

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

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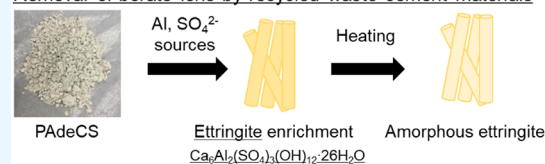
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**ABSTRACT:** The removal of boron from model wastewater using PAdeCS, a material derived from waste concrete, was studied. Three different types of boron removal methods were examined: adsorption with untreated PAdeCS, adsorption with heat-treated 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 ( $\text{Ca}:\text{Al}:\text{SO}_4^{2-} = 6:2:3$ ). 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.

## Removal of borate ions by recycled waste cement materials



How is the boron-removal performance of adsorbents derived from recycled cement waste material in the solution? by

- Direct addition of PAdeCS.
- Addition of ettringite enriched, heat-treated PAdeCS.
- Coagulation with PAdeCS for ettringite preparation in the solution
- Coagulation method shows highest performance of boron removal

## 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 ( $\text{B}(\text{OH})_3$ ) under acidic conditions and borate ions ( $\text{B}(\text{OH})_4^-$ ) 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.<sup>1,2</sup> 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.<sup>3</sup> 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.<sup>4</sup> Japanese effluent standards stipulate that the concentration of boron in wastewater should be 10 mg/L or lower.<sup>5</sup>

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,<sup>6–10</sup> activated carbons,<sup>11–13</sup> double-layered hydroxides,<sup>14–16</sup> oxides or hydroxides,<sup>17,18</sup> and adsorbents derived from industrial

wastes.<sup>19–21</sup> The coagulation–sedimentation method is also effective for the removal of boron in water.<sup>22–25</sup> 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 adsorbent 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 ( $\text{Ca}_6\text{Al}_2(\text{SO}_4)_3(\text{OH})_{12}\cdot 26\text{H}_2\text{O}$ ), 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,<sup>26–29</sup> and the boron removal ability can be enhanced

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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.<sup>28,30,31</sup> In this study, we use PAdeCS as a calcium source for the removal of boron in water. First, we prepared an ettringite-enriched PAdeCS by reacting calcium in PAdeCS with an aluminum source and a sulfate source and heat-treated ettringite-enriched PAdeCS by the heat treatment. The heat-treated ettringite-enriched PAdeCS 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 PAdeCS 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 PAdeCS.** PAdeCS (SP-00, 15–30  $\mu\text{m}$  in diameter) was provided by Nippon Concrete Industries Co., Ltd., Japan. The specific surface area is 107  $\text{m}^2/\text{g}$  by the nitrogen adsorption method (Belsorp mini, Bel Japan Inc., Tokyo, Japan). The calcium composition in PAdeCS is 28.9% based on the measurement with X-ray fluorescence (XRF, Rigaku ZSX Primus II).

The ettringite-enriched PAdeCS was prepared by the following method. A water slurry (the ratio of water to PAdeCS at 60.2 g/g, optimal conditions determined from previous experiments) was mixed with the water solutions of aluminum acetate ( $\text{Al}_2\text{O}(\text{CH}_3\text{COO})_4 \cdot n\text{H}_2\text{O}$ ; purchased from Wako Pure Chemical Industries Ltd., Osaka, Japan, purity of 85.0%) as an aluminum source and sodium sulfate ( $\text{Na}_2\text{SO}_4$ ; 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  $\text{Ca}:\text{Al}:\text{SO}_4^{2-}$  at 6:2:3 in ettringite ( $\text{Ca}_6\text{Al}_2(\text{SO}_4)_3(\text{OH})_{12} \cdot 26\text{H}_2\text{O}$ ). The mixture was then stirred at 400 rpm at 80  $^\circ\text{C}$  for 24 h. Then, the mixture was vacuum-filtered through a nitrocellulose filter paper (pore size: 0.1  $\mu\text{m}$ ). The solid residues were washed with distilled water and dried at 25  $^\circ\text{C}$  for 24 h. The dried solid so prepared is referred to as ettringite-enriched PAdeCS. The ettringite-enriched PAdeCS was then heat-treated in a constant-temperature oven at 100  $^\circ\text{C}$  for 24 h to prepare heat-treated ettringite-enriched PAdeCS.

The crystal phases of the solid samples were determined by X-ray diffraction (XRD; Rigaku, Ultima IV, Japan;  $\text{Cu K}\beta$  ( $\lambda = 1.3847 \text{ \AA}$ ); the voltage and current for X-ray generation were 40 kV and 40 mA, respectively, the  $2\theta$  range was 5–70 $^\circ$ , the step size was 0.02 $^\circ$ , and the scan speed was 2.0 $^\circ/\text{min}$ ).

