK}_a = 9.15 \]

indicating that at pH 10 for 2.0% dose, more than 95% of boric acid in the solution should be dissociated to boric ions, which are subject to be ion-exchanged with sulfate ions in ettringite. With higher doses of PAdeCS, the portion of dissociated boric acid would be close to 100%. Thus, the higher removal performance at higher dose can be attributed to the degree of formation of ettringite.

### 3.5. Comparison of Adsorbents for Boron Adsorption

The relationship between the amount of boron removal \(q_m\) (mg/g) and concentration in wastewater \(C_e\) (mg/L) would be expressed by the Langmuir equation (eq 1),

\[ q_m = \frac{K_q C_e}{1 + K_q C_e} \]

where \(q_m\) (mg/g) is the monolayer capacity, and \(K\) (L/mg) is the Langmuir constant. The Langmuir plots for the results of the boron removal obtained in this study (after 24 h dose) are shown in Figure 9 based on eq 2.

\[ \frac{C_e}{q_m} = \frac{1}{K_q} + \frac{1}{K_q q_m} \]

For each case, a linear relationship was obtained from the equilibrium concentration \(C_e\), demonstrating that the relationship between the boron removal amount \(q_m\) and the concentration in water \(C_e\) can be expressed by the Langmuir-type equation (eq 1), and the determined parameters, \(q_m\) and \(K\), are shown in Table 4.

### Table 4. Langmuir Parameters for Boron Removal

| Material                  | \(q_m\) (mg/g) | \(K\) (L/mg) | \(R^2\) |
|---------------------------|----------------|--------------|---------|
| untreated PAdeCS          | 1.83           | 0.138        | 0.819   |
| heat-treated PAdeCS       | 3.39           | 0.125        | 0.993   |
| coagulation–sedimentation  | 3.02           | 2.17         | 0.998   |

The parameter \(q_m\) that appeared in eq 1, which denotes the maximum capacity of the adsorbent or removal of boron obtained in this study, is compared with the literature data in Table 5. The observed boron adsorption capacities in this study \((q_m)\) were comparable with those of pure ettringite reported in the literature.

### Table 5. Comparison of the Boron Removal Capacities of This Study and Other Solid Materials

| Material                  | Capacity (mg B/g) | Remarks                      | Reference |
|---------------------------|-------------------|------------------------------|-----------|
| activated carbon          | 2.37              | initial concentration: 100 mg/L. | 17        |
| Palm tree bark was treated to prepare the activated carbon. | | | |
| NMDG@PAF                  | 18.4              | initial concentration: 140 mg/L. | 14        |
| NMDG@PS-DVB               | 13.2              | initial concentration: 70 mg/L. | 13        |
| Mg-Al-LDH nanosheets       | 21.6              | initial concentration: 200 mg/L. | 20        |
| Monolayered nanosheets of Mg-Al-LDHs | | | |
| Mg-Al-CLDH nanosheets      | 77.8              | initial concentration: 140 mg/L. | 20        |
| Calcinated monolayered nanosheets of Mg-Al-LDHs | | | |
| ettringite                | 0.6               | initial concentration: 94 mg/L. | 28        |
| meta-ettringite           | 2.9               | initial concentration: 94 mg/L. | 28        |
| untreated PAdeCS          | 1.83              | initial concentration: 100 mg/L. | this study |
| heat-treated PAdeCS       | 3.39              | initial concentration: 100 mg/L. | this study |
| coagulation–sedimentation  | 3.02              | initial concentration: 100 mg/L. | this study |

For the practical applications, the effect of the coexisting anions on the boron removal should be clarified because anions in water could compete with boric ions for ion exchange with ettringite. After boron removal, the adsorbent could be disposed of because PAdeCS is a waste-derived, cheap material. After removal, the pH in wastewater increases to the alkaline region at about 10 to 12. This may require further treatment of wastewater to neutralize with some acids. In this case, bubbling with CO₂ would be appropriate because dissolved calcium ions can be removed and neutralized as calcium carbonate.

