Treatment of high boron concentration wastewater by chemical oxo-precipitation (COP) at room temperature

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ABSTRACT

Chemical oxo-preceipitation (COP) process that combined the oxidant treatment and precipitation using metal salts was developed for boron containing water disposal under relatively milder conditions (room temperature, pH 10) than a precipitation process. Among the selected boron compounds in 1000 mg-B L^{-1}, including boric acid (H_3BO_3), metaborate ($NaBO_2$), borax ($Na_2B_4O_7$) and perborate ($NaBO_3$), the precipitation process using calcium chloride reduced 80% boron in perborate solution, and was unable to treat the rest of boron compounds immediately. COP then adopted the hydrogen peroxide (H_2O_2) to pretreat the boric acid and substantially increased the boron removal of chemical precipitation from less than 5% to 80%. In addition, of alkaline earth metals, barium ion was the most efficient precipitant increased the 80% of boron removal to 98.5% as the mole ratios of H_2O_2/B and Ba/B were adjusted to 1.5 and 1, respectively. The residue boron in end water of COP was 15 ppm-B, a value never reached by the conventional coagulation processes.

Keywords: Boric acid; Perborate; Hydrogen peroxide; Barium

1. Introduction

The elemental boron is rarely found in nature, and forms a number of complex compounds, such as boric acid, borate, perborate, etc. High level of boron released into environment due to human activity is majorly from agriculture and industrial developments. Boron can be applied to synthesis a variety of productions including fertilizers, insecticides, buffer, dyestuffs, bleaching, and borosilicate glasses (Yilmaz *et al.* 2007, Irawan *et al.* 2011). The manufacture of thin film transistor liquid crystal display (TFT-LCD) is one of important industries in Taiwan. The processing of polarizer, an essential component of TFT-LCD, uses boron acid solution to improve their durability and mechanical strength by creating a cross-linked internal structure (Miyazaki *et al.* 2010). The manufacturing generates boron wastewater of high concentrations, which would be in a range of hundreds ppm and variable depending on productivity (Kentjono *et al.* 2010). World Health Organization (WHO) and European Union (EU) have set up a limitation of boron level of 0.5 mg/L in potable water (Hilal *et al.* 2011), while the

Environmental Protection Administration (EPA) in Taiwan regulates a boron level of 1 mg/L discharged from plants. Hence, it is necessary to explore an efficient and cost-effective method to disposal and recover boron in wastewater.

The boron removal technologies of updating include precipitation, reverse osmosis, ion exchange, and adsorption membrane filtration (AMF) (Turek *et al.* 2007, Tu *et al.* 2010, Bryjak *et al.* 2009, Kabay *et al.* 2010, Irawan *et al.* 2011, Kipcak and Ozdermir 2012, Polowczyk *et al.* 2013). Boron presenting in water in several types of chemical configurations, as well as their variable quantities depending on the purpose, are the difficulties as considering a simple and economic treatment method. Precipitation and crystallization are more suitable for boron water in high concentration than other methods that are normally used to manage the trace amounts of boron. A modified electrocoagulation has been developed for treating 500-1000 ppm of boron water, and could remove 94% of boron using an aluminum precipitant at pH 8.0 (Yilmaz *et al.* 2007). Lime ($Ca(OH)_2$), generally applied in coagulation process, could also successfully achieve a boron removal of 87% from boric acid in a level of 750 ppm by heating at 45-80°C (Irawan *et al.* 2011). However, the production of a large amount of sludge lowered the interesting of the co-precipitation methods that were conditioned using high concentration of metal hydroxide. Besides, the kinetic study suggested that the precipitation of boron with calcium hydroxide required heating to increase the reaction rate (Remy *et al.* 2005, Tsai and Lo 2011).

Boric acid is in equilibrium with borate anion of which the predominant is dependent of pH in water (Xu and Jiang 2008)

$$B(OH)_3 + H_2O \rightarrow B(OH)_4^- + H^+ \qquad K_a = 10^{-9.2}\ M \tag{1}$$

The major species is the uncharged $B(OH)_3$ molecule at pH lower than 9, and is a fully hydrated form of $B(OH)_4^-$ anion at pH higher 9. To obtain a high efficiency of boron removal, the conventional precipitation processes using metal salts, therefore, have to work at high pH values, usually above 12 (Yoshikawa *et al.* 2012). The reactivity between boric acid and hydrogen peroxide has been discussed (Sadovskii *et al.* 2012). The momo- and diperoxoborate formation through rapid equilibrium with hydrogen peroxide in boric acid solution was proposed (Pizer and Tihal 1987, Davies *et al.* 2005, Durrant *et al.* 2011)

