

Boron Removal from Aqueous Solution by Bipolar Electrodialysis

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Abstract

Boron removal process using electrodialysis method combined with bipolar membrane water splitting reaction was investigated. By using bipolar membrane electrodialysis, pH value of boron contained solution will immediately increase and the dissociation reaction of boric acid into borate ions was enhanced. Therefore, boron can be effectively removed from boron contained solution. Experimental results confirm that bipolar membrane electrodialysis has an advantage over existing electrodialysis. Effect of initial concentration was investigated. It was confirmed that energy requirement for boron removal increase when the initial boron concentration increase.

Keywords: Boron; Electrodialysis, Bipolar membrane; Water

Introduction

Boron compounds in water at high concentration are known to be toxic to humans and plants. The World Health Organization (WHO) has limited boron concentration in drinking water to less than 0.5 mg-B/L. Because of the increased use of desalinated seawater and underground water for drinking water and large amount of boron emissions via wastewater from the manufacturing process, the removal of boron from aqueous solutions has been an important issue in recent years.

In aqueous solutions, boron is mainly present in the form of boric acid. According to the dissociation reaction, boric acid will form into

borate ion at alkaline condition.



There are several methods investigated for removing boron from aqueous solutions, such as precipitation^[1], adsorption^[2], solvent extraction^[3] and ion-exchange^[4]. However, the precipitation and the adsorption methods are efficient only under high boron concentration. In the case of the solvent extraction and the ion-exchange, post regeneration process causes cost increases.

Electrodialysis is one of the considerable options for boron removal from aqueous solution^[5]. Using electrodialysis, borate ion will be efficiently removed from aqueous solution. However, borate ion only exist at alkaline condition, existing electrodialysis method cannot be utilized to acidic solutions.

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To resolve this problem, we focus on water splitting reaction caused by bipolar membrane. Combining the water splitting reaction and electro dialysis, the dissociation reaction of boric acid into borate ions will be enhanced and boron removal will become available in acidic solutions.

In this study the boron removable process using electro dialysis method combined with bipolar membrane water splitting reaction was investigated.

Process description

In a bipolar membrane electro dialysis (BPED) system, a number of bipolar membranes and anion exchange membranes are stacked in an alternating pattern between a cathode and an anode (Fig. 1). The repeating unit is called a cell pair, which consists of a bipolar membrane, a compartment filled with a boron contained solution (feed cell), and an anion exchange membrane and a compartment filled with an electrolyte solution (concentrate cell).

When an electrical potential is applied across the system, water molecules in the bipolar membranes will be split into protons and hydroxyl

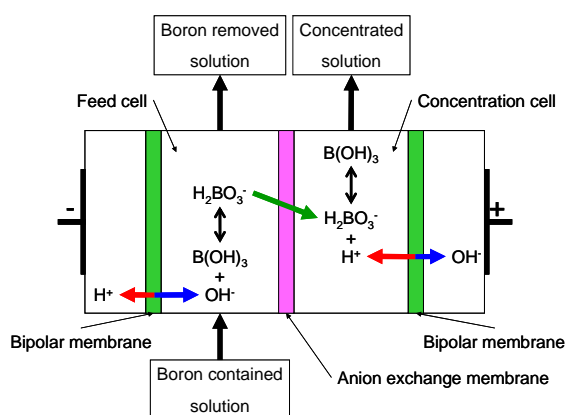


Fig. 1. Schematic of the bipolar membrane electro dialysis system for boron removal.

ions. According to the electrical field applied across the system, hydroxyl ions will be transported to the feed compartment. Due to the increase of hydroxyl ions, pH of the boron contained solution will increase and the dissociation of boric acid into borate ions will be enhanced. Generated borate ions will be transported from feed compartment to concentrate compartment via the anion exchange membrane by function of the electrical field. Thus boron will be removed from boron contained solution and concentrated in the electrolyte solution.

Experimental

An experimental study was conducted in a laboratory-scale electro dialysis apparatus (AGC). This apparatus contains three cell pairs between two electrodes at the both end. Neosepta BP-1E (Tokuyama) was employed as a bipolar membrane and Selemion AMV (AGC) was employed as an anion exchange membrane. The membrane effective area was 117.5 cm² and the distance between two membranes was 1.5 mm.

