

Continuous-flow detoxification treatment of boron-containing wastewater under hydrothermal conditions

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To develop a practical method of treating boron-containing wastewater, we custom designed two laboratory-scale continuous-flow-type hydrothermal mineralization apparatuses. We carried out a hydrothermal treatment using a continuous-flow apparatus, using $\text{Ca}(\text{OH})_2$, CaCl_2 , and both $\text{Ca}(\text{OH})_2$ and CaCl_2 as mineralizers, under various pH conditions. Our results show that using CaCl_2 under optimal pH conditions ($\text{pH} \approx 12$) allowed for the stable removal of boron from wastewater. One of the precipitates obtained in this process was parasibirskite, which is a natural boron mineral. Finally, because the residual concentration of boron could not be reduced below 10 mg/dm^3 , we propose a realistic boron removal wastewater treatment system incorporating the hydrothermal mineralization method.

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1. Introduction

Boron is distributed widely in the environment, mainly as boric acid, and is an important micronutrient for plants, animals, and humans. However, an excessive intake of boron has a detrimental impact on plants, animals, and human bodies. For example, the tolerable limit of boron for citrus and some agricultural crops is 2 or 3 mg/dm^3 . Thus, the World Health Organization has recommended a limit on the amount of boron in drinking water of 0.3 mg/dm^3 in the European Union.^{1)–3)} Recently, the Japanese quality standard for discharged wastewater containing boron was set at 10 mg/dm^3 (230 mg/dm^3 if discharged into the sea). However, boric acid is also an important industrial resource and is widely used in a wide variety of manufacturing processes such as in semiconductor, ceramic, and plating industries. An effective removal technique is needed because the wastewater generated in these industrial processes produces several hundreds to several thousands mg/dm^3 of boron in a day.

Recently, we suggested a novel wastewater treatment technique based on the hydrothermal mineralization mechanism, which is one of mechanisms according to which minerals are produced in the earth's crust.^{4)–15)} In this method, the wastewater with toxic, but valuable, anions is sealed in a pressure vessel together with a mineralizer such $\text{Ca}(\text{OH})_2$. The pressure vessel is then placed in an oven at an appropriate temperature for a specified treatment time. This method can not only reduce the concentration of various toxic anions dissolved in the wastewater to less than the Japanese effluent standard but also recover toxic anions as natural minerals. Previously, we have succeeded in detoxifying wastewater with various toxic but valuable anions (cf. Table 1). Moreover, it was found that in the present

treatment, the residual concentration depended only on the solubility of the minerals in the aqueous solution; that is, the residual concentration was approximately independent of the initial concentration of the anions in the wastewater. However, it was difficult to reduce the boron concentration in wastewater to below 10 mg-B/dm^3 using this batch hydrothermal mineralization method. This is because the mineral Ca-B, parasibirskite, produced by the hydrothermal mineralization mechanism has high solubility in water at room temperature. It is well known that the solubility of many minerals in water decreases with an increase in temperature. We have previously confirmed that the residual concentration of boron in wastewater under hydrothermal condition is lower than that of wastewater obtained by solid-liquid separation at room temperature. Thus, to effectively detoxify the wastewater by using our method, it is necessary to carry out the solid-liquid separation under hydrothermal conditions.

In order to apply this method to practical wastewater treatment, a flow-type apparatus is required. In this study, we manufactured two laboratory-scale flow-type apparatuses and used them to investigate the detoxification of the model wastewater containing dissolved boron.

