Study on the Existence Form and Removal of Boron Acid

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Abstract. Boron, as a microelement, in the form of boric acid, borate, borosilicate in aqueous solution, has advantages and disadvantages for human production and life. When the concentration of boron is too high, it will affect the surrounding environment and biological survival. The chemical precipitation, adsorption (mainly resin method) and membrane separation method are the main methods for removing boron from sewage. The paper introduces the existence form of boron acid and the principle of these methods, but with the development of science and technology, we need to upgrade and optimize the original method to achieve efficient, energy-saving, environmentally friendly environmental governance.

1. Introduction

There are three kinds of forms, boric acid, borate and borosilicate, of boron existed in nature. Meanwhile, there is no elemental boron. Boron plays an important role in human’s production and life. It is widely used in steel and alloy industry, chemical industry, agricultural and other fields [1-2]. However, with the rapid development of boron-related industries, the boron content of environment increased dramatically, which caused serious environmental pollution and waste of resources. In addition, the increasing of boron in environment affected human health directly or indirectly [3]. For example, the boron content of fracturing fluid must be controlled when the fracturing fluid is reused in the oil field, otherwise the reaction of crosslinking of boron with guar will occur, the excessive crosslinking ratio will lead to the block of the liquid distribution pipeline [4]. Furthermore, long-term exposure in atmosphere of boron-containing substances can damage human’s nervous system, reproductive system, and even cause death [5]. However, the regulations on boron content vary from different regions of different countries. "Standards for Drinking Water Hygiene" of China strictly stipulates that the boron content in drinking water is less than 0.5 mg/L, the maximum value of boron concentration is 1 mg/L in South Korea, Japan, Britain and other countries. And thus, how to effectively remove boron from water medium becomes an inevitable problem. In this paper, the existence form of boric acid in solution is mainly introduced. In addition, various boron acid removal methods such as chemical precipitation, adsorption (especially resin) and membrane separation have been compiled.

2. The Existence Form of Boric Acid in Solution

The form of boric acid in solution can be illustrated by the following chemical equation:

$$H_3BO_3 + H_2O \rightleftharpoons [B(OH)_4]^- + H^+ \quad (1)$$

It can be seen that $[B(OH)_4]^- \rightleftharpoons [B(OH)_4]^- + H^+$ is stable in an alkaline environment, and $H_3BO_3$ is dominant under acidic conditions. Theoretically, when the pH is 12, the molar ratio of $[B(OH)_4]$ and $H_3BO_3$ in the solution is $10^{-2.76}:1$, and pH decreasing, the equilibrium proceeds to the left. When the pH is 6, the molar ratio of $[B(OH)_4]$ and $H_3BO_3$ in the solution becomes $1:10^{3.24}$, at which time the boron in the
solution exists almost in the form of $\text{H}_3\text{BO}_3$.[4,6]

In the solution, when the concentration of boric acid is below 1500 mg/L, it mainly exists in the form of $\text{H}_3\text{BO}_3$ and $[\text{B(OH)}_4]^-$.

From equation (1), it is known that the lower the pH, in the form of boron is mainly $\text{H}_3\text{BO}_3$, $[\text{B(OH)}_4]^-$ is very low. With the pH value increases, the $[\text{B(OH)}_4]^-$ begins to increase and the $\text{H}_3\text{BO}_3$ begins to decrease, but the pH=9.4, the $[\text{B(OH)}_4]^-$ accounts for 80%; when the boric acid concentration is above 1500 mg/L, a variety of polyborate ions can be formed, such as $[\text{B}_3\text{O}_3(\text{OH})_4]^-$, $[\text{B}_4\text{O}_5(\text{OH})_4]^2-$, $[\text{B}_3\text{O}_3(\text{OH})_5]^2-$ and $[\text{B}_5\text{O}_6(\text{OH})_4]^-$, etc. While the presence of boric acid in aqueous solution, the tetrahedral configuration of $[\text{B(OH)}_4]^-$ allows it to form a stable complex with the ortho-cis hydroxy group, which provides the way to remove boron acid from solution.[7].

