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Review

Removal technology of boron dissolved in aqueous solutions – A review

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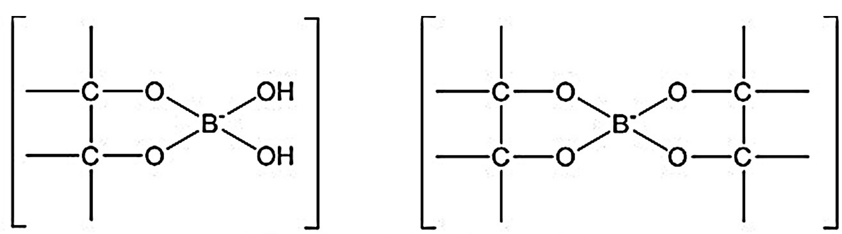
HIGHLIGHTS

- Introduce importance and relevant problem of boron.
- Update study on removal of boron dissolved in water.
- Present solutions for boron pollution.

GRAPHICAL ABSTRACT



Structure of borate complex

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ABSTRACT

Boron is an essential micronutrient for plants, humans and animals, which is also an important component used in various industries. Along with the wide spread of boron application, more and more boron waste pollutes the drinking water sources, and leads to a series of environment and health problems. This paper reviews the reported boron removal technology from aqueous solutions, including adsorption process, membrane process, hybrid process and other methods, presenting available choices to solve the problem of boron pollution.

Contents

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1. Introduction

Boron is a nonmetallic element, which is widely distributed in the world. Elemental boron is never found in nature, it is a ubiquitous element in surface and water in various forms of boric acid and borates. Its concentration in nature is very low. In the earth crust, the average concentration of boron is approximately 10 mg/kg [1]. In soil, the average concentration is 30 mg/kg. In seawater, the content of boron is about 4.5 ppm, while the concentration in ground water range from 0.3 to 100 ppm [2].

1.1. Importance of boron

Boron is an essential micronutrient for plants, humans and animals. For plants, it is a structural component of cell wall, plays an important role in the structural stability [3], and relates to cell wall formation and lignification. It also affects pollen germination, enzyme reaction, the metabolism of phenol and carbohydrate, nucleic acid synthesis, and membrane transportation [4–6]. If boron deficiency occurs in the plant growth, it will lead to thick leaf, excessive branch, and poor germination [7]. For humans and animals, it relates to the organism of immune function [8], and affects hormone action and bone metabolism [9]. Boron deficiency disarranges embryo development for vertebrates [10], and impedes absorption of the element such as calcium magnesium and phosphorus [11].

Although boron is essential for organisms in many ways, it changes to be toxic while its amount is slightly higher than required. Excessive boron inhibits photosynthesis and root cell division, impedes deposition of lignin and chlorophyll [12], causes yellowish spots on the leaves, less fruit, dwarf even death for plants [11]. In fact, the gap of boron amount between deficiency and excess is narrow. The required amount of boron is different among different plants, and boron excess is more difficult to control than boron deficiency [13]. Tu et al. [14] divided the crops into three groups by their boron toleration, they are sensitive, semi-sensitive and tolerant with below 1.0 ppm, 1.0–2.0 ppm and above 2.0 ppm separately.

For humans and animals, the adverse effects of boron could not be ignored. Moderate boron is a beneficial nutrient, but a long-term chronic absorption of boron may cause a series of harmful impacts, such as growth retardation, the change of blood composition, nervous and reproductive system [15]. Boron is found in fruits, vegetables, nuts and wine. Humans can absorb enough boron from normal diet without any other special feed [16].

1.2. Uses of boron and related problems

Boron has been used extensively in many industries, such as glass, ceramics, porcelain, cosmetics, semiconductors, carpets and fireproofing fabrics. Among them, the biggest user is the glass industry, more than half of the boron compounds are consumed in the glass industry. Beside, boron products are also used in fertilizer, welding, cleaning product, fuels, and catalysts. Boron has two stable