$$B(OH)_3 + H_2O_2 \rightarrow HOOB(OH)_3^- + H^+ \tag{2}$$

$$HOOB(OH)_3^- + H_2O_2 \rightarrow (HOO)_2B(OH)_2^- + H_2O \tag{3}$$

At higher pHs (8-11), it has been proved that another complex form, which was named monoperoxodiborate, would be generated (Rey and Davies 2005, Deary *et al.* 2013)

$$B(OH)_4^- + HOOB(OH)_3^- \rightarrow (HO)_3BOOB(OH)_3^{2-} + H_2O \tag{4}$$

On the assumption that the boric acid derived compounds, namely $(HO)_3BOOH^-$ and $(HO)_2B(OOH)_2^-$ ions and also the $(HO)_3BOOB(OH)_3^{2-}$ ion, is more easily hydrolyzed at near neutral pH, an oxidant pretreatment of the target boron compound should substantially improve the precipitation in water. Thus, this work aimed at development of a novel chemical oxo-precipitation (COP) concept that combined oxidant treatment and chemical precipitation for boron removal. The selected boron compounds, including boric acid, perborate, borax and metaborate, were in a level of 1000 ppm-B, and the optimization of species and dosage of oxidants and precipitants were evaluated at room temperature.

2. Methods and materials

All reagents were of analytical grade, and used without further purification. The synthetic solution of boric acid (H_3BO_3, Sigma-Aldrich), perborate ($NaBO_3 \cdot 4H_2O$, Fluka), borax ($Na_2B_4O_7 \cdot 10H_2O$, Sigma-Aldrich) and metaborate ($NaBO_2 \cdot 4H_2O$, Alfa Aesar) were selected as the target boron-containing wastewater. Chemicals used as oxidants included hydrogen peroxide (H_2O_2, Merck), sodium peroxide (Na_2O_2, Alfa Aesar), permanganate ($KMnO_4$, J.T. Baker), and peroxidisulfate ($Na_2S_2O_8$, Merck). Four kinds of alkaline earth metal salts, Ca^{2+} ($CaCl_2$, Alfa Aesar), Mg^{2+} ($MgCl_2 \cdot 6H_2O$, Sigma-Aldrich), Ba^{2+} ($BaCl_2 \cdot 2H_2O$, J.T. Baker) and Sr^{2+} ($SrCl_2 \cdot 6H_2O$, J.T. Baker), were the precipitants. All solutions were prepared with deionized water that was purified using a laboratory-grade RO-ultrapure water system.

Batch oxidation and precipitation experiments were carried out by jar-testing in a 1-L beaker at room temperature. 500 mL of the weighted boron compounds that could give 1000 ppm-B concentration in 1 L were pre-conditioned with a specific mole ratio of oxidants (related to boron) at a specific pH value. After transferring another 500 mL of solution containing metal salts (in a specific mole ratio related to boron) into the beaker, the mixture was stirred at 100 rpm for 5 min and then at 30 rpm for 15 min, during which the pH value was adjusted using NaOH and HCl. After stirring, the mixtures were settled for 1 hour. The supernatants withdraw were immediately filtered using 0.45 μm PVDF membrane and analyzed by an inductively coupled plasma optical emission spectrometer (ICP-OES, ULTIMA 2000, HORIDA) for boron and metal ion concentration. The determination of boron removal was from the difference between the initial and the final concentrations. The precipitates collected were rinsed several times and then dried at 110 ℃ for one day. The crystal structure and the composition of boron precipitate were verified by X-ray power diffraction (XRD, Rigaku, RX III).