2. Experimental

2.1 Apparatus

In Fig. 1, the two types of experimental apparatuses, custom designed by Taiatsu Techno®, are shown. In the single-flow-channel-type apparatus [cf. Fig. 1(a)], a syringe pump continuously pumps wastewater through a preheater into a reactor. The double-flow-channel-type apparatus [cf. Fig. 1(b)] uses one channel for the continuous feed of wastewater into the reactor and the second channel to add various additive aqueous solutions. Treated wastewater is discharged from the reactor by self-pressure in the reactor through the sampling unit, which consists of a sampling tube, sintered-metal filter, and cooling

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Table 1. Summarized previous experimental results by hydrothermal mineralization treatment

Elements	B	F	P			As		Cr
Valence	V		I	III	V	III	VI	VI
Attained concentration (mg/dm ³)	4.0–30.0	0.1	0.1	3.0	10.0	0.02		0.03
Recovered mineral	Ca ₂ B ₂ O ₅ ·H ₂ O	CaF	Ca ₁₀ (PO ₄) ₆ (OH) ₂	Ca(HPO ₃)·H ₂ O		Ca ₅ (AsO ₄) ₃ (OH)		CaCrO ₄
Effluent standard (mg/dm ³)	10.0 (230.0)	8.0		16.0		0.1		0.1

condenser. The reactor can be used at temperatures of up to 300°C, can withstand pressures of up to 30 MPa, and can contain volumes of up to 100 cm³.

2.2 Materials

Sodium tetraborate (Na₂B₄O₇·10H₂O: Kishida Reagents Chemicals) and sodium metaborate (NaBO₂·4H₂O: Wako Pure Chemicals Industries Ltd.) were used without further purification as boron reagents. Calcium hydroxide [Ca(OH)₂: Kishida Reagents Chemicals] was used as a mineralizer, and calcium chloride (CaCl₂: Wako Pure Chemicals Industries Ltd.) was used as an additive. Model wastewaters containing boron were prepared by dissolving sodium tetraborate or sodium metaborate into distilled and deionized water, and when necessary, their pH was adjusted using NaOH (Kishida Reagents Chemicals).

2.3 Hydrothermal treatment with Ca(OH)₂

Using the single-flow-channel-type apparatus [cf. Fig. 1(a)], 2.0 g of Ca(OH)₂ was sealed into the reactor and heated up to 150°C. Then, 500 mg/dm³ of sodium tetraborate aqueous solution was fed into the sealed reactor through the preheater (set at 180°C) at a flow rate of 10 cm³/min. The treated wastewater was collected every minute, starting at the 6-min mark, using a sampling unit with a filter and cooling condenser.

2.4 Hydrothermal treatment with Ca(OH)₂ and CaCl₂

Using the double-flow-channel-type apparatus [cf. Fig. 1(b)], 2.0 g of Ca(OH)₂ was sealed into the reactor and heated up to 150°C. Then, 1000 mg/dm³ of sodium tetraborate (pH = 9.4), sodium metaborate (pH = 11.1), or sodium metaborate and NaOH (pH = 13.2) aqueous solution were fed from inlet 1 and 3708 mg/dm³ of calcium chloride aqueous solution (C/B = 1.0) was fed from inlet 2 simultaneously into the sealed reactor at a flow rate of 5 cm³/min. Only the boron-containing wastewater was preheated to 180°C. The treated wastewater was collected every minute, starting at the 6-min mark, using a sampling unit with a filter and cooling condenser.

2.5 Hydrothermal treatment with CaCl₂

The empty reactor of the double-flow-channel-type apparatus [cf. Fig. 1(b)] was sealed and heated up to 150°C. The sealed reactor was simultaneously fed with an aqueous solution of 1000 mg/dm³ of sodium metaborate and NaOH (pH = 13.2) from inlet 1 and an aqueous solution of 3708–7416 mg/dm³ of calcium chloride (C/B = 1.0–2.0) from inlet 2, both at a flow rate of 5 cm³/min. The treated wastewater was collected every minute, starting at the 6-min mark, using a sampling unit with a filter and cooling condenser.

