



# Boron removal and recovery from concentrated wastewater using a microwave hydrothermal method

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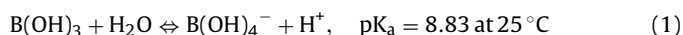
## ABSTRACT

Boron compounds are widely-used raw materials in industries. However, elevated boron concentrations in aqueous systems may be harmful to human and plants. In this study, calcium hydroxide ( $\text{Ca}(\text{OH})_2$ ) alone and  $\text{Ca}(\text{OH})_2$  with phosphoric acid ( $\text{H}_3\text{PO}_4$ ) addition (P-addition) were used to remove and recover boron from wastewater using hydrothermal methods. A microwave (MW) hydrothermal method was used and compared with the conventional heating (CH) method in batch experiments. Physicochemical properties of the precipitates obtained from both methods were analysed by XRD, SEM with EDX and BET. For the case of  $\text{Ca}(\text{OH})_2$  alone and the MW method, experimental results showed that boron recovery efficiency reached 90% within 10 min, and crystals of  $\text{Ca}_2\text{B}_2\text{O}_5 \cdot \text{H}_2\text{O}$  were found in the precipitates as indicated by the XRD analysis. For the case of P-addition and the MW method, boron recovery efficiency reached 99% within 10 min, and calcium phosphate species ( $\text{CaHPO}_4 \cdot \text{H}_2\text{O}$ ,  $\text{CaHPO}_4$  and  $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ ) were formed. The experimental results of this study indicate that the required reaction time of the MW method was much less than that of the CH method, and the MW method is an effective and efficient method for boron removal and recovery from concentrated wastewater.

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## 1. Introduction

Boron exists in many compounds, including borax, borosilicate and boric acid [1]. Boric acid,  $\text{B}(\text{OH})_3$ , and borate ions,  $\text{B}(\text{OH})_4^-$ , are common constituents in sea water. Fractionation of these two species is pH-dependent [2]:



Boron is also an essential trace nutrient for human, animals and plants [3,4]. However, elevated levels of boron may be harmful and fatal [5,6]. The recommended limits for boron in drinking water are 0.5 and 1.0 mg/L by World Health Organization (WHO) and the European Union, respectively.

Boron has been used in many industrial products, such as semiconductor (as an electronic receptor), ceramic (as a product enhancer), borosilicate glass, and detergent [7]. Wastewaters from these manufacturing processes often contain elevated concentrations of boron. In Taiwan, the Environmental Protection Agency (EPA) imposes boron discharge limit of 1 mg/L.

Several boron removal technologies have been developed in the past decade. Ion exchange (IE) and reverse osmosis (RO) provide stable treatment and are often used in drinking water treatment

[8–10]. However, they are costly and may not perform well for concentrated wastewater. Adsorption removal by metal hydroxide [11] and other materials, such as calcined alunite [12], fly ash [13] and coal [14] may be cheaper: however, these materials have low boron removal efficiencies and would generate plenty of sludge. Recently, several innovative approaches have been proposed, such as adsorption by cellulose [15] and plant uptake [16,17], but they are still in the developmental stage. To meet the stringent discharge limit of 1 mg/L, more technically and economically effective methods for boron removal from concentrated water and wastewater are warranted. Mineralization of boron by metal hydroxide is effective for concentrated wastewater [18]. The addition of phosphoric acid could prevent the re-dissolution of precipitates that were formed from calcium hydroxide and boric acid [19]. Furthermore, the precipitates can be recovered and used as raw material for boron industries. However, this technique requires a long reaction time and lots of energy for heating, and microwave technique may be a better alternative to deal with these two disadvantages.

Microwave technique has been developed and used in many applications for a long period of time. Microwave radiation provides many advantages, including uniform heating, quick start up/stop, and material-selective heating [20]. It has been used not only in food preparation and electrical communication industries, but also widely applied in environmental engineering field, including recycle of fly ash [21], measurement of chemical oxygen demand [22] and degradation of perfluorooctanoic acid [23].

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The objective of this study was to compare two hydrothermal methods (conventional heating, microwave radiation) on mineralization of calcium hydroxide for boron recovery from concentrated wastewater. Optimal operating conditions by microwave radiation (e.g., reaction temperature, calcium hydroxide doses) were developed and effects of phosphoric acid addition on boron recovery were evaluated. Mechanisms of boron recovery by mineralization were also proposed.

## 2. Materials and methods

### 2.1. Materials

In this study, calcium hydroxide was the source of cation for mineralization and purchased from Vacalai Tesque Co. (Japan). Boron solution was prepared from boric acid (Merck Co., Germany) with deionized water. Thirty (30) mL solutions containing 500 mg/L of boron were used in each of the batch experiments. In addition, the influence of phosphoric acid (Sigma–Aldrich Co., Germany) addition (P-addition) in mineralization and boron removal was evaluated in this study.

### 2.2. Boron recovery experiments

For boron recovery, two heating methods and one control were implemented; they were conventional heating (CH) using a circulator oven, microwave radiation (MW) using a microwave digestion oven (Milestone Ethos Touch Control, USA) at 500 W power setting, and the control was added with the same chemical dosages but under the room temperature (25 °C). They were investigated at different reaction times (10 min–4 h). The heating experiments were carried out under different reaction temperatures (55–160 °C), dosages of calcium hydroxide (0.1–4 g per 30 mL of solution) and pH values (6–13). The precipitates were then separated from liquid by a centrifuge (Z32HK, Hermle, Germany) at 10,000 rpm for 5 min and then dried at –58 °C by a freeze dryer (FD3-12P, KINGMECH, Taiwan). Throughout this study, boron recovery efficiencies were determined and compared using the following equation:

$$\text{Boron recovery efficiency (\%)} = \left[ \frac{C_0 - C_e}{C_0} \right] \times 100 \quad (2)$$

where  $C_e$  is the concentration of the boron solution (mg/L) at the end of the experiment and  $C_0$  is the initial boron concentration (mg/L).