3. The Method of Boron Acid Removal

3.1. Chemical Precipitation

In the 1970s and 1980s, some researchers studied the removal of boric acid by a series of inorganic and organic precipitants [8]. The principle of boron removal by chemical precipitation is to convert boron in solution into borate precipitate or boric acid with low solubility. The precipitant is divided into organic precipitant (polyvinyl alcohol, hydroxyl carboxylic acid, etc.) and inorganic precipitant (oxides and hydroxides containing elements of calcium, magnesium, iron and aluminum). Because of the difference of acid properties of precipitant, the precipitation method can be divided into acid precipitation and alkali precipitation [9].

The acid precipitation is based on the principle that the solubility of $\text{H}_3\text{BO}_3$ in the inorganic acid is small. So hydrochloric acid or sulfuric acid was added into the solution to convert boron into boric acid with lower solubility. Xiao et al [10] used hydrochloric acid as precipitant to achieve preliminary boron removal from brine. The alkali precipitation means that the metal oxide reacts with boron acid in solution to form an insoluble borate precipitate under weak alkaline conditions. For example, ferrous hydroxide can react with boron acid to form boron-ferrate that is poorly soluble in water [11]. In addition, Lu et al.[12] removed boron acid from water medium by the mixture of calcined product obtained from magnesite with ammonium chloride under heating condition. The removal rate of boron was more than 90%. Remy et al.[13] used calcium hydroxide powder to remove boron from wastewater. When the content of calcium hydroxide powder was 50 g/L, the temperature was 90 °C, and the treatment time was 2 h, the boron removal was better, and the boron acid content was reduced from 700 mg/L to 50 mg/L. Complexes can be formed between hydroxyl-carboxylic acids and boric acid. The stoichiometry of the complex is dependent on the number of groups (hydrous or carboxylic) available for binding to boron, the pH value of the solution, the relative concentrations of ligand and borate, and the mode of preparation [14]. The chemical precipitation is mostly used for the removal of high concentration boron. The raw materials of precipitant are easy to be obtained and its cost is low. However, the large consumption of the precipitating agent produces a large amount of sludge, which increases the difficulty of subsequent processing.

3.2. Adsorption

The adsorption utilizes different kinds of porous adsorbents to remove boron from the solution. Guan et al.[15] summarized several adsorbents, including chelating resins, activated carbon, fly ash and industrial waste, oxides and hydroxides, and layered double hydroxide et al, for removing boron. Li et al.[16] studied the adsorption properties of layered double hydroxide Mg/Al-LDO towards boron and explored the effects of solution pH, adsorbent dosage, adsorption time and adsorption temperature on adsorption properties of boron. The results showed that the removal of boron was 94.47% and the adsorption amount was 47.24 mg/g. The amount of adsorbent of 0.20 g, optimum pH of 9.5, initial boron concentration of 100 mg/L, reaction time of 100 minutes and solution temperature of 303 K were kept constant in the experiment.

The remove principle of resin towards boron concludes complexation and adsorption. The complexation reaction is the complexation of polyhydroxy functional group with $[\text{B(OH)}_4]^-$ and acidic polyhydroxy functional group with $\text{H}_3\text{BO}_3$.[5,17]. So the resin can also be used as a special adsorption method. Yu et al [18] introduced research status of ion exchange resin of boron from meglumine,
polyol, saccharide, polystyrene, polyacrylate, inorganic-organic composite resin and natural polymer and also summarized the application of boron ion exchange resin in water treatment, environmental protection, extraction and separation. Joanna [19] modified the Purolite A170 resin into GLY-resin by using glycerol. The GLY-resin was applied to the removal of oxoborate in solution and post-crystallization lye. When pH of solution was 9.5, the maximum adsorption capacity was 1.6 mg/g and the maximum removal rate was 98.5%. The adsorption is also mostly used for the removal of high concentration of boron. Although the effect of adsorption is relatively high, the disadvantages, large consumption of adsorbent and difficulty in regeneration, may cause the expensive cost of boron removal. The resin is mostly suitable for the removal of low concentration boron. Due to its high selectivity and high adsorption, most studies concentrate this field of boron removal.

3.3. Membrane Separation

The membrane separation is that the raw material components are separated selectively through a separation medium of selective semipermeable membrane and the driving force (such as concentration difference, pressure difference, potential difference) on both sides of semipermeable membrane. The membrane separation includes reverse osmosis, forward osmosis, nanofiltration and electrodialysis.