2.6 Characterization

The white powders produced by the three treatments were identified using X-ray diffraction analysis (XRD: RINT-2000 from RIGAKU). Boron and calcium concentrations before and

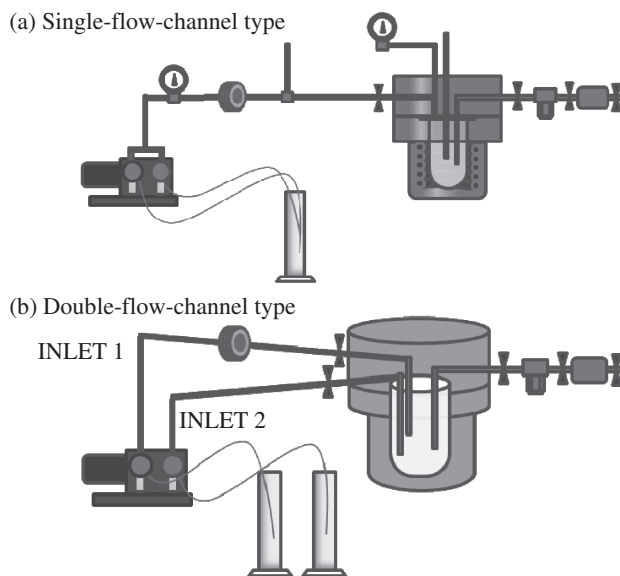


Fig. 1. Schematic illustration of laboratory-scale flow-type apparatus.

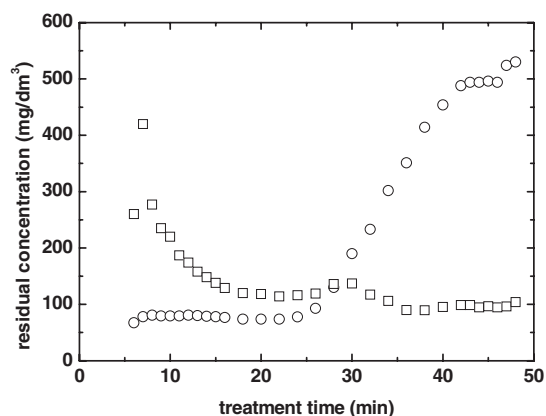


Fig. 2. Dependence of residual concentration on treatment time. Boron and calcium represented using ○ and □, respectively.

after treatment were quantitatively determined by inductive coupled plasma-atomic emission spectroscopy (ICP-AES: OPTIMA 3300DV from Perkin Elmer Co., Ltd.). The pH values of the wastewater before and after treatment were measured using a pH meter (F-51 from HORIBA Ltd.).

3. Results and discussion

3.1 Hydrothermal mineralization treatment with Ca(OH)₂

Figure 2 shows both the boron and calcium residual concentrations plotted against the treatment time. From the starting point up to 24 min (total treatment volume of wastewater was 240 cm³), the residual boron concentration was constant at approximately

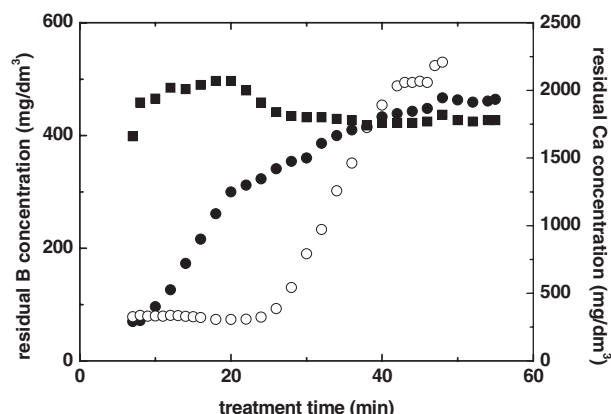


Fig. 3. Dependence of residual concentration of boron (○ and ●) and calcium (■) on treatment time. Mineralizers used were $\text{Ca}(\text{OH})_2$ alone (○) and both $\text{Ca}(\text{OH})_2$ and CaCl_2 (● and ■).