3. Results and discussion

3.1 Boron removal by chemical precipitation using calcium ion

Removal of four types of boron synthetic wastewaters, including boric acid, borax, metaborate and perborate, by chemical precipitation with Ca^{2+} ($CaCl_2$) at pH 10 was investigated. As shown in Fig. 1, of the boron compounds, it is found that perborate can be most efficiently reduced; a maximum removal of 78% is obtained for perborate, while

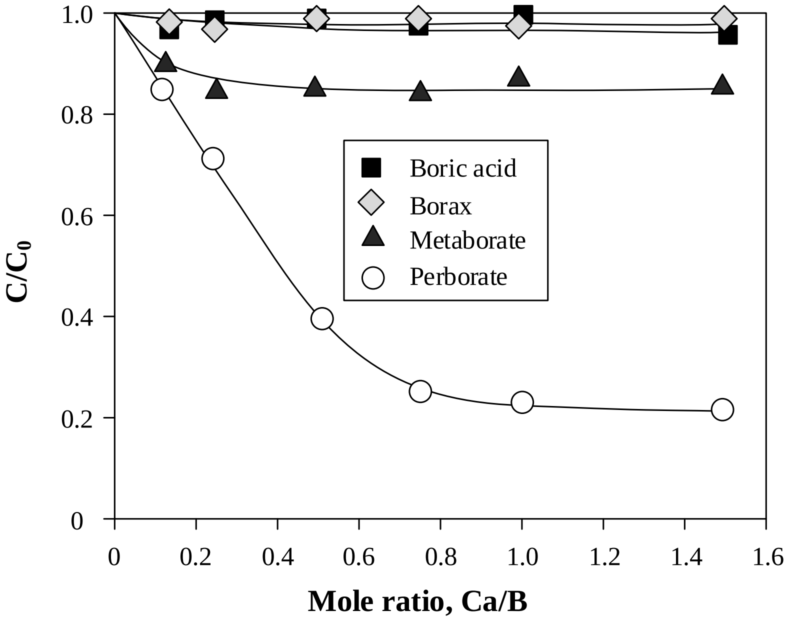

Fig. 1 Effect of mole ratio of calcium to boron on precipitation removal of boric acid, borax, metaborate and perborate. ([B]i = 1000 ppm, pH = 10)

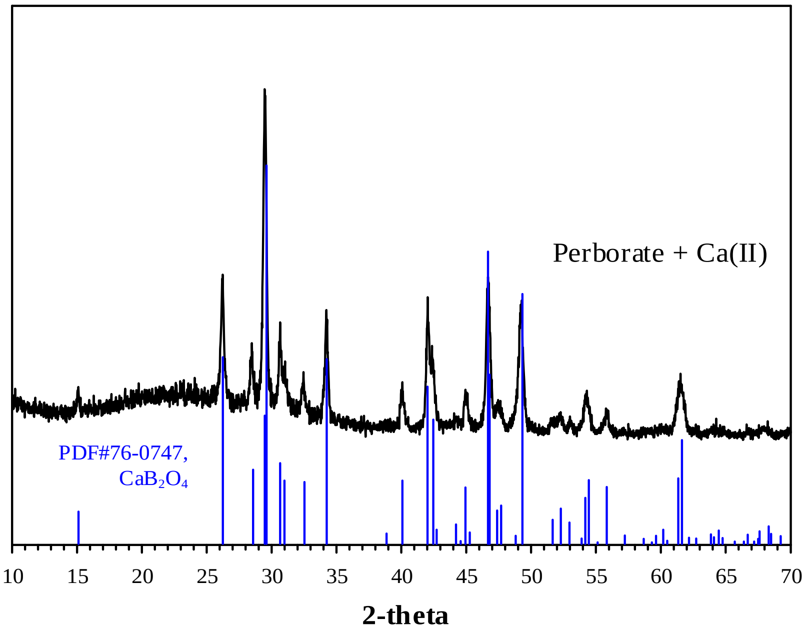

Fig. 2 XRD analysis of precipitates of calcium chloride and sodium perborate

only 18% of metaborate and less than 5% of boric acid and borax are removed at a mole ratio of Ca/B of 1. The rate of precipitation reaction increased with increasing initial mole ratio of Ca/B, and maintained at a fixed value as mole ration of Ca/B higher than 1.

Fig. 2 displays XRD structural analysis of precipitates collected from chemical precipitation process of Ca^{2+} and perborate, of which the diffraction peaks can be well fitted by a JCPDS standard sample of CaB_2O_4, calcium borate. $NaBO_3 \cdot 4H_2O$ is a simplistic form of perborate to represent its chemical composition, and generally polymerizes into a dimer anion - $B_2O_4(OH)_4^{2-}$ that is joined by two peroxo-bridges in a chair shaped ring (Weiger *et al.* 1993). Thus, a proposed reaction of calcium precipitation can be proposed

$$Ca^{2+} + 2BO_3^- + H_2O \rightarrow CaB_2O_4(OH)_4\downarrow \tag{5}$$

Formation of calcium borate precipitates resulted in high efficiency of boron removal in alkaline solution might be attributed to a relatively high soluble form of perborate hydrates at room temperature (Sahin and Bulutcu, 1999). On the other hand, a solid type of perborate is a soluble form of $H_2O_2 \cdot B(OH)_4^-$. It means that the perborate can be seen as an insertion of a peroxide agent into the network of boron and oxygen atoms in boric acid. According to valence balance of chemical formula in the selected boron compounds, peroxo anions (HOO^-) in perborate is at an oxidation state. This implied that the oxidant pretreatment for boron compounds, except for perborate, would probably improve boron removal from solution.