3.3.1. Reverse osmosis. Reverse osmosis is to apply an external force on the high concentration side, so that the high concentration zone penetrates into the low concentration zone through the selective semipermeable membrane under the action of external force. Wu et al[20] introduced the principle and application status of removing boron about reverse osmosis process at domestic and abroad, and the removal characteristics of boron and scope of application also were summarized, concluding SWRO (conventional seawater reverse osmosis), SWRO+BWRO (brackish water reverse osmosis), SWRO+BWRO-BSR (boron selection resin) and SWRO+EDR (electrodialysis). However, reverse osmosis is easily affected by the pH of the solution, the applied pressure, and the species of the membrane. D. Prats et al[21] studied the effect of pH and pressure on the boron removal when the conventional reverse osmosis membrane was used into the treatment of brackish water. The results showed that the removal of boron was about 50% when pH was below 9.5; but when pH was 10.5, the removal rate of boron is almost 100%, and the boron removal increases with the increase of pressure.

3.3.2. Forward Osmosis. Forward osmosis is that the solution from a low concentration zone automatically permeates to a high concentration zone through selective semipermeable membrane. It is the advantages that are no external force addition, low energy consumption, low environmental pollution and high water recovery rate compared with the reverse osmosis. So forward osmosis has been attracted much attention in recent years. Ding et al [22] analyzed the difference between forward and reverse osmosis technology and introduced the application of forward osmosis in the fields of energy recovery and wastewater treatment, seawater desalination. Meanwhile, Ding also pointed out the defects of forward permeation in membrane performance and extracting liquid. This method is also affected by the pH of the solution on removing boron. W. Fam et al. [23] utilized this method to remove boron acid. Under neutral conditions, the boron removal was only 45%; however, the rate of boron removal was 94% when the pH value of solution was 11, because boron in the solution contains larger-size borate species, and thus increases boron rejection rate up to 94% by electrostatic repulsion.

3.3.3. Nanofiltration. Nanofiltration is a pressure-driven membrane separation technique, whose filtration accuracy is between ultrafiltration and reverse osmosis. It is used for the reduction of hardness and the removal of small molecules matter in solution. Liu [24] studied seawater desalination and its performance of boron removal by the technology of nanofiltration, when the initial concentration of boron was determined as 5.59 mg/L. The results indicated that the final effluent boron concentration is about 1.0 mg/L under the conditions of two-stage nanofiltration and second-stage influent pH 10.3; the final effluent boron concentration is below 0.1 mg/L in the case of two-stage nanofiltration, complexation reaction and second-stage influent pH 10.3.

3.3.4. Electrodialysis. Because of the selective permeability of the ion exchange membrane, the
substance separation can be completed by electrodialysis under the action of an external DC electric field. The ion exchange membrane can be divided into cation exchange membrane that only allows cations to pass through and anion exchange membrane that allows anions to pass through and repel the cations. The boron removal of electrodialysis is mainly affected by voltage, membrane’s types, solution pH and initial boron concentration. N. Kabay et al.[25] used TS-I-I0 electrodialyzer and a Neosepta cation and anion exchange membrane to carry out boron removal in boric acid solution. Meanwhile, the effects of pH and boron concentration on boron removal were carried out. When the pH of solution is increased from 9 to 10.5, the boron removal is increased from 20% to 80%. Furthermore, the rate of boron removal increased as the increasing of initial boron concentration when pH value of solution is 10.5. Electrodialysis can be applied difficultly due to the large consumption of electric energy. While the membrane separation is used to remove boron, the boron removal is higher, but it usually needs a higher pH (10-11), which causes an increase in alkalinity and facilitates precipitation of calcium, magnesium, aluminum, and iron and so on in the solution, thereby causing damage to the membrane and causing membrane pollution.

4. Conclusion
In summary: if the boron content is high in solution, the boron content can be reduced by pretreatment such as precipitation and adsorption so that reducing the economic cost in the subsequent treatment, and then the resin or the membrane separation is used to remove boron deeply to meet the requirements of drinking water and industrial water. Due to boron is present in the aqueous solution in the form of H₃BO₃ or [B(OH)₄]. It can be seen from the foregoing that the introduction of polyhydroxy functional groups on the materials for modification is a thought worthy of further investigation, thereby improving the boron removal and achieving a high-efficiency, energy-saving and environmentally-friendly concept.

5. References
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