80 mg/dm³. This result indicates that the hydrothermal mineralization treatment can effectively remove boron from wastewater under flow conditions. The precipitation obtained by flow-type hydrothermal treatment was of the same mineral, $\text{Ca}_2\text{B}_2\text{O}_5 \cdot \text{H}_2\text{O}$, as in the batch case.^{4,5)} The residual boron concentration gradually increased from 25 min to 42 min and stayed constant at approximately 500 mg/dm³ for times over 42 min. The residual boron concentration observed after 42 min is the same as the initial boron concentration, 500 mg/dm³; thus, 42 min is the breakthrough point. At this breakthrough point, we theorize that all of the added $\text{Ca}(\text{OH})_2$ is consumed in the formation of calcium borate, even though the consumption rate of the added $\text{Ca}(\text{OH})_2$ is 60 mol %. It was found in our previous work⁴⁾ that the reaction between dissolved boron and $\text{Ca}(\text{OH})_2$ occurs on the surface of the $\text{Ca}(\text{OH})_2$ crystal. Thus, the low consumption rate of added $\text{Ca}(\text{OH})_2$ can be explained by the following reaction mechanism: (1) Calcium borate crystals begin to form on the surface of the $\text{Ca}(\text{OH})_2$ hexagonal plate-like crystal. (2) The mineral formation reaction proceeds until the surface of the $\text{Ca}(\text{OH})_2$ particle is completely masked by calcium borate. (3) The mineral formation reaction stops before all of the added $\text{Ca}(\text{OH})_2$ is consumed. Therefore, the unreacted $\text{Ca}(\text{OH})_2$ particles remain at the center of $\text{Ca}(\text{OH})_2$ and are covered by calcium borate crystals. The dissolved Ca^{2+} concentration decreased exponentially with increasing treatment time and was constant at approximately 100 mg/dm³ after 24 min. This time was almost the same as the starting point of the boron concentration increase. Thus, the lower Ca^{2+} concentration will also be a reason for the low consumption rate of $\text{Ca}(\text{OH})_2$.

3.2 Hydrothermal mineralization treatment with both $\text{Ca}(\text{OH})_2$ and CaCl_2

To know the effect of dissolved Ca^{2+} concentration on the residual boron concentration, the hydrothermal mineralization treatment with both $\text{Ca}(\text{OH})_2$ and CaCl_2 was investigated using the double-flow-channel-type apparatus [cf. Fig. 1(b)]. Here, an aqueous solution of 1090 mg/dm³ of sodium tetraborate was fed into the sealed reactor through inlet 1 at a rate of 4.9 cm³/min, and an aqueous solution of 3660 mg/dm³ of CaCl_2 was fed in through inlet 2 at a rate of 4.7 cm³/min, along with 2.0 g of $\text{Ca}(\text{OH})_2$ powder, which was preheated to 150°C. **Figure 3** shows the treatment time dependence of residual concentration of the boron and calcium. Considering the $\text{Ca}(\text{OH})_2$ result, it could be predicted that the residual boron concentration would be

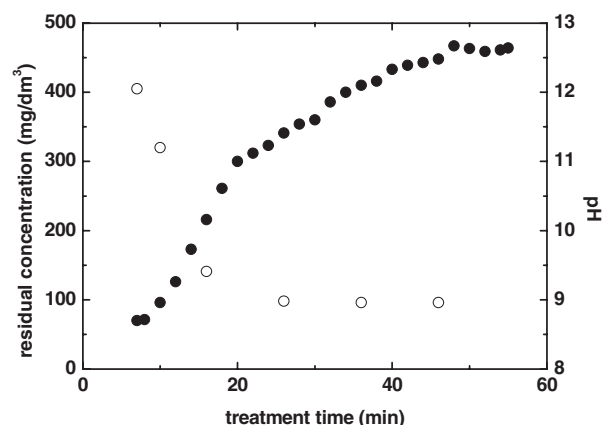
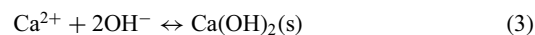
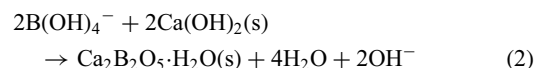
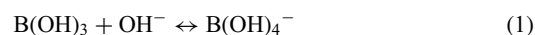


Fig. 4. Dependence of residual concentration of boron (●) and pH (○) on treatment time.