### 2.2. Boron Removal Experimental Methods.

**2.2.1. Boron Removal by Adsorption.** A model wastewater was prepared by dissolving sodium tetraborate decahydrate (borax) ( $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ ; Wako Pure Chemical Industries Ltd., Osaka, Japan, purity > 99.0%) in distilled water with the boron concentration of 100 mg/L. The adsorbent, heat-treated ettringite-enriched PAdeCS, hereafter, was added in the model wastewater. The mass ratio of added PAdeCS (dose) was changed in the range of 1.0–8.0%. The mixture was stirred with a magnetic stirrer at 400 rpm at room temperature. The liquid phase was sampled with a syringe filter (pore size: 0.2  $\mu\text{m}$ ), and the boron concentration in the sample was measured with inductively coupled plasma atomic emission spectrometry (ICPA-6000, Thermo Fisher Scientific, CA, USA). The pH of

the mixture was measured with a pH meter (Horiba, Kyoto, Japan). After 24 h, the mixture was vacuum-filtered using a nitrocellulose filter (pore size: 0.1  $\mu\text{m}$ ), and the solid residue was dried at 25  $^\circ\text{C}$  for 24 h. The dried solid sample was analyzed with XRD (Rigaku, Ultima IV, Japan;  $\text{Cu K}\beta$  ( $\lambda = 1.3847 \text{ \AA}$ ); the voltage and current for X-ray generation were 40 kV and 40 mA, respectively) to identify the crystalline phases.

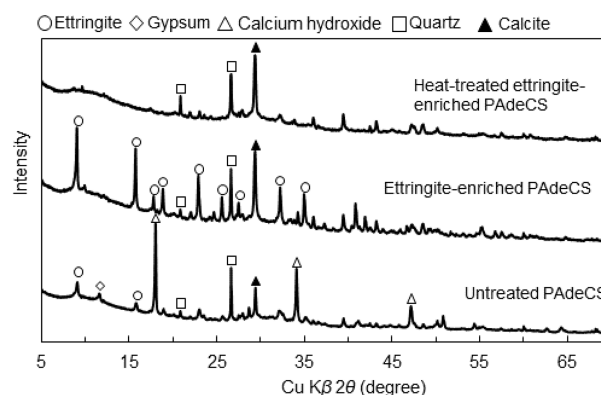
### 2.2.2. Boron Removal by Coagulation–Sedimentation.

Untreated PAdeCS and aluminum sulfate ( $\text{Al}_2(\text{SO}_4)_3$ ), a source for aluminum and sulfate, were mixed in the model wastewater. The mass fraction of PAdeCS 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 PAdeCS 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. The liquid phase was sampled through filtration, the boron concentration in the sample was measured with inductively coupled plasma atomic emission spectrometry (ICPA-6000, Thermo Fisher Scientific, CA, USA), and the pH of the mixture was measured with a pH meter (Horiba, Kyoto, Japan). After 24 h, the mixture was vacuum-filtered using a nitrocellulose filter (pore size: 0.1  $\mu\text{m}$ ), the solid residue was dried at 25  $^\circ\text{C}$  for 24 h, and the crystalline phases were analyzed with XRD (Rigaku, Ultima IV, Japan;  $\text{Cu K}\beta$  ( $\lambda = 1.3847 \text{ \AA}$ ); the voltage and current for X-ray generation were 40 kV and 40 mA, respectively).

## 3. RESULTS AND DISCUSSION

### 3.1. Preparation of Ettringite-Enriched PAdeCS and Its Heat Treatment.

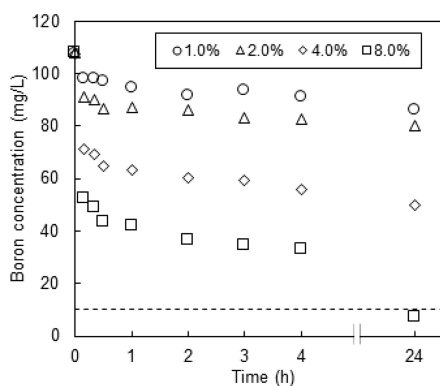
Figure 1 shows XRD patterns of



**Figure 1.** X-ray diffraction patterns of untreated PAdeCS, ettringite-enriched PAdeCS, and heat-treated ettringite-enriched PAdeCS.