### 2.3. Analytical methods

Compositions of the precipitates were analysed by X-ray diffraction (XRD) (X'Pert PRO, PANalytical, Netherlands), equipped with a Cu target operated at 45 kV and 40 mA. The surface structures of the precipitates were observed by scanning electron microscopy (SEM) (JSM-6500F, JEOL, Japan) with energy dispersive X-ray spectrometry (EDX) (Energy 300, OXFORD INCA, England). The specific surface areas of the precipitates were determined from  $N_2$  adsorption and desorption isotherms using a surface area and porosity analyzer (BET) (TriStar 3000, Micromeritics, USA).

Boron concentrations in solutions were measured by azomethine-H method [24] with a UV-visible spectrophotometer (Cintra 20, GBC, Australia) at 410 nm.

## 3. Results and discussion

### 3.1. Effects of the heating methods on boron recovery

Two heating methods (CH and MW) were conducted in 30 mL solutions containing 2 g of  $Ca(OH)_2$  and 500 mg/L of boron at 130 °C

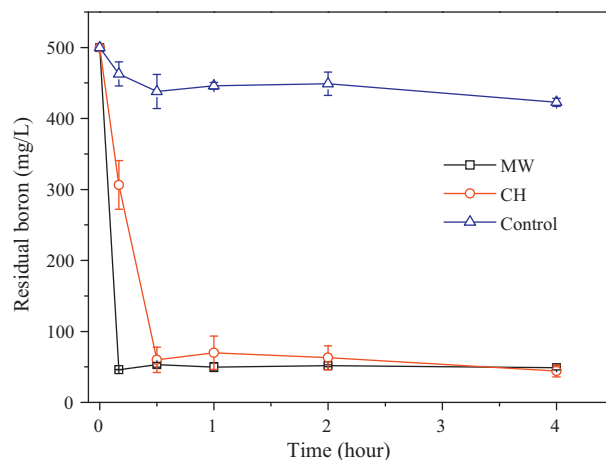


Fig. 1. Boron concentrations versus reaction time by two heating methods (130 °C) and control (B = 500 mg/L,  $Ca(OH)_2$  dosage = 2 g and 30 mL solution).

from 10 min to 4 h and the results are shown in Fig. 1. For the MW method, boron concentrations dropped rapidly to 48 mg/L within 10 min, and stayed essentially the same afterwards. When compared to the MW method, the rates of boron recovery by the CH method were slow. Boron concentrations dropped to 306 mg/L after 10 min, 60 mg/L after 30 min, and stayed essentially the same afterwards. For the control, the boron concentrations decreased only slightly: the concentration stayed around 450 mg/L after 4 h. The experimental results implied that the energy transfer rate was faster by the MW method, so the initial boron removal rate was much faster. However, after a long enough reaction time (e.g., 30 min), the overall boron recovery rates of both heating methods were comparable.

XRD patterns of the precipitates made by the MW and CH methods are shown in Fig. 2. After 10 min of heating, the diffraction peaks of  $Ca_2B_2O_5 \cdot H_2O$  were observed in the precipitates from the MW method, while the corresponding peaks were too weak to be identified in the precipitates made by the CH method (Fig. 2). After 4 h of treatment, peak intensities of  $Ca_2B_2O_5 \cdot H_2O$  of the precipitates from both heating methods became similar (figures not shown). The results implied the MW method can produce faster crystallization of  $Ca_2B_2O_5 \cdot H_2O$ .

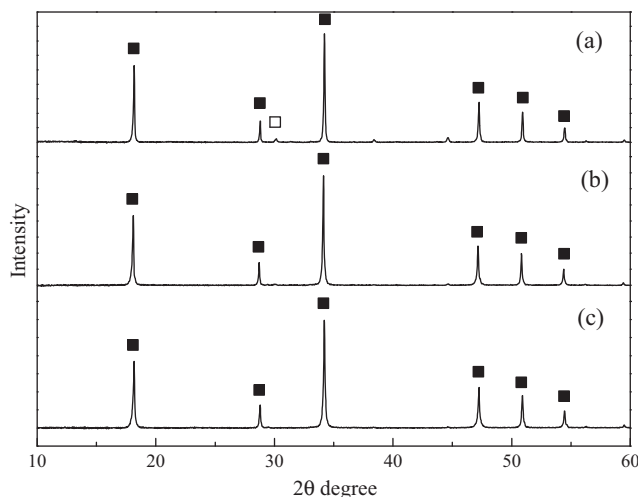
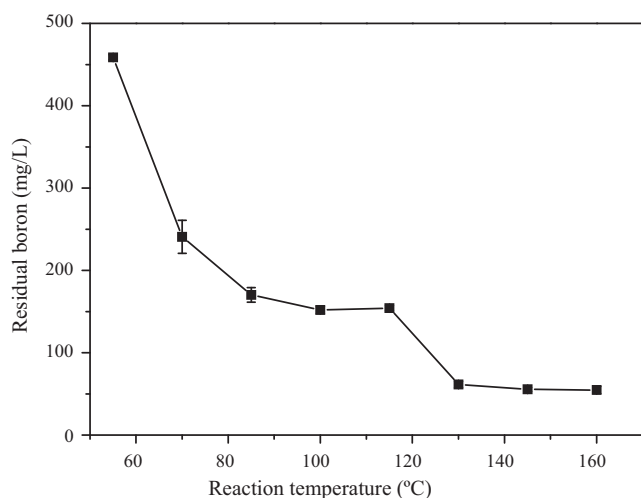


Fig. 2. XRD patterns of precipitates made by (a) MW (130 °C), (b) CH (130 °C) and (c) control (B = 500 mg/L,  $Ca(OH)_2$  dosage = 2 g, 30 mL solution,  $t = 10$  min). ■:  $Ca(OH)_2$  and □:  $Ca_2B_2O_5 \cdot H_2O$ .