constant at approximately 80 mg/dm³, up to at least 24 min. However, the residual boron concentration monotonically increased with increasing treatment time in the early stage of the hydrothermal mineralization treatment, and after approximately 48 min, became a constant at approximately 460 mg/dm³. **Figure 4** shows the treatment time dependence of residual boron concentration and the pH value of the collected wastewater. The pH value decreased with an increase in the residual boron concentration. We propose the following series of reactions to explain the observations:



By using chemical reaction formula (2), it is found that the pH value increases when parasibirskite ($\text{Ca}_2\text{B}_2\text{O}_5 \cdot \text{H}_2\text{O}$) is formed. However, the produced OH^- will be consumed by the formation of $\text{Ca}(\text{OH})_2$ precipitates and $\text{B}(\text{OH})_4^-$ oxo-ions. Because the produced OH^- will be excessively consumed, the pH value decreases. Moreover, the amount of OH^- produced will decrease because the surfaces of the $\text{Ca}(\text{OH})_2$ crystal are being covered by parasibirskite ($\text{Ca}_2\text{B}_2\text{O}_5 \cdot \text{H}_2\text{O}$), which causes the pH value of the aqueous solution to decrease further. Thus, the formation of $\text{Ca}_2\text{B}_2\text{O}_5 \cdot \text{H}_2\text{O}$ was inhibited when the pH value decreased because the amount of $\text{B}(\text{OH})_3$ in the aqueous solution had increased. Thus, it is postulated that the pH value will be one of the more important factors for effectively removing boron from wastewater when the continuous-flow-type hydrothermal mineralization treatment is used.

Model boron wastewaters with three different pH values (pH = 9.4, 11.1, and 13.2) were treated using both $\text{Ca}(\text{OH})_2$ and CaCl_2 using the double-flow-channel-type apparatus [cf. Fig. 1(b)]. In **Fig. 5**, the residual boron concentration and pH value of the collected aqueous solution are plotted against the treatment time. When the initial pH value of the model wastewater was 9.4, the residual boron concentration gradually increased with an increase in the treatment time, and the pH value of the collected aqueous solution rapidly decreased. At an initial pH of 11.1, the residual boron concentration could be kept at less than 100 mg/dm³ for up to approximately 30 min. After that, both the residual boron concentration and the pH value increased with increasing treatment time. When the initial pH value of the model wastewater

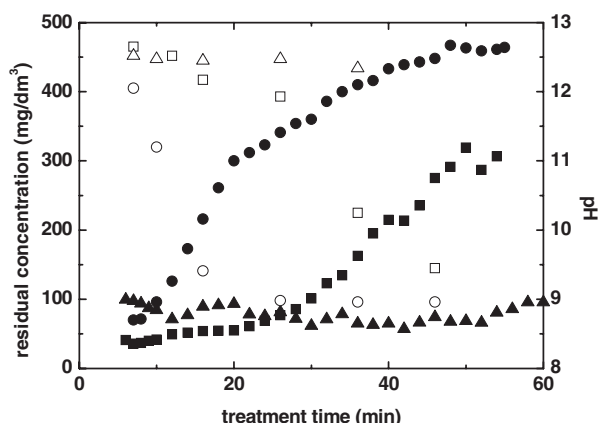


Fig. 5. Dependence of residual concentration of boron (filled) and pH (open) on treatment time. The pH values are 9.4 (● and ○), 11.1 (■ and □), and 13.2 (▲ and △).

was 13.2, the residual boron concentration could be kept constant in the range from 80 to 100 mg/dm³ during the present treatment time scale. Moreover, the pH value of the aqueous solution slightly decreased throughout the treatment; however, the pH value could be kept at a relatively high level (approximately 12.5). These results indicate that the pH value is the most important factor for realizing the stable boron removal treatment from wastewater using a hydrothermal mineralization treatment.