3.2 Effects of oxidants and precipitants on boron removal by oxo-precipitation

Boric acid (1000 ppm) was pretreated with the common oxidants, including $S_2O_8^{2-}$, MnO_4^-, Na_2O_2 and H_2O_2 (mole ratio of oxidant to boron is 3) at various pH values (3-10), and the chemical precipitation was carried out at pH 10 by using Ca^{2+} as precipitant, which was named an oxo-precipitation (COP, mole ratio of Ca to boron is 1), as shown in Fig. 3. Among the selected oxidants, Na_2O_2 and H_2O_2 are capable of largely increasing the calcium borate precipitation; the boron removal can reach 70% and 80%, respectively. By contrast, 26% and a less than 5% of boron could be reduced by adding MnO_4^- and without oxidant. Besides, the boron removals using Ca^{2+}-COP are independent of pH value during oxidant treatment. Except for MnO_4^- having an oxidation state of Mn(VII), all the rest of oxidants contain peroxo-group (O_2^{2-}) of which the oxygen atoms have an oxidation state of -1, whereas only hydrogen peroxide has OOH^- groups that can form a polymeric structure between borate molecules (Adams and Clark, 1983; Flanagan *et al.* 1989). In fact, H_2O_2 could magnify the removal efficiency of chemical precipitation by modifying the distribution diagram of boric acid (Pizer and Tihal 1987). Hydrogen peroxide in boric acid (borate) activated a catalyzed reaction for the oxidation of organic substance has been investigated; several boron derivatives from interaction with hydrogen peroxide (Eqs. (2)-(4)) were easily hydrolyzed in a less alkaline to neutral pH solution as compared with boric acid itself (pKa = 9.2) (Davies *et al.* 2005). Restated, the production of boron anions arise from nucleophilic substitution (Lobachev *et al.* 2007) by hydrogen peroxide is the main reason boric acid is efficiently reduced by COP.

Alkaline earth metal salts, Mg^{2+}, Ca^{2+}, Sr^{2+}, and Ba^{2+}, are studied as precipitants for the removal of hydrogen peroxide treated boron solution as shown in Fig. 4. Extent of removal as a function of pH for the selected cations is in an order: $Ba^{2+} > Sr^{2+} > Ca^{2+} > Mg^{2+}$; boron concentration sharply decreases from pH 6 to 9 and tends to equilibrium at pH above 9, except for Mg^{2+} that reduces boron at pH 9-10 apparently. The maximum removals at relative optimal pH are 37.6%, 85.2%, 86.3%, and 98.5% for Mg^{2+}, Ca^{2+},

Sr^{2+}, Ba^{2+}, respectively. The difference of extent in the removal of boron and its pH dependent between selected precipitants should be as a results of these metal borates formation having the varied solubility product constants (Ksp).