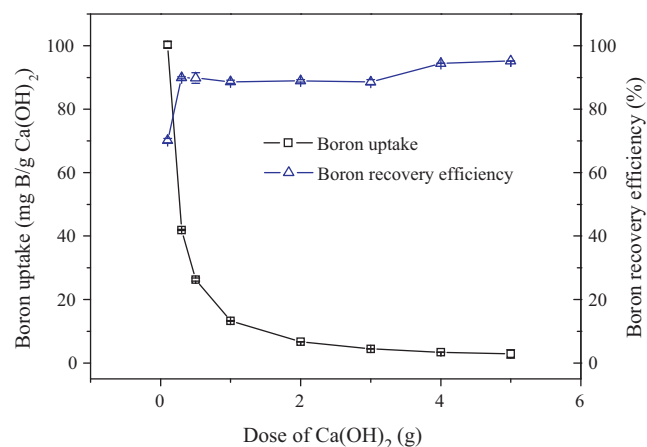
**Fig. 3.** Effects of reaction temperatures on residual boron concentrations by microwave radiation ( $B=500$  mg/L,  $\text{Ca}(\text{OH})_2$  dosage = 0.5 g, 30 mL solution and  $t=0.5$  h).

### 3.2. Reaction temperature

Effects of reaction temperatures on boron recovery by the MW method were shown in Fig. 3. The solutions were subjected to microwave radiation at a 500 W power setting for 30 min, the final boron concentrations decreased as temperature increased (from 55 °C to 130 °C). XRD analyses were conducted on the precipitates made under different reaction temperatures. At lower reaction temperatures, diffraction peaks of  $\text{Ca}(\text{OH})_2$  were the predominant ones. As the reaction temperature increased, the diffraction peaks of  $\text{Ca}_2\text{B}_2\text{O}_5 \cdot \text{H}_2\text{O}$  started to appear. From 70 °C to 100 °C, intensities of  $\text{Ca}_2\text{B}_2\text{O}_5 \cdot \text{H}_2\text{O}$  peaks had a significant increase, and became stable after 130 °C. The results indicate that reaction temperature is an important factor for inducing mineralization of  $\text{Ca}_2\text{B}_2\text{O}_5 \cdot \text{H}_2\text{O}$ , and 130 °C was chosen as the reaction temperature in the subsequent experiments.

### 3.3. Calcium hydroxide doses

Effects of  $\text{Ca}(\text{OH})_2$  doses were evaluated in 500 mg/L of boron solutions for 0.5 h of microwave radiation at 130 °C. Fig. 4 shows percentage boron removals and masses of boron removed unit mass of  $\text{Ca}(\text{OH})_2$  with different doses of  $\text{Ca}(\text{OH})_2$  (0.1–5.0 g). The mass of boron removal per unit mass of  $\text{Ca}(\text{OH})_2$  dropped with increasing  $\text{Ca}(\text{OH})_2$  doses. For boron recovery efficiency, it reached 90% as  $\text{Ca}(\text{OH})_2$  dose was increased to 0.3 g, and became essentially the



**Fig. 4.** Effects of  $\text{Ca}(\text{OH})_2$  doses on boron recovery by microwave radiation ( $B=500$  mg/L, 30 mL solution,  $T=130$  °C and  $t=0.5$  h).

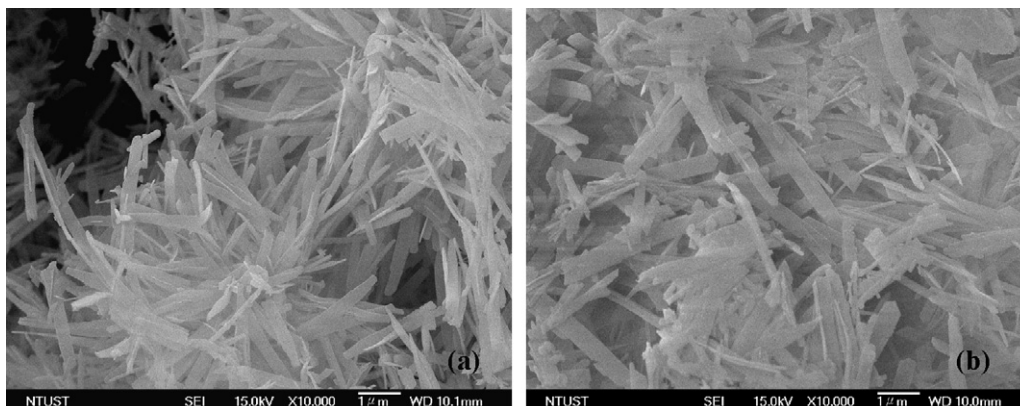
**Table 1**

BET analysis of the precipitates from reactions with different amount of  $\text{Ca}(\text{OH})_2$  addition (initial boron concentration = 500 mg/L, 30 mL solution,  $T=130$  °C and  $t=0.5$  h).

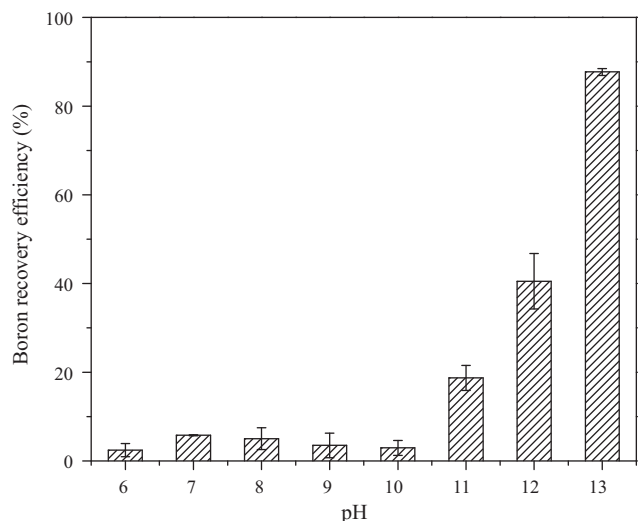
Amount of $\text{Ca}(\text{OH})_2$ added (g)	Surface area ( $\text{m}^2/\text{g}$ )	Pore volume ( $\text{cm}^3/\text{g}$ )
0.1	28.4	0.068
0.3	14.6	0.037
0.5	12.7	0.031

same until 5 g. Fig. 5 shows the SEM photographs of precipitates from two  $\text{Ca}(\text{OH})_2$  doses (0.1 and 0.3 g). For the 0.1 g dose, stick-shape crystals were observed and their width was about 400 nm (Fig. 5(a)). These crystals aggregated together and were identified as  $\text{Ca}_2\text{B}_2\text{O}_5 \cdot \text{H}_2\text{O}$  from the XRD analysis. For the 0.3 g dose, wider stick-shape crystals, consisted of  $\text{Ca}(\text{OH})_2$  and  $\text{Ca}_2\text{B}_2\text{O}_5 \cdot \text{H}_2\text{O}$ , were observed, the width of the crystals was greater, at around 600 nm (Fig. 5(b)).

