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Precipitation recovery of boron from aqueous solution by chemical oxo-precipitation at room temperature [☆]

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HIGHLIGHTS

- 99.7% of boron was recovered as barium perborate salts at room temperature.
- Dissolved oxygen served as an indicator to estimate the progress of the reaction.
- Phase transformation of precipitates was revealed.
- The mechanisms of COP were proposed.

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ABSTRACT

This work investigated the effective precipitation recovery of boron by chemical oxo-precipitation (COP), which uses hydrogen peroxide (H_2O_2) to transform aqueous boron to easy-precipitating perborates at room temperature. By using barium hydroxide ($Ba(OH)_2$) as a precipitant, the boron removal enhanced with treatment time and the boron level was eventually reduced from 1000 ppm to 3 ppm in four hours. The transformation of the precipitates from amorphous to crystalline was assumed to be responsible for such high boron removal. The aqueous data and the characterization of the precipitates, including elemental analysis, dissolved oxygen, XRD and Raman microscopy, reveal that the phase transformation of perborate species in the precipitates carried out with time during the COP. Mechanisms of COP that describe the precipitates transformation from $BaB(OH)_3OOB(OH)_3$ and $Ba(B(OH)_3OOH)_2$ to $BaB(OH)_2(OO)_2B(OH)_2$ were proposed.

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1. Introduction

The development of renewable energy is an urgent challenge during the past decade in order to replace CO_2 -emitting fossil fuels. Polymer electrolyte membrane fuel cells (PEMFCs) that utilize hydrogen as fuel are promising candidates due to their high power density, low working temperature and zero emission [1,2]. Meanwhile, hydrogen storage technologies have been intensely studied to store hydrogen safely and affordably for mobile and portable applications [3,4]. Boron-based materials (BBMs), such as sodium

borohydride ($NaBH_4$), ammonia borane (NH_3BH_3) and hydrazine borane ($N_2H_4BH_3$), are promising chemical hydrogen storage materials due to their high hydrogen capacity and good stability [5]. Generally, the hydrogen stored in BBMs can be released by hydrolysis reactions, which can be catalyzed by heterogeneous metal compounds in aqueous solution under mild conditions [5,6]. The concentrated boron wastewater generated after dehydrogenation remains a problem due to its potential toxicity to the environment [7–9]. Thus, effective boron recovery methods are necessary for removing boron from the concentrated boron wastewater and producing reusable boron product.

Various types of boron removal technologies have been developed, such as chemical precipitation, adsorption, reverse osmosis and ion exchange [10,11]. Adsorption and ion exchange methods are suitable for low boron concentration due to their high boron selectivity and excellent efficiency [12,13]. However, they are impractical to deal with concentrated boron wastewater without

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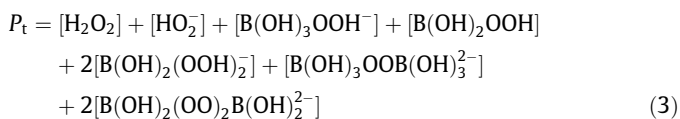
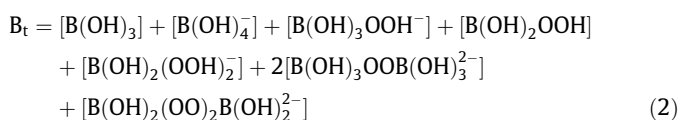
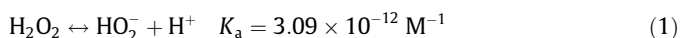
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pretreatment [14]. Reverse osmosis has been widely applied for desalination, nevertheless, the required operation pH at 10–11 is relatively high that often causes the hydroxides of metals to scale the membrane [15,16]. Chemical precipitation, which is most commonly adopted in industry to remove contaminants at high concentration from water, has the potential to treat concentrated boron wastewater in an easy and cost-effective way.

Conventional precipitation methods recover boron as borate ores, however, high temperature and pH are required to resemble the hydrothermal process in the nature [11]. Using lime ($\text{Ca}(\text{OH})_2$) alone can provide 87% of boron removal from boric acid solution containing 750 ppm of boron at 60 °C [17]. In addition, co-precipitation methods that combined lime with sulphuric acid or phosphoric acid have been studied under 50–90 °C using conventional heating and 130 °C using microwave radiation [18,19]. Electrocoagulation, a modified co-precipitation method utilizing aluminium, iron or zinc plate as sacrificial anode, has been developed to improve the efficiency of boron removal [20–22]. Under the optimal pH at 8, about 85% of boron can be removed from 1000 ppm boron solution using electrocoagulation method without heating [23].