### 4. CONCLUSIONS

The highest boron removal performance was achieved for the coagulation–sedimentation method using untreated PAdeCS (4.0 or 5.0%) with aluminum sulfate (0.82%), with which the ratio of calcium is about double (4.0%) or higher (5.0%) than the stoichiometric conditions of ettringite \(\text{Ca}:\text{Al}:\text{SO}_4^{2-} = 3:1:3\).
The heat-treated ettringite-enriched PAdeCS showed much higher boron removal performances compared with untreated PAdeCS. This is due to the higher accessibility for the ion exchange of boric ions with sulfate ions during the transformation of meta-ettringite to ettringite in water. The ion-exchanged ettringite by borate ions should be charlesite, but no peaks assigned to charlesite were detected by XRD ion-exchanged ettringite by borate ions should be charlesite, transformation of meta-ettringite to ettringite in water. The ion-exchange of boric ions with sulfate ions during the transformation of meta-ettringite to ettringite in water. The ion-exchange of boric ions with sulfate ions during the transformation of meta-ettringite to ettringite in water. This is due to the higher accessibility for the fact that the post-treatment of water to neutralize the alkaline condition (pH 11–12) is required.

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### Notes

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## REFERENCES

(1) Howe, P. D. A review of boron effects in the environment. *Biol. Trace Elem. Res.* 1998, 66, 153–166.

(2) Wolska, J.; Bryjak, M. Methods for boron removal from aqueous solutions — A review. *Desalination* 2013, 310, 18–24.

(3) Guan, Z.; Lv, J.; Bai, P.; Guo, X. Boron removal from aqueous solutions by adsorption — A review. *Desalination* 2016, 383, 29–37.

(4) Guidelines for Drinking-Water Quality, 4th ed.; World Health Organization, 2011.

(5) Ministry of the Environment Government of Japan Website; https://www.env.go.jp/en/water/wq/nes.html (accessed May 27, 2022).

(6) Remy, P.; Muhr, H.; Plasari, E.; Ouerrdiane, I. Removal of boron from wastewater by precipitation of a sparingly soluble salt. *Environ. Prog.* 2005, 24, 105–110.

(7) Xu, Y.; Jiang, J. Q. Technologies for boron removal. *Ind. Eng. Chem. Res.* 2008, 47, 16–24.

(8) Yilmaz, A. E.; Boncukcuoglu, R.; Bayar, S.; Fil, B. A.; Kocakerim, M. M. Boron removal by means of chemical precipitation with calcium hydroxide and calcium borate formation. *Korean J. Chem. Eng.* 2012, 29, 1382–1387.

(9) Yoshikawa, E.; Sasaki, A.; Endo, M. Removal of boron from wastewater by the hydroxyapatite formation reaction using acceleration effect of ammonia. *J. Hazard. Mater.* 2012, 237-238, 277–282.

(10) Ersan, H. Y.; Pinarbası, S. Boron removal by glucamine-functionalized hydrogel beads in batch fashion. *J. Appl. Polym. Sci.* 2011, 121, 1610–1615.

(11) Ikeda, K.; Umeno, D.; Saito, K.; Koide, F.; Miyata, E.; Sugo, T. Removal of boron using nylon-based chelating fibers. *Ind. Eng. Chem. Res.* 2011, 50, 5727–5732.

(12) Recepoglu, Y. K.; Kabay, N.; Ipek, I. Y.; Arda, M.; Yuksel, M.; Yoshizuka, K.; Nishihama, S. Packed bed dynamic study for boron removal from geothermal brine by a chelating fiber and breakthrough curve analysis by using mathematical models. *Desalination* 2018, 437, 1–6.

(13) Recepoglu, Y. K.; Kabay, N.; Yilmaz-Ipek, I.; Arda, M.; Yuksel, M.; Yoshizuka, K.; Nishihama, S. Deboronation of geothermal water using N-methyl-D-glucamine based chelating resins and a novel fiber adsorbent: batch and column studies. *J. Chem. Technol. Biotechnol.* 2017, 92, 1540–1547.

(14) Kanchev, J.; Taylor, M. K.; Shin, D.-M.; Jarenwattananon, N. N.; Colwell, K. A.; Long, J. R. Functionalized porous aromatic frameworks as high-performance adsorbents for the rapid removal of boric acid from water. *Adv. Mater.* 2019, 31, 1808027.