BET analyses were conducted on the precipitates made with different  $\text{Ca}(\text{OH})_2$  doses were carried out and the results are shown in Table 1. Surface areas and pore volumes decreased with increasing doses of  $\text{Ca}(\text{OH})_2$ . The surface area of the precipitate with the presence of 0.3 g  $\text{Ca}(\text{OH})_2$  was only half of that with 0.1 g of  $\text{Ca}(\text{OH})_2$ . BET results also supported the results of the crystal sizes from the SEM photographs: precipitates from dosing of 0.1 g  $\text{Ca}(\text{OH})_2$  yielded smaller crystals and had larger surface areas than 0.3 g.



**Fig. 5.** SEM photographs of precipitates from the reactions with (a) 0.1 and (b) 0.3 g of  $\text{Ca}(\text{OH})_2$  by microwave radiation ( $B=500$  mg/L,  $T=130$  °C and  $t=0.5$  h).



**Fig. 6.** Effects of pH values on boron recovery efficiency by microwave radiation ( $B = 500 \text{ mg/L}$ ,  $\text{Ca(OH)}_2$  dosage =  $0.5 \text{ g}$ ,  $30 \text{ mL}$  solution,  $T = 130^\circ\text{C}$  and  $t = 0.5 \text{ h}$ ).

### 3.4. Effects of pH

To carry out this study, the pH of each solution containing  $0.5 \text{ g}$   $\text{Ca(OH)}_2$  and  $500 \text{ mg/L}$  of boron was adjusted by adding HCl or NaOH and then heated by microwave radiation at  $130^\circ\text{C}$  for  $0.5 \text{ h}$ . Fig. 6 is a presentation of boron recovery efficiencies for each pH value (6–13). The result showed boron recovery efficiencies were highly depended on pH values and the efficiencies were dropped sharply with decreasing pH values. For higher pH values (above 11), the efficiencies of boron recovery were relatively high and reached 90% at pH of 13. At pH values between 6 and 10, the efficiencies were below 10%. It was due to the fact that lower pH values would raise the concentration of hydrogen ions ( $\text{H}^+$ ) which competed with boron for available  $\text{Ca(OH)}_2$ .

### 3.5. Influence of P-addition

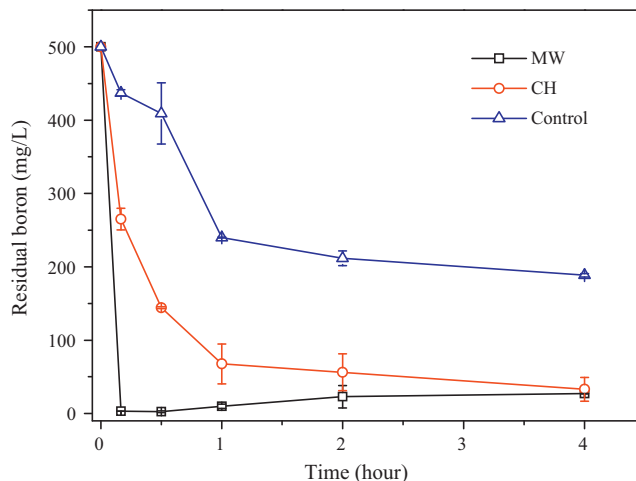
#### 3.5.1. Effects of heating methods

Effects of phosphoric acid addition on boron recovery were investigated by adding  $2 \text{ g}$  of  $\text{Ca(OH)}_2$  and  $1.5 \text{ g}$  of  $\text{H}_3\text{PO}_4$  in  $30 \text{ mL}$  solutions containing  $500 \text{ mg/L}$  of boron. The boron concentrations decreased sharply to  $5 \text{ mg/L}$  within the first  $10 \text{ min}$  by the MW method (Fig. 7), which is much less than  $48 \text{ mg/L}$  when no phosphoric acid was added. However, the boron level showed a slight increasing trend afterwards. For the CH method, boron level stayed above  $50 \text{ mg/L}$  within the first hour and decreased gradually afterwards. For the control, the boron level fell to  $240 \text{ mg/L}$  in  $1 \text{ h}$  and decreased gradually afterwards. Then boron concentration decreased to approximately  $200 \text{ mg/L}$  at the end of  $4 \text{ h}$ .

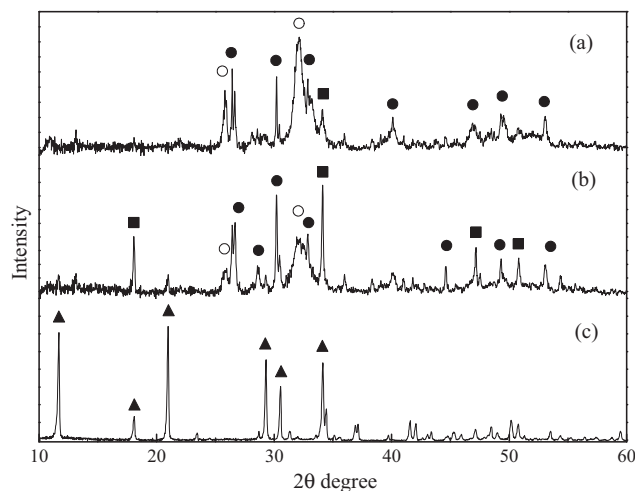
XRD analysis was conducted on the precipitates. XRD diffraction peaks of  $\text{Ca(OH)}_2$ ,  $\text{CaHPO}_4$  and  $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$  were identified in the MW and CH samples after one half an hour of reaction (Fig. 8). For the MW method, peaks of  $\text{Ca(OH)}_2$  were not as strong as those from the CH method, but their peaks of  $\text{CaHPO}_4$  and  $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$  were stronger. The stronger appearance of  $\text{CaHPO}_4$  and  $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$  implies higher boron recovery efficiencies [19].