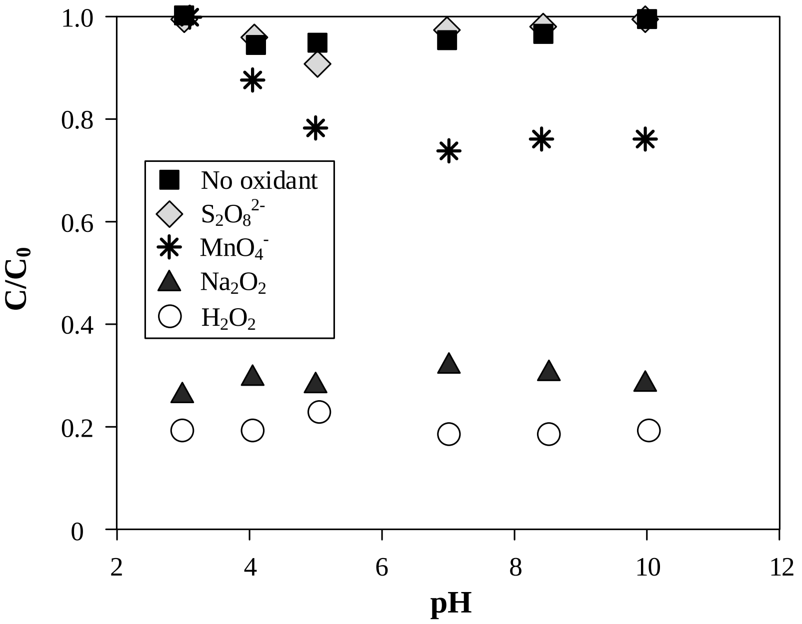

Fig. 3 Effect of oxidant at various pH values (3-10) on precipitation removal of boric acid using calcium precipitant. ([B]i = 1000 ppm, Ca/B = 1, oxidant/B = 3, pH of precipitation process = 10)

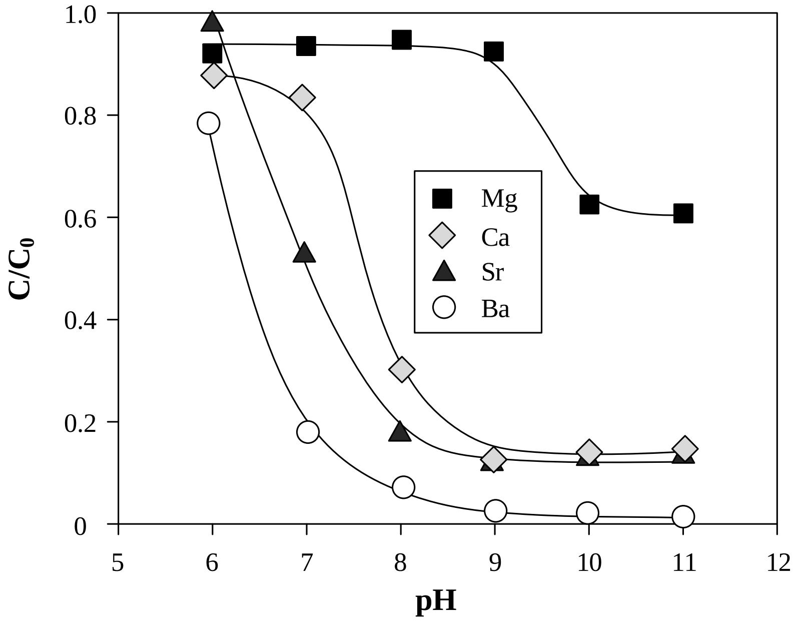

Fig. 4 Boric acid removal as a function of pH using Mg, Ca, Sr, and Ba precipitants. ([B]i = 1000 ppm, $H_2O_2/B = 3$, precipitant/B = 1)

3.3 Optimization of oxo-precipitation removal for boron compounds

Hydrogen peroxide (H_2O_2) and barium ion (Ba^{2+}) have successfully been used as the oxidant and the precipitant for boron removal from boric acid solution. Based on the results of Fig. 1 that attributed the higher removal of perborate to its peroxo anion that is absence in the rest of selected boron compounds, COP adopting H_2O_2 and Ba^{2+} were carried out for the treatment of boric acid, borax and metaperborate. As shown in Fig. 5, the selected boron compounds ([B] = 1000 ppm) are pretreated by H_2O_2 that is varied as