untreated PAdeCS, ettringite-enriched PAdeCS, and heat-treated ettringite-enriched ettringite. The untreated PAdeCS contains calcium hydroxide ( $\text{Ca}(\text{OH})_2$ ), quartz ( $\text{SiO}_2$ ), and calcite ( $\text{CaCO}_3$ ) with traces of ettringite and gypsum ( $\text{CaSO}_4$ ). The ettringite-enriched PAdeCS showed the stronger peaks assigned to ettringite at 9 $^\circ$  and 16 $^\circ$ , and peaks assigned to calcium hydroxide at 18 $^\circ$  and 34 $^\circ$  were undetected. This result suggests that ettringite was generated from calcium hydroxide in PAdeCS reacted with added aluminum acetate and  $\text{Na}_2\text{SO}_4$ . The peaks assigned to ettringite were not detected after heat treatment, suggesting that the crystalline ettringite was converted to meta-ettringite, an amorphous phase, by the heat treatment.<sup>28–31</sup>

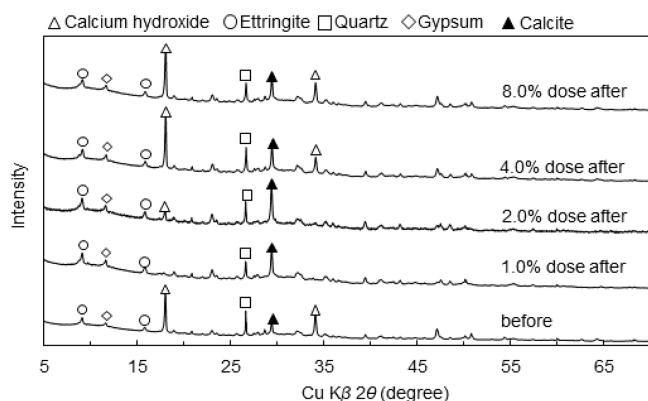
### 3.2. Boron Removal Performance of Untreated PAdeCS. Figure 2 shows the time change of the boron



**Figure 2.** Time dependence of boron concentration for untreated PAdeCS. The dashed line shows the Japanese effluent standard for the boron concentration (10 mg/L).

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



**Figure 3.** X-ray diffraction patterns of untreated PAdeCS before and after the boron removal experiments.

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.

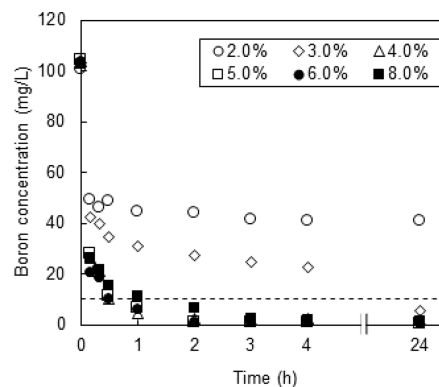
Table 1 summarizes the results of boron removal using ettringite-enriched PAdeCS. A higher dose (8.0%) and longer

**Table 1. Boron Removal Performance of Untreated PAdeCS for Various Dose Conditions**

dose (mass %)	initial concentration (mg/L)	concentration after 24 h (mg/L)	removal ratio (%)
1.0	107.6	86.21	19.9
2.0	108.1	80.21	25.8
4.0	107.7	49.87	53.7
8.0	107.9	7.0	93.5

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

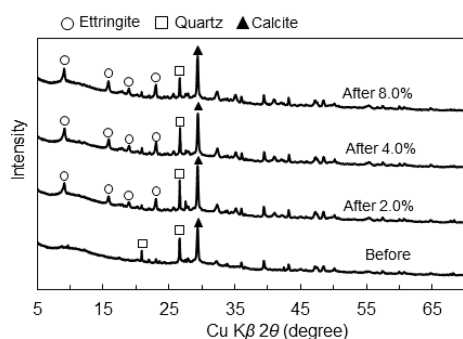


**Figure 4.** Time dependence of boron concentration in solution using heat-treated ettringite-enriched PAdeCS from an initial boron concentration of 100 mg/L.

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



**Figure 5.** X-ray diffraction patterns of heat-treated PAdeCS before and after boron removal experiments at different adsorbent concentrations.

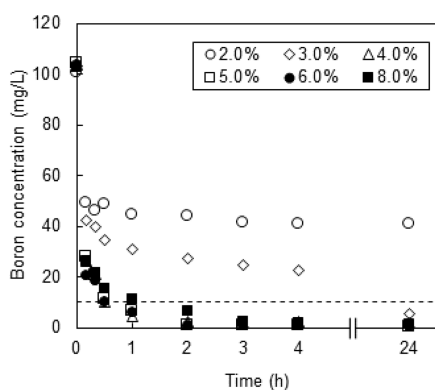
the boron removal performances with heat treatment could be due to the enhancement of the accessibility of boric ions into the crystalline structure of ettringite during the recrystallization.<sup>30,31</sup>

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.