#### 3.5.2. Effects of $\text{Ca(OH)}_2$ and $\text{H}_3\text{PO}_4$ doses

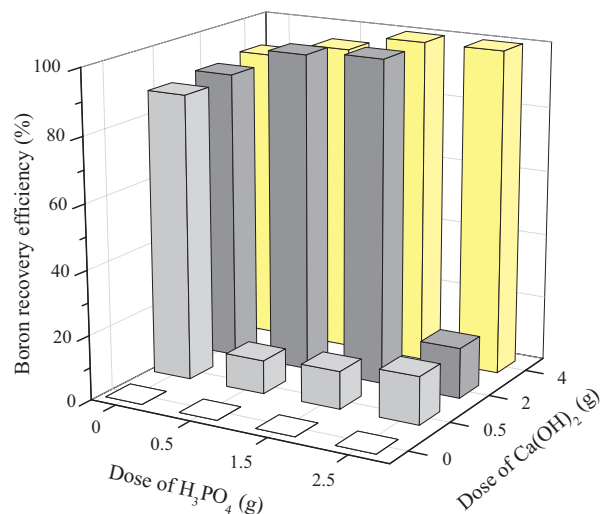
Effects of  $\text{Ca(OH)}_2$  and  $\text{H}_3\text{PO}_4$  doses were investigated in  $500 \text{ mg/L}$  of boron solutions for  $10 \text{ min}$  of microwave radiation at  $130^\circ\text{C}$ . Fig. 9 shows boron recovery efficiencies with different doses of  $\text{Ca(OH)}_2$  ( $0.5$ – $4.0 \text{ g}$ ) and  $\text{H}_3\text{PO}_4$  ( $0.5$ – $2.5 \text{ g}$ ). The boron recovery



**Fig. 7.** The boron concentration with different reaction time by two heating methods ( $130^\circ\text{C}$ ) and control ( $B = 500 \text{ mg/L}$ ,  $\text{Ca(OH)}_2$  dosage =  $2 \text{ g}$ ,  $\text{H}_3\text{PO}_4$  dosage =  $1.5 \text{ g}$  and  $30 \text{ mL}$  solution).



**Fig. 8.** XRD patterns of the precipitates obtained from (a) MW ( $130^\circ\text{C}$ ), (b) CH ( $130^\circ\text{C}$ ) and (c) control with P-addition ( $B = 500 \text{ mg/L}$ ,  $\text{Ca(OH)}_2$  dosage =  $2 \text{ g}$ ,  $\text{H}_3\text{PO}_4$  dosage =  $1.5 \text{ g}$ ,  $30 \text{ mL}$  solution,  $t = 0.5 \text{ h}$ ). ■:  $\text{Ca(OH)}_2$ , ●:  $\text{CaHPO}_4$ , ▲:  $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ , ○:  $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ .



**Fig. 9.** Effects of  $\text{Ca(OH)}_2$  and  $\text{H}_3\text{PO}_4$  doses on boron recovery by microwave radiation ( $B = 500 \text{ mg/L}$ ,  $30 \text{ mL}$  solution,  $T = 130^\circ\text{C}$  and  $t = 10 \text{ min}$ ).

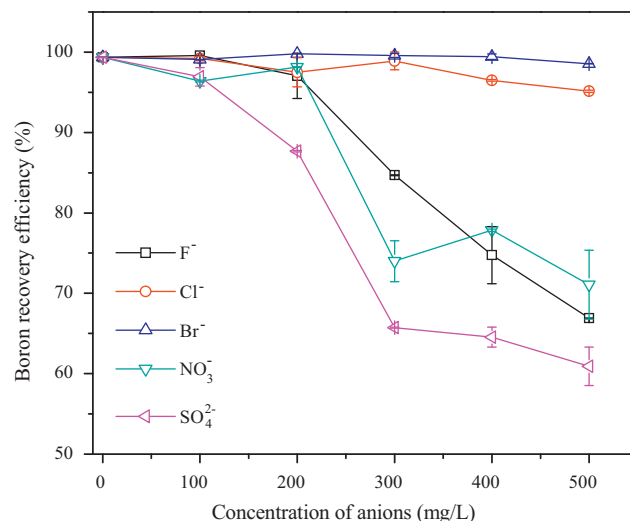


ery efficiency depended greatly on the dose ratios of  $\text{Ca}(\text{OH})_2$  and  $\text{H}_3\text{PO}_4$  addition. On the left of the figure,  $\text{Ca}(\text{OH})_2$  alone ( $\text{H}_3\text{PO}_4$  addition = 0 g), the recovery efficiencies stayed above 90% with various  $\text{Ca}(\text{OH})_2$  doses. However, the recovery efficiency dropped to 10% as  $\text{H}_3\text{PO}_4$  addition raised to 0.5 g and 1.5 g with 0.5 g  $\text{Ca}(\text{OH})_2$ . Moreover, the recovery efficiency reached 99% as 1.5 g of  $\text{H}_3\text{PO}_4$  and more than 2 g of  $\text{Ca}(\text{OH})_2$  were added. It implies that lower  $\text{Ca}(\text{OH})_2/\text{H}_3\text{PO}_4$  addition ratio yielded a worse recovery, and 2 g of  $\text{Ca}(\text{OH})_2$  and 1.5 g of  $\text{H}_3\text{PO}_4$  were chosen as the dosage in the subsequent interference experiment.