Solution for feed cell (feed solution, 1 L), solution for concentrate cell (concentrate solution, 1 L) and electrode rinse solution (0.1 M Na₂SO₄ aq, 1L) was circulated using magnetic pumps. The flow rates of three solutions were all set at 1.0 L/min. The electro dialysis experiments were operated with a constant electrical potential at 10 V.

Results and discussion

Comparison of BPED and existing electro dialysis

Comparison study of BPED and existing electro dialysis (ED) system was performed. For

ED apparatus, cation exchange membrane, CMV (AGC), was employed instead of bipolar membrane.

$\text{Na}_2\text{B}_4\text{O}_7$ solution having 100 mg-B/L was employed for the feed solution. Initial pH values of the feed solution were set at 2.6 and 9.2 by adding HCl and NaOH (the concentration of Cl^- in the feed solution was controlled at 0.01 M). The concentrate solution was 0.01 M NaOH solution.

When the electrical potential was applied, the current value increased with time in BPED cases. While in ED cases, current value decreased with time and reached 0 in 30 minutes. This is due to the increase in the electrical resistance in the feed solution. Since ED process employed cation exchange membrane instead of bipolar membrane, the ion concentration in the feed solution decreased with time (Fig. 2a).

The pH value of the feed solution increased immediately in BPED cases, while the change of pH value was smaller in ED cases (Fig. 2b). The pH value of the concentrate solution decreased immediately in BPED cases, while the change of pH value was smaller in ED cases.

The decrease of boron concentration was observed in all cases (Fig. 2c). In BPED cases, more than 90% of boron in the feed solutions was removed in both acidic and alkaline conditions. This result suggests that dissociation reaction of boric acid into borate ion was enhanced by water splitting reaction by bipolar membrane. On the other hand, in ED case, 50% of boron was removed in alkaline condition, 42% of boron was removed in acidic condition. This difference in boron removal would be due to difference of pH value in the feed solutions, which fix the degree of