3.3 Hydrothermal mineralization treatment with CaCl₂

In the hydrothermal treatment of the model boron wastewater using both Ca(OH)₂ and CaCl₂ at a high pH, it can be predicted that the Ca²⁺ added as CaCl₂ in an aqueous solution will be converted to Ca(OH)₂ and precipitated in a reactor during treatment. Considering the formation reaction of Ca(OH)₂, it will not be necessary to add the Ca(OH)₂ powder as a mineralizer. The hydrothermal mineralization treatment of the model boron wastewater using CaCl₂ at pH = 13.2 and 150°C was investigated by using the double-flow-channel-type apparatus [cf. Fig. 1(b)]. **Figure 6** shows the treatment time dependence of the residual boron concentration and pH value of the aqueous solution. It was found that boron could be removed by the hydrothermal mineralization treatment without using Ca(OH)₂. Both the residual boron concentration and pH value depended on the atomic ratio between calcium and boron (Ca/B). In the case of Ca/B = 1.0, the residual boron concentration and pH value showed a slight treatment time dependence. The reason for this would be the lack of Ca²⁺ in wastewater. At more than Ca/B = 1.5, the residual boron concentration was almost constant at approximately 70 mg/dm³, and the pH value could be kept constant at approximately 12.1. From the XRD analysis of precipitates obtained after the treatment, the collected precipitate was found to be parasibirskite, even when the Ca/B ratio was different and when Ca(OH)₂ was not used. These results indicate that it is highly feasible to achieve continuous boron removal by the hydrothermal mineralization treatment.

3.4 Proposal of industrial boron-containing wastewater treatment systems using hydrothermal mineralization process

In this study, it was found that boron could be removed from aqueous media by hydrothermal mineralization treatment using a

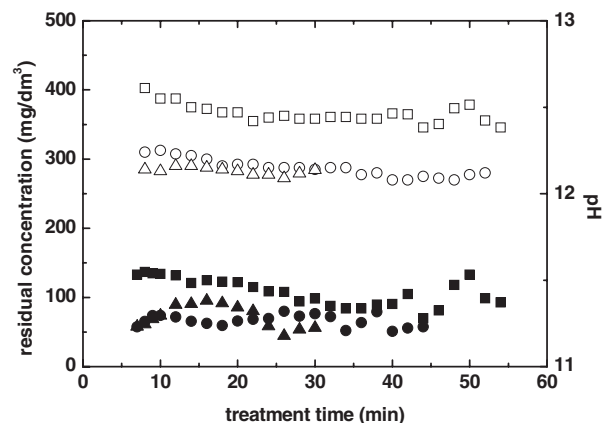


Fig. 6. Dependence of residual concentration of boron (filled) and pH (open) on treatment time. The atomic ratios (Ca/B) between added calcium and boron dissolved in wastewater are 1.0 (■ and □), 1.5 (● and ○), and 2.0 (▲ and △).

flow-type apparatus. Moreover, the hydrothermal mineralization treatment has the following merits: (1) The addition of Ca(OH)₂ powder, which was essential in batch systems, is not required when Ca²⁺, which is used for the formation of parasibirskite, is supplied in the form of an aqueous solution. (2) Stable boron removal (residual boron concentration ≤ 100 mg/dm³) is feasible for many hours; that is, the breakthrough of the residual boron concentration is not observed. (3) The precipitates in the reaction vessel could be used in borax processes as an industrial resource. Meanwhile, some problems must still be solved before the practical use of this treatment method is possible: (1) The end-point concentration of boron in wastewater after treatment should be reduced below 10 mg/dm³, although the Japanese effluent standard for boron discharge to the sea (230 mg/dm³) has already been attained. (2) In the present apparatus, the precipitate could not be collected during the hydrothermal mineralization treatment. Of course, the precipitation can be collected after cooling and opening the reaction vessel. However, when the precipitate is collected under ambient conditions, the residual boron concentration increases because parasibirskite has a very high solubility in aqueous media under ambient conditions. Thus, a new system should be developed for recovering the precipitates without redissolving parasibirskite in an aqueous media. (3) Practical industrial wastewater contains various ions and contaminants. The effect of contaminants on the treatment efficiency needs to be investigated. (4) It is very difficult to evaluate the economical viability of the proposed system by using the laboratory-scale experimental results. However, the exact economic evaluation, which includes energy consumption, operation and maintenance costs, and income from selling the precipitate as valuable industrial resource, should be carried out. Consequently, the industrial systems used for wastewater treatment can be improved by incorporating the hydrothermal mineralization treatment. In **Fig. 7**, we show the schematic diagram of the proposed industrial treatment system for boron-containing wastewater by utilizing the hydrothermal mineralization mechanism discussed here. In the proposed system, the double-flow-type process for the hydrothermal mineralization treatment is combined with the existing boron-containing wastewater treatment process, which uses an anion exchange column. This is helpful as it dilutes the wastewater containing boron, possibly to the extent of achieving the Japanese effluent standard (10 mg/dm³).