### 3.6. Interference of other anions

In addition to boron, wastewater contains many other anions which might interfere with boron recovery efficiency. To evaluate the potential interferences by other anions,  $\text{F}^-$ ,  $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{NO}_3^-$  and  $\text{SO}_4^{2-}$ , concentrations ranging from 100 to 500 mg/L were added to the solutions containing 2 g  $\text{Ca}(\text{OH})_2$ , 1.5 g  $\text{H}_3\text{PO}_4$  and 500 mg/L of boron and then microwaved at 130 °C. As shown in Fig. 10, boron recovery efficiencies were only slightly affected in the presence of  $\text{Cl}^-$  and  $\text{Br}^-$ , and they stayed above around 95%. However, in the presence of excess  $\text{F}^-$ ,  $\text{NO}_3^-$  and  $\text{SO}_4^{2-}$ , the recovery efficiencies were found to drop sharply.

In the presence of 500 mg/L of  $\text{F}^-$  ion, the recovery efficiency decreased from 99 to 68%. XRD analysis was conducted on the precipitates. XRD diffraction peaks of  $\text{Ca}_5(\text{PO}_4)_3\text{F}$  (fluorapatite) and  $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$  were identified. The formation of  $\text{Ca}_5(\text{PO}_4)_3\text{F}$  would reduce amount of  $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$  crystal, and it may lead to lower boron recovery efficiency. In the presence of 500 mg/L of  $\text{NO}_3^-$  and  $\text{SO}_4^{2-}$ , the recovery efficiencies also decreased significantly. After XRD analysis, there were not other crystals which were identified in the precipitates; both of their XRD diffraction



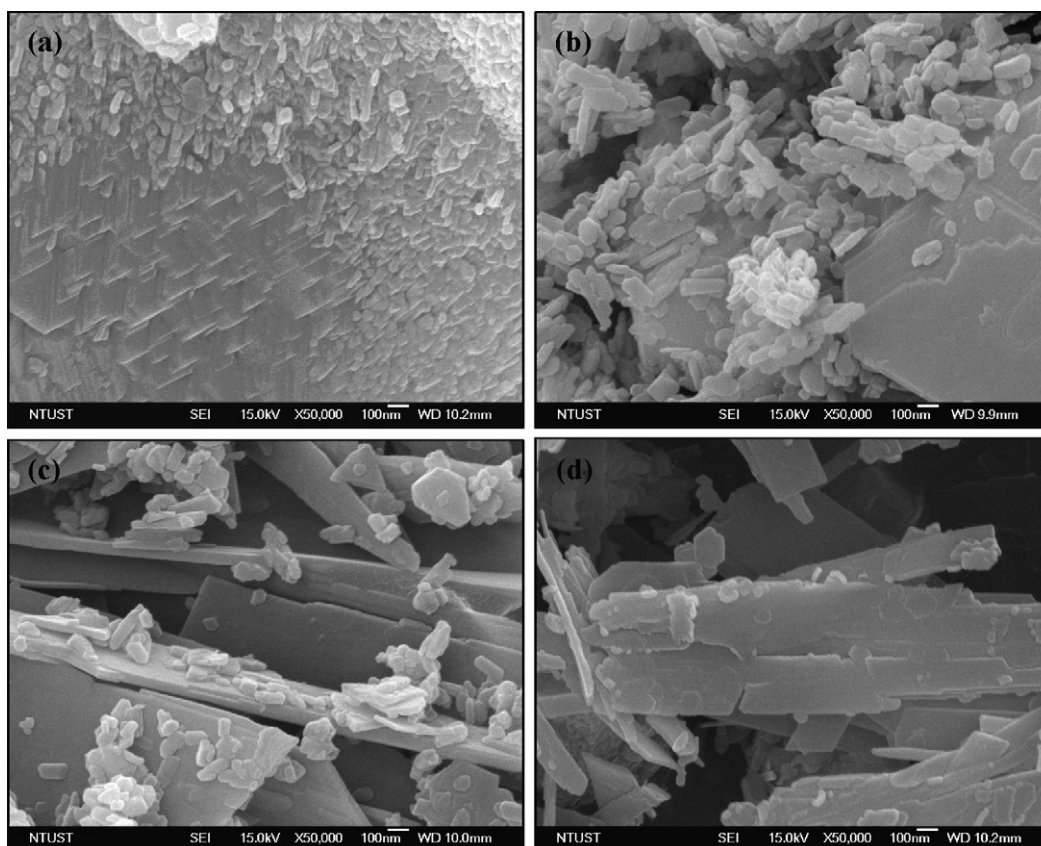
**Fig. 10.** Effects of other anions on boron recovery efficiency by microwave radiation ( $B = 500$  mg/L,  $\text{Ca}(\text{OH})_2$  dosage = 0.5 g,  $\text{H}_3\text{PO}_4$  dosage = 1.5 g, 30 mL solution, pH = 13,  $T = 130$  °C and  $t = 10$  min).

peaks were identified as  $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ . It implies the competitions of  $\text{NO}_3^-$  and  $\text{SO}_4^{2-}$  ions with boron ions for being contained in the precipitates, and these two ions may have higher affinity than boron ions [25].

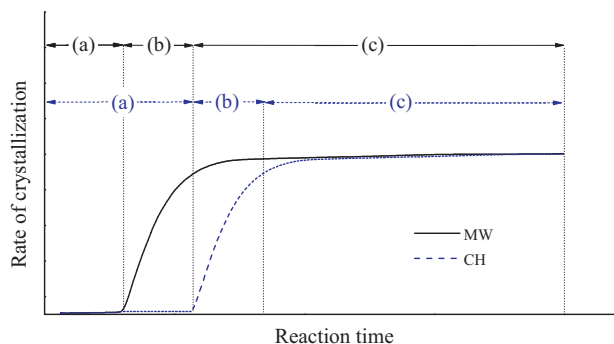
### 3.7. Mechanisms of boron recovery by mineralization

#### 3.7.1.1. $\text{Ca}(\text{OH})_2$ alone

For the case of  $\text{Ca}(\text{OH})_2$  alone (without phosphoric acid addition), the main mechanism for boron recovery is precipitation of



**Fig. 11.** SEM photographs of various precipitates (a) 0.5 g of  $\text{Ca}(\text{OH})_2$  in 30 mL solution, (b) the condition of  $B = 0$  mg/L,  $T = 130$  °C and  $t = 0.5$  h of microwave radiation, (c) the condition of  $B = 500$  mg/L,  $T = 100$  °C,  $t = 0.5$  h and (d) the condition of  $B = 500$  mg/L,  $T = 130$  °C and  $t = 0.5$  h.