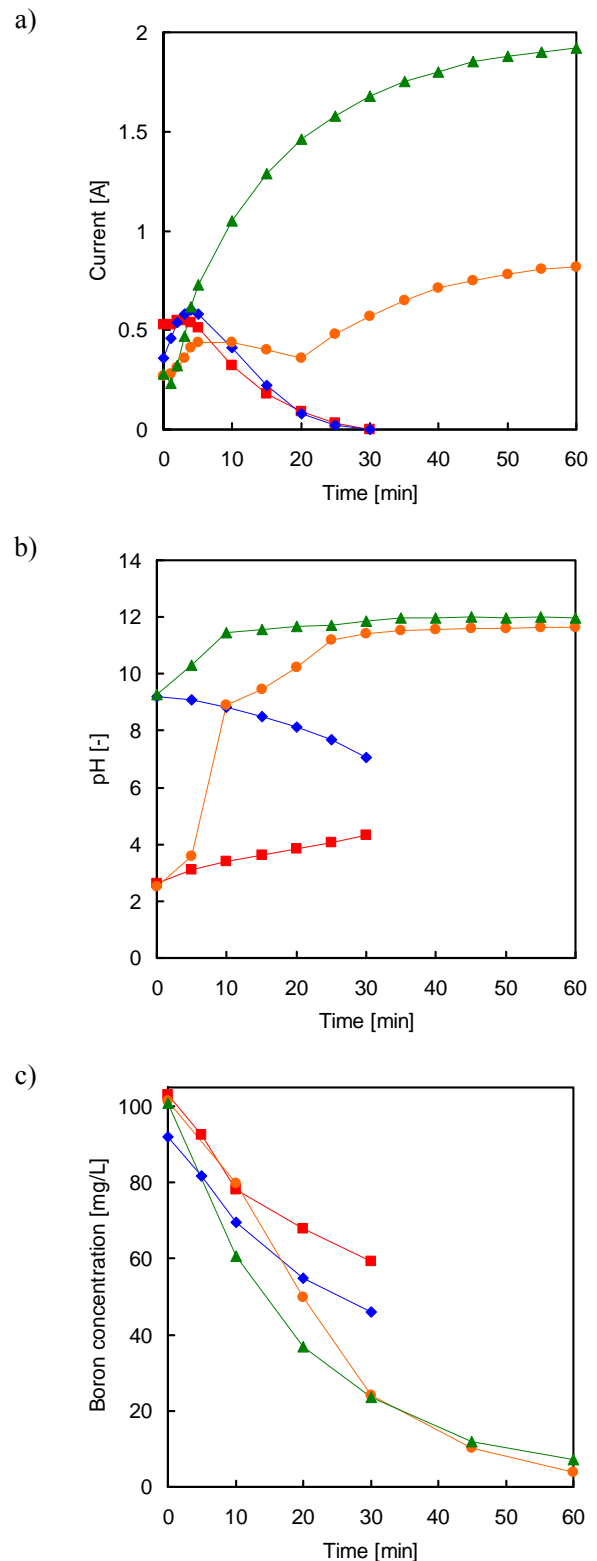


Fig. 2. Comparison of BPED and ED. a) Current, b) pH value of feed solution, c) concentration of boron. ● BPED pH 2.6, ▲ BPED pH 9.2, ■ ED pH 2.6, ◆ ED pH 9.2.

ionization of boric acid.

Effect of initial boron concentration

The effect of initial boron concentration in the solution was investigated. $\text{Na}_2\text{B}_4\text{O}_7$ solution having 50, 100, 200 mg-B/L was employed for the feed solution and concentrate solution.

In case of 50 mg-B/L, 90% of boron was removed in 30 minutes and boron concentration in the feed solution reached less than 1.0 mg-B/L in 60 minutes.

In case of 100 mg-B/L, 90% removal in 60 minutes and <1.0 mg-B/L in 120 minutes.

In case of 200 mg-B/L, boron concentration in the feed solution did not reach below 20 mg/L in this experiment.

The effect of initial concentration on the energy requirement for boron removal calculated from the experiment was shown in Fig. 4. It suggests that energy requirement for boron removal increases with the initial boron concentration increase.

Conclusions

Boron removable process using bipolar membrane electrodialysis was investigated. Water splitting reaction in bipolar membrane enhanced the dissociation reaction of boric acid into borate ion. Therefore, boron in the feed solution was effectively removed and concentrated.

More than 90% of boron was removed in 30 minutes and boron concentration in the feed solution reached less than 1.0 mg-B/L in 60 minutes in the best case studied.

It was confirmed that energy requirement will increase when the initial boron concentration increased.

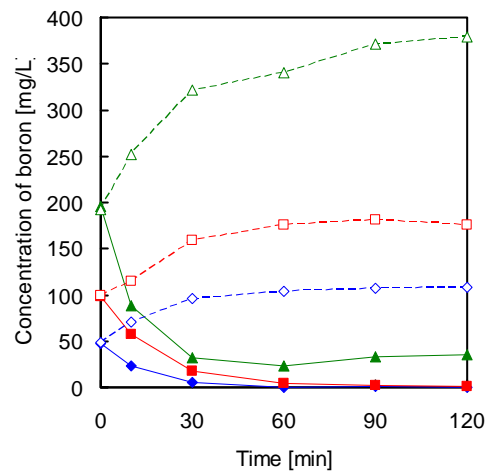


Fig. 3. Effect of initial boron concentration on boron removal. \blacklozenge feed 50 mg-B/L, \diamond concentrate 50 mg-B/L, \blacksquare feed 100 mg-B/L, \square concentrate 100 mg-B/L, \blacktriangle feed 200 mg-B/L, \triangle concentrate 200 mg-B/L.

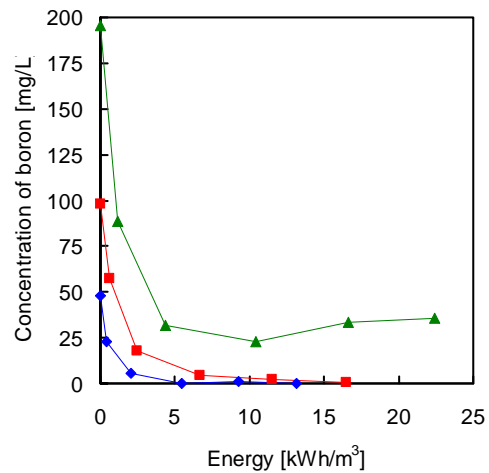


Fig. 4. Energy requirement for boron removal. \blacklozenge feed 50 mg-B/L, \diamond concentrate 50 mg-B/L, \blacksquare feed 100 mg-B/L, \square concentrate 100 mg-B/L, \blacktriangle feed 200 mg-B/L, \triangle concentrate 200 mg-B/L.

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