Chemical oxo-precipitation (COP), another modified precipitation method, has been developed in our recent work [27]. COP is capable of removing boron extensively from solution at room temperature and relatively neutral pH. COP adopted hydrogen peroxide to promote the precipitation of metal perborate *salts* from the boric acid solution. As shown in Fig. 1, boric acid would take series nucleophilic substitution reactions with hydrogen peroxide and form various types of perborates. The perborates, particularly the species 3 and 7, dominate the $\text{B}(\text{OH})_3/\text{H}_2\text{O}_2/\text{H}_2\text{O}$ system at pH 8.5–12.5 as shown in Fig. 2, whose equilibrium constants are arranged in Table 1. Eq. (1) is the dissociation reaction of hydrogen peroxide, followed by the two mass balance reactions in Eqs. (2) and (3).



Unlike the conventional precipitation method, COP method can be performed with lower dosages of precipitants at room temperature. The perborates that are transformed from boric acid using hydrogen peroxide can easily and directly precipitate with alkaline earth metals at room temperature. The COP method that uses barium as a precipitant is the most effective one in alkaline earth metals. The boron level can be reduced from 1000 ppm to

15 ppm in 20 min. This work aims to study the reaction mechanisms of COP that uses barium as precipitant and to evaluate the proper procedure to perform COP. The duration of COP was extended to 12 h in this work and the states of precipitates were examined in details. Eventually, the mechanism of COP was proposed through controlling the reaction pH.

2. Materials and methods

All reagents were of analytical grade, and used without further purification. The synthetic wastewater was prepared by boric acid ($\text{B}(\text{OH})_3$, Showa) which is the common boron contaminate species in wastewater, particularly in the alkaline wastewater after the hydrolysis of NaBH_4 [28]. Hydrogen peroxide (H_2O_2 , Merck) was used to transform boric acid or borate ion to perborates; barium hydroxide ($\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$, Panreac) was used as precipitant. All solutions were prepared with a deionized water that was purified using a laboratory-grade RO-ultrapure water system.

The COP batch experiments were carried out in a jar-test at 150 rpm and room temperature. 500 ml of $\text{Ba}(\text{OH})_2$ solution was mixed with another 500 ml of the synthetic wastewater of 1000 ppm boron concentration, then H_2O_2 was transferred into the mixture to yield $[\text{H}_2\text{O}_2]/\text{B}$ and $[\text{Ba}]/[\text{B}]$ in mole ratios of 2 and 0.8, respectively. The initial pH of the solution was reduced from around 11.8 to 9 by adding HCl (Shimakya, 32%). The reaction was kept for 12 h; at specific intervals, 10 ml of a solution was withdrawn and filtered through a 0.45 μm filter (Advantec). The reaction pH was maintained at 10.5 by NaOH and HCl.

Dissolved oxygen (DO) was measured by dissolved oxygen meter (Oxi 3210, WTW). The sampling that was filtered using 0.45 μm PVDF membrane was titrated by 0.01 M permanganate (KMnO_4 , Showa) in 100 ml 3% H_2SO_4 solution to determine the concentration of aqueous active oxygen, and also was analyzed by an inductively coupled plasma optical emission spectrometer (ICP-OES, ULTIMA 2000, HORIBA) to detect boron and barium ion concentration. The precipitates collected were rinsed several times and then dried at 60 °C for one day. The crystal structure and functional groups in the collected precipitates were verified by XRD (Rigaku, RX III) and Raman microscopy (DRX, Thermo Scientific) using a 780 nm laser. The precise boron, barium and O_{act} composition was verified by elemental analysis of the precipitates. After dissolving 0.1 g dried precipitate with 25 ml of 14% HNO_3 , the barium/boron ratio of the precipitate was determined by ICP. The amount of active oxygen (O_{act}) in the precipitate was quantified by permanganate titration method after dissolving 0.1 g dried precipitate with 25 ml of 10% H_2SO_4 .

3. Results and discussion

3.1. Effect of reaction time on COP

The effects of reaction time on COP were investigated using $\text{Ba}(\text{OH})_2$ as the precipitant to replace the wide utilization of $\text{Ca}(\text{OH})_2$ in conventional precipitation. Various species of perborate are formed at pH 8.5–12.5, and therefore the initial pH was set to be 9.

As presented in Fig. 3a, the boron level is varied greatly with the reaction time. The boron concentration was reduced from 1000 ppm to 3 ppm in six hours, and to less than 2.4 ppm in eight hours. The decrease of pH in 8–12 h might lead to the slight raise of boron level. Fig. 3b plots the relationship between barium concentration and pH. Both pH and barium level increased markedly in 2–6 h probably because some barium hydroxide dissolved during the precipitation process. The blank experiment found that about 3.4% of barium hydroxide was undissolved. The long-term reaction

Table 1
Equilibrium constants for the reactions shown in Fig. 1.

Equilibrium constant	Value	Refs.
K1	$1.05 \times 10^{-9} \text{ M}$	[24]
K2	20 M^{-1}	[25]
K3	2×10^{-8}	[25]
K4	0.01 M^{-1}	[24]
K5	2 M^{-1}	[24]
K6	4.3 M^{-1}	[26]
K7	61 M^{-1}	[24]
K8	$2 \times 10^{-6} \text{ M}^{-1}$	[25]

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