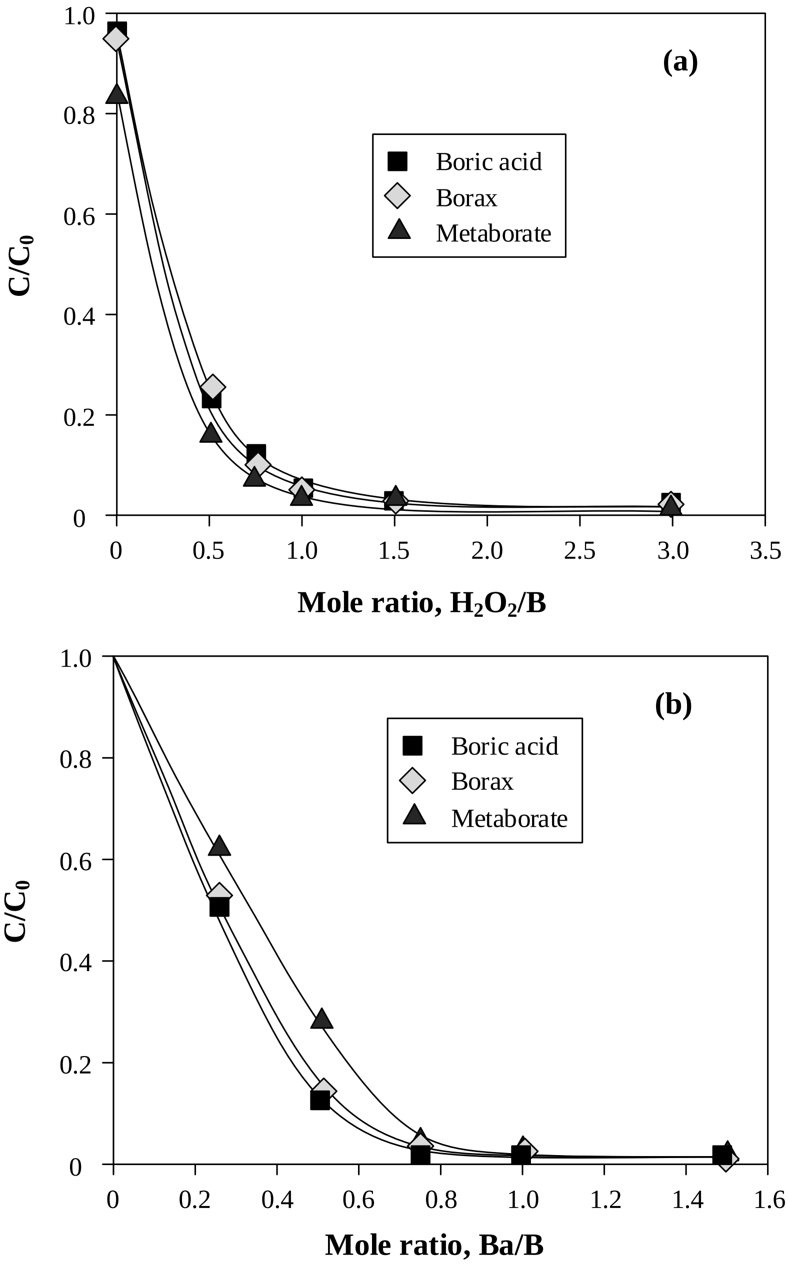

Fig. 5 Boron removal of boric acid, borax, and metaborate as a function of mole ratio of (a) hydrogen peroxide to boron (Ba/B = 1) and (b) barium to boron (H_2O_2/B = 3). ([B]i = 1000 ppm, pH = 10)

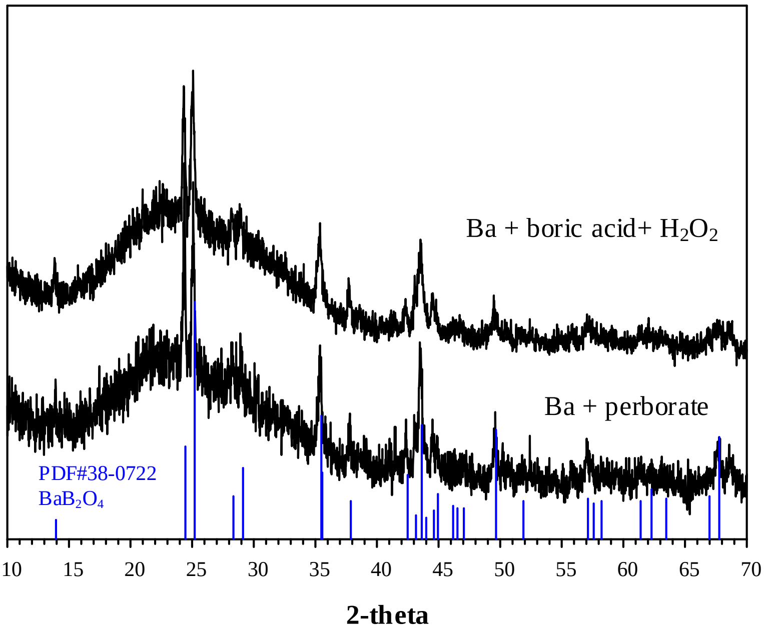

Fig. 6 XRD analyses of barium borates recovered from chemical precipitation of perborate and oxocoagualtion of H_2O_2 treated boric acid