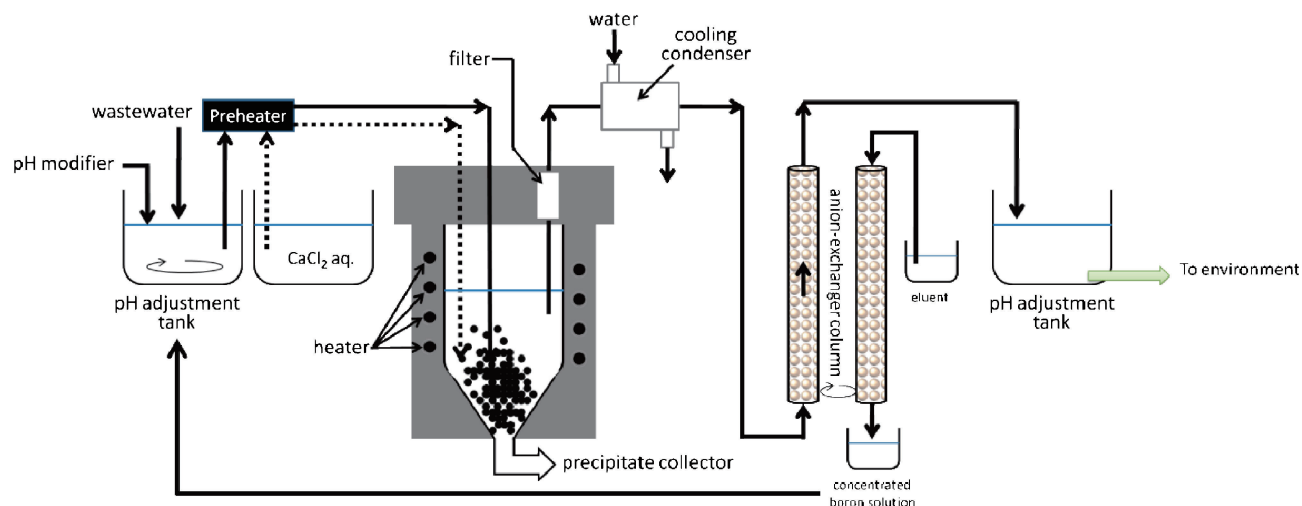


Fig. 7. (Color online) Proposed schematic diagram of industrial boron-containing wastewater treatment system based on hydrothermal mineralization mechanism.

4. Conclusions

We succeeded in carrying out the detoxification of wastewater containing boron using a laboratory-scale continuous-flow-type hydrothermal mineralization apparatus. It was found that the residual boron concentration in wastewater after hydrothermal mineralization treatment could be reduced below 100 mg/dm^3 by allowing both boron-containing wastewater with an adjusted pH = approximately 12 and a CaCl_2 aqueous solution to flow through a reaction vessel. Adding Ca(OH)_2 powder was not required. These results indicate that the hydrothermal mineralization technique can be practically applied. While the residual boron concentration was still higher than the standard effluent value for fresh water (10 mg/dm^3), the standard effluent value for seawater could be satisfied (230 mg/dm^3). Thus, post processing for detoxifying the treated wastewater is still required. Therefore, we propose to combine the hydrothermal mineralization treatment method with an ion-exchange system for removing boron from treated wastewater (cf. Fig. 7).

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