**Fig. 12.** Different rates in precipitation for formation of  $\text{Ca}_2\text{B}_2\text{O}_5 \cdot \text{H}_2\text{O}$  by the MW and CH methods. (a) Induction phase, (b) crystallization phase and (c) stationary phase.

$\text{Ca}_2\text{B}_2\text{O}_5 \cdot \text{H}_2\text{O}$ . In order to evaluate transformation of precipitates during microwave hydrothermal treatment, SEM analyses were made on different precipitates (Fig. 11). Two types of crystals were observed in virgin  $\text{Ca}(\text{OH})_2$  (Fig. 11(a)): smooth octahedral crystals in the bottom-left of the photograph and irregular beam-shape crystals in the top-right. From the EDX results, it was found that the ratio of oxygen element in the beam-shape crystal was larger than that of the octahedral crystal. Without the presence of boron, the amount of beam-shape crystal increased from fission of octahedral crystals after microwave irradiation at  $130^\circ\text{C}$  for half an hour (Fig. 11(b)). With the presence of boron (500 mg/L), plate-like crystals, identified as  $\text{Ca}_2\text{B}_2\text{O}_5 \cdot \text{H}_2\text{O}$  by EDX, were formed by the mineralization of beam-shape  $\text{Ca}(\text{OH})_2$  and boron after microwave irradiation at  $100^\circ\text{C}$  for half an hour (Fig. 11(c)). With an increasing of temperature from 100 to  $130^\circ\text{C}$ , the plate-shape crystal of  $\text{Ca}_2\text{B}_2\text{O}_5 \cdot \text{H}_2\text{O}$  became longer and finer and turned as a wood stick shape (Fig. 11(d)).

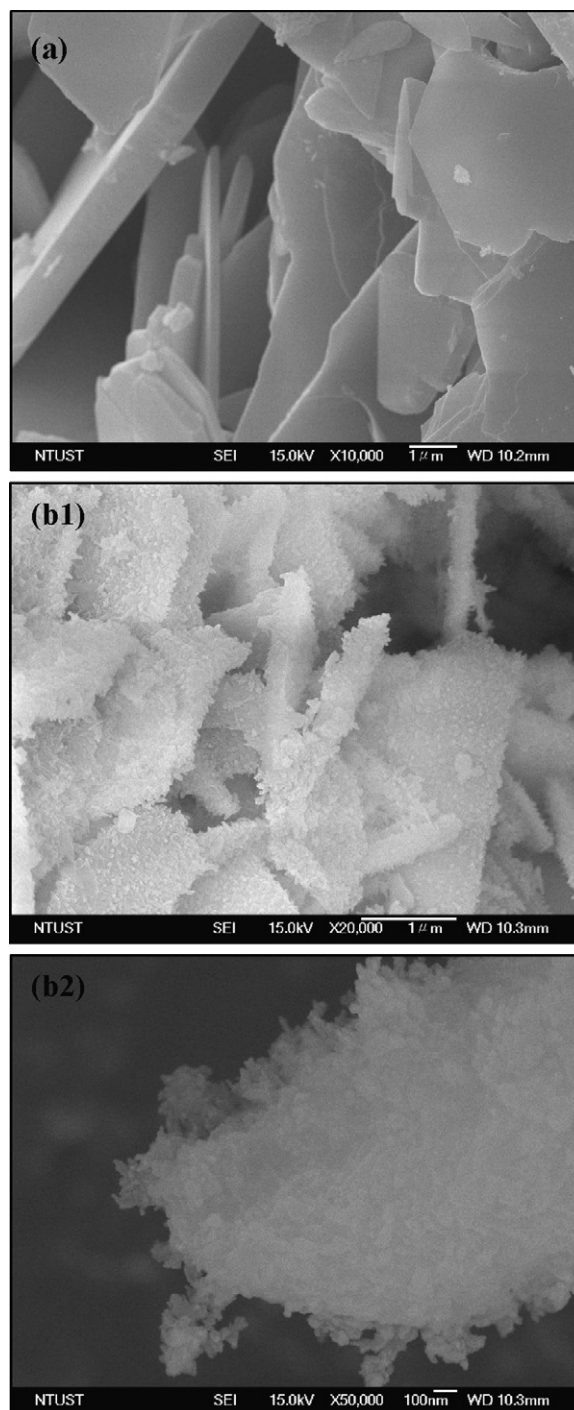
In general, precipitation could be categorized into three phases: induction, crystal growth and stationary. In the induction phase, the main activities are ions diffusion and nucleation, and the rate of critical nucleus formation ( $J$ ) for nucleation can be represented by [26]:

$$J = P \exp \left[ \frac{-\Delta G^*}{kT} \right] \quad (3)$$

where  $P$  is related to collision efficiency,  $\Delta G^*$  is the activation energy for nucleation,  $k$  is the Boltzmann constant and  $T$  is absolute temperature. Based on the experimental results, differences in rates of variety of precipitation for formation of  $\text{Ca}_2\text{B}_2\text{O}_5 \cdot \text{H}_2\text{O}$  by two heating methods are proposed and illustrated in Fig. 12. For the MW method, the microwave radiation not only provides uniform heating and raises the diffusion rate, enhances Brownian motion, and increases collision frequency for calcium ions and boron ions. As shown in Eq. (3), microwave radiation method can increase the collision frequency ( $P$ ) to shorten the reaction time in the induction phase. In the crystal growth phase, the nuclei grow to critical sizes and get crystallized rapidly. Because of the same reaction temperature, crystallization by the MW and CH methods exhibited similar rates of crystal growth. Finally, when the crystallization becomes stable, boron concentrations and the amount of crystals formed reach equilibrium.