a function of mole ratio of H_2O_2 to boron (H_2O_2/B), and then are removed by precipitation at pH 10 using Ba^{2+} that is varied as a function of mole ratio of Ba^{2+} to boron (Ba/B). The results suggest that for all types of boron the removal obviously increases with increasing H_2O_2 and Ba^{2+}, and reaches a maximum as H_2O_2/B and Ba/B were higher than 1.5 and 1, respectively. 98.5% of a final boron removal could be obtained as the conditions, H_2O_2/B and Ba/B, were appropriately adjusted. To the optimization of treating boron level of 1000 ppm by COP, the stoichiometric amounts of H_2O_2 and Ba^{2+} required were around 4.7 and 12.7 g L^{-1}, respectively, and left a residue level of boron of 15 ppm in solution. The cost of chemicals and energy consumption by COP performed at room temperature can be much less than by a traditional chemical process using lime ($Ca(OH)_2$) and heating (Remy *et al.* 2005, Irawan *et al.* 2011). In addition, the effluent level from the concentrated wastewater was around 15 ppm of boron which was quite suitable as a feed to further low-level boron treatments, such as ion exchange, to ultimately meet the environmental standards.

Accordingly, borates (not boric acid) is a form of peroxy compounds that combines with hydrogen peroxide or its anion (David and Bossoutrot 1996; John and Colin D., 2013). Two peroxoboron predominate between pH 7 and 9 ($HOOB(OH)_3^-$ and $(HOO)_2B(OH)_2^-$) (Eqs. (2) and (3)) are presented as the reactions in which H_2O_2 in perborate produces peroxoborate anion with displacement of protons from H_2O_2 (Deary *et al.* 2013). The results of the similar tendencies of boron removal with increasing H_2O_2 and Ba^{2+} dosage among the selected boron compounds in Fig. 5 imply the nucleophilic substitution of boric acid to perborate also occurred in borax and metaborate as equal ratios of H_2O_2 relative to boron were added.

$$2B(OH)_3 + 2H_2O_2 \rightarrow B_2O_4(OH)_4^{2-} + 2H^+ + 2H_2O \qquad (6)$$

$$B_4O_5(OH)_4^{2-} + 4H_2O_2 \rightarrow 2B_2O_4(OH)_4^{2-} + 2H^+ + H_2O \qquad (7)$$

$$2BO_2^- + 2H_2O_2 \rightarrow B_2O_4(OH)_4^{2-} \qquad (8)$$

Therefore, COP using Ba^{2+} proved to be capable of most efficiently removing boric acid in alkaline earth metals and be an effective method for the removal of borax and metaborate by formation of barium borate hydrates.

Fig. 6 depicts the XRD patterns of precipitates collected from the synthetic wastewaters of perborate and boric acid treated by Ba^{2+} and COP using H_2O_2 and Ba^{2+}, respectively. Both of the precipitation samples present the identical diffraction peaks and are indexed as a standard structure of barium borate, BaB_2O_4, of JCPDS database (#38-0722). The borate compound of COP same as that of perborate precipitation explains rationally the high effectiveness in boron removal from the boric acid wastewater, as well as the borax and metaborate wastewaters, which have been treated with H_2O_2.

4. Conclusions

To improve the inconveniences of the conventional coagulation process in boron removal, such as high temperature and high pH, this investigation developed a modified precipitation method in which the target boron compounds were pretreated with the specific oxidant, named chemical oxo-precipitation (COP). Among the selected boron compounds (boric acid, metaborate, borax, and perborate), calcium chloride was capable of achieving 78% of boron removal for the perborate at pH10, but not for the rest of boron compounds. Accordingly, perborate can be seen a borate molecule constructed with peroxo-groups (OOH^-). Thus, peroxide was an effective oxidant to substantially enhance the boron removal (from less 5% to 80%) of boric acid solution via chemical precipitation using Ca^{2+}. Further, Ba^{2+} was the most efficient precipitants in alkaline earth metals for treating the H_2O_2 treated boron compounds. The boron removal attained 98.5% as the mole ratios of H_2O_2/B and Ba/B were adjusted to 1.5 and 1, respectively. XRD patterns indicated that the precipitate recovered from COP of boric acid using Ba^{2+} was a $BaB_2O_4(OH)_4$ phase, which was identical to that from direct precipitation of perborate. The results of highly efficient boron removal at a relative low pH and room temperature proved the COP developed in this study to be a superior method to the present coagulation and its derived processes.

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