**Table 2. Boron Removal Performance of Heat-Treated PAdeCS for Various Additive Conditions**

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



**Figure 6.** Time dependence of boron concentration during coagulation–sedimentation.

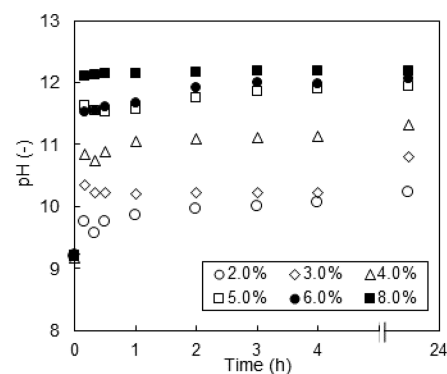
change of boron concentration during coagulation–sedimentation. Boron removal performance was significantly improved compared with the cases with heat-treated PAdeCS. The boron concentration decreased rapidly at the initial stage of the treatment and leveled off. The boron concentration dropped dramatically 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%.

**Table 3. Boron Removal by the Coagulation–Sedimentation Method with PAdeCS and  $Al_2(SO_4)_3$**

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

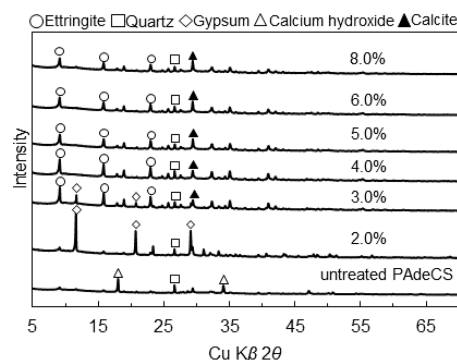
Figure 7 shows the time changes of pH during coagulation–sedimentation. The pH was almost unchanged during the



**Figure 7.** Time changes of pH during coagulation–sedimentation.

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.

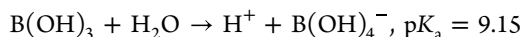
Figure 8 shows the XRD patterns of the solids before and after coagulation–sedimentation. The peak assigned to ettringite was detected for the cases with a dose higher than 3.0%. The peak strengths for ettringite were higher for the



**Figure 8.** X-ray diffraction patterns of solid residues of coagulation–sedimentation.

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 ( $\text{CaSO}_4$ ), 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,



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 ( $q_e$ ; mg/g) and concentration in wastewater ( $C_e$ ; mg/L) would be expressed by the Langmuir equation (eq 1),

$$\frac{q_e}{q_m} = \frac{KC_e}{1 + KC_e} \quad (1)$$

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.

$$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{Kq_m} \quad (2)$$

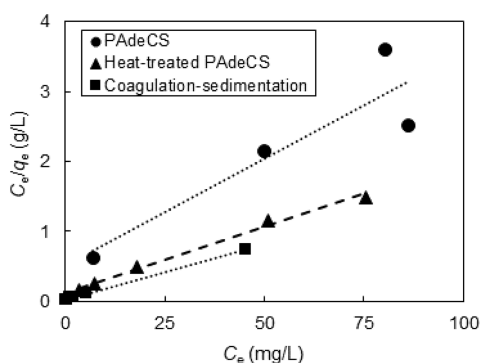


Figure 9. Langmuir plots for boron removal performances after 24 h.

For each case, a linear relationship was obtained from the equilibrium concentration ( $C_e$ ), demonstrating that the relationship between the boron removal amount ( $q_e$ ) 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

	$q_m$ (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. Palm tree bark was treated to prepare the activated carbon.	17
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. Monolayered nanosheets of Mg-Al-LDHs	20
Mg-Al-CLDH nanosheets	77.8	initial concentration: 140 mg/L. Calcinated monolayered nanosheets of Mg-Al-LDHs.	20
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 with PAdeCS	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  $\text{CO}_2$  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 ( $\text{Ca}:\text{Al}:\text{SO}_4^{2-} =$

6:2:3). 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 analysis, presumably due to the low exchange rate of sulfate ions in ettringite or because the solid was amorphous. The boron removal capacity, represented by the monolayer capacity of the Langmuir sorption equation ( $q_m$ ), was in the range of 1.83 mg/g (untreated PAdeCS) to 3.39 mg/g (heat-treated PAdeCS). The Japanese effluent standard of boron concentration at 10 mg/L was achieved for all the methods despite the fact that the post-treatment of water to neutralize the alkaline condition (pH 11–12) is required.

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### Notes

The authors declare no competing financial interest.

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