### 3.7.2. With P-addition

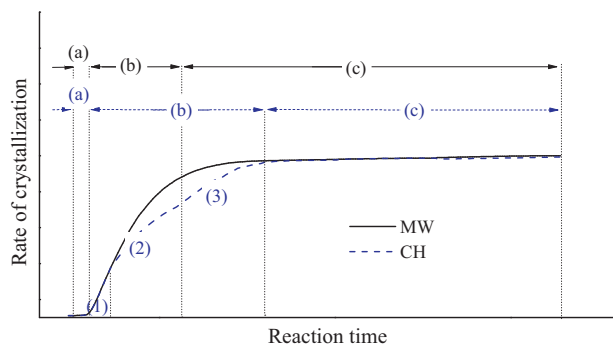
With the addition of  $\text{H}_3\text{PO}_4$ ,  $\text{Ca}(\text{OH})_2$  and  $\text{B}(\text{OH})_3$ ,  $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$  were formed rapidly and boron was contained in the  $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$  crystals. Fig. 13(a) shows the flake-shape crystals of  $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ , the surfaces are smooth. These flake-shape crystals contain lots of boron ions; however, their solubility is relatively high ( $K_{\text{sp}} = 10^{-6.6}$ ) [26], and a part of boron will re-dissolve back to the solution (see



**Fig. 13.** SEM photographs of the precipitates obtained with 2 g of  $\text{Ca}(\text{OH})_2$  and 1.5 g  $\text{H}_3\text{PO}_4$  in (a) the condition of  $B = 500 \text{ mg/L}$ ,  $T = 25^\circ\text{C}$ , (b1) the condition of  $B = 500 \text{ mg/L}$ ,  $T = 130^\circ\text{C}$  and (b2) higher magnification photographs of (b1).

Fig. 7). During the heating,  $\text{CaHPO}_4$  and  $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$  were formed on the surfaces of  $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$  crystals (Fig. 13(b1)). The sizes of  $\text{CaHPO}_4$  and  $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$  crystals were smaller with both diameters of around 50 nm (Fig. 13(b2)). In these crystalline phases, it was difficult for boron to re-dissolve due to the lower solubility of  $\text{CaHPO}_4$  ( $K_{\text{sp}} = 10^{-6.9}$ ) and  $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$  ( $K_{\text{sp}} = 10^{-117.1}$ ) [27].

There are three different crystal species in the case of P-addition, and nucleation only occurred during crystallization of  $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ . Because formations of  $\text{CaHPO}_4$  and  $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$  were solid phase transformation, the induction phase only



**Fig. 14.** Different rates in precipitation for three calcium phosphate species, (1)  $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ , (2)  $\text{CaHPO}_4$  and (3)  $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$  by the MW and CH methods. (a) Induction phase, (b) crystallization phase and (c) stationary phase.

appeared in the formation of  $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$  (Fig. 14). For the formation of  $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ , the rates of crystallizations were similar for both the MW and CH methods during the induction and the crystal growth phases. It is due to the relatively fast chemical reaction rate for  $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$  formation, the reaction enthalpy is around  $-65,813 \text{ cal/mol}$  [28]. For formations of  $\text{CaHPO}_4$  and  $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ , the reactions are endothermic and a large amount of energy was required, especially for  $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ . That two reaction enthalpies are  $4400 \text{ cal/mol}$  [29] and  $30,710 \text{ cal/mol}$  [30], respectively. For high energy requirements, the MW method exhibited advantages of uniform and rapid heating, it provided sufficient energy in a short period of time for the reaction and enhanced rate of crystal growth.

#### 4. Conclusion

An effective and efficient method for boron recovery from concentrated wastewater was developed. By microwave radiation with  $\text{Ca}(\text{OH})_2$  alone, the recovery efficiency reached around 90% within 10 min of reaction time. The main mechanism of boron recovery is the mineralization of  $\text{Ca}_2\text{B}_2\text{O}_5 \cdot \text{H}_2\text{O}$  by  $\text{Ca}(\text{OH})_2$  and  $\text{B}(\text{OH})_3$ . It is an endothermic reaction and the optimum temperature in this study was found to be around  $130^\circ\text{C}$  and the optimum dose of  $\text{Ca}(\text{OH})_2$  was  $0.3 \text{ g}$  in  $30 \text{ mL}$  solution. The shapes of crystals formed were different with different doses of  $\text{Ca}(\text{OH})_2$ . For the case of  $\text{H}_3\text{PO}_4$  addition, formation of sparingly soluble calcium phosphate species is the major mechanism for boron recovery, and the recovery efficiency achieved 99% within 10 min of reaction time. The optimum dose of  $\text{Ca}(\text{OH})_2$  and  $\text{H}_3\text{PO}_4$  were  $2.0$  and  $1.5 \text{ g}$  in  $30 \text{ mL}$  solution, respectively. Presence of high concentrations of fluoride, nitrate and sulfate ions would retard the boron recovery. Even  $\text{H}_3\text{PO}_4$  addition will improve boron recovery, the precipitates formed in the  $\text{Ca}(\text{OH})_2$  alone case, mainly consist of  $\text{Ca}_2\text{B}_2\text{O}_5 \cdot \text{H}_2\text{O}$ , and they are more suitable for uses in manufacturing of ceramic, glass and borax. To enhance the boron recovery and removal, a combined recovery process should be considered. In the first step of the combined process, only  $\text{Ca}(\text{OH})_2$  is added to recover the majority of boron from wastewater, and the residual boron ions are then removed by  $\text{H}_3\text{PO}_4$  addition to meet the stringent discharge standard.

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