(15) Kluczka, J.; Ciba, J.; Trojanowska, J.; Zolotajkin, M.; Turek, M.; Dydo, P. Removal of boron dissolved in water. *Environ. Prog.* 2007, 26, 71–77.

(16) Can, B. Z.; Ceylan, Z.; Kocakerim, M. M. Adsorption of boron from aqueous solutions by activated carbon impregnated with salicylic acid: equilibrium, kinetic and thermodynamic studies. *Desalination* 2012, 40, 69–76.

(17) Melliti, A.; Kheriji, J.; Bessaies, H.; Hamrouni, B. Boron removal from water by adsorption onto activated carbon prepared from palm bark: kinetic, isotherms, optimisation and breakthrough curves modeling. *Water Sci. Technol.* 2020, 81, 321–332.

(18) Jiang, J. Q.; Xu, Y.; Quill, K.; Simon, J.; Shettle, K. Laboratory study of boron removal by Mg/Al double-layered hydroxides. *Ind. Eng. Chem. Res.* 2007, 46, 4577–4583.

(19) Theiss, F. L.; Ayoko, G. A.; Frost, R. L. Removal of boron species by layered double hydroxides: A review. *Colloid Interface Sci.* 2013, 402, 114–121.

(20) Gao, Z.; Xie, S.; Zhang, B.; Qiu, X.; Chen, F. Ultrathin Mg-Al layered double hydroxide prepared by ionothermal synthesis in a deep eutectic solvent for highly effective boron removal. *Chem. Eng. J.* 2017, 319, 108–118.

(21) Seki, Y.; Seyhan, S.; Yurdakoc, M. Removal of boron from aqueous solution by adsorption on Al₂O₃ based materials using full factorial design. *J. Hazard. Mater.* 2006, 138, 60–66.

(22) Kasahara, S.; Takasu, T.; Nagano, N.; Mikoshi, Y.; Itou, H.; Sakamoto, N. Removal of boron from aqueous solution using zeolite magnesia granules. *Mater. Trans.* 2020, 61, 1930–1939.

(23) Polat, H.; Vengosh, A.; Pankratov, I.; Polat, M. A new methodology for removal of boron from water by coal and fly ash. *Desalination* 2004, 164, 173–188.

(24) Kluczka, J.; Trojanowska, J.; Zolotajkin, M. Utilization of fly ash zeolite for boron removal from aqueous solution. *Desalination*. *Water Treat.* 2015, 54, 1839–1849.

(25) Polowczyk, L.; Ulatowska, J.; Koźlecki, T.; Bastryk, A.; Sawiński, W. Studies on removal of boron from aqueous solution by fly ash agglomerates. *Desalination* 2013, 310, 93–101.

(26) Csetenyi, L. J.; Glasser, F. P. Borate Substituted Ettringites. *MRS Online Proc. Libr.* 1992, 294, 273.

(27) Hiraga, Y.; Shigemoto, N. Boron Uptake Behavior During Ettringite Synthesis in the Presence of H₃BO₃ and in a Suspension of Ettringite in H₃BO₃. *J. Chem. Eng. Jpn.* 2010, 43, 865–871.

(28) Hongo, T.; Tsunashima, Y.; Sakai, Y.; Iizuka, A.; Yamasaki, A. A comparative borate adsorption study of ettringite and metaehttringite. *Chem. Lett.* 2011, 40, 1269–1271.
(29) Sun, Q.; Li, J.; Wang, J. Effect of borate concentration on solidification of radioactive wastes by different cements. *Nucl. Eng. Des.* 2011, 241, 4341−4345.

(30) Zhou, Q.; Lachowski, E. E.; Glasser, F. P. Metaettringite, a decomposition product of ettringite. *Cem. Concr. Res.* 2004, 34, 703−710.

(31) Fuchida, S.; Hobo, S.; Tsuchiya, K.; Tanaka, Y.; Nakamura, T.; Tokoro, C. Experimental Investigation of Boron Removal Mechanism from Wastewater by Calcined Ettringite. *Water, Air, Soil Pollut.* 2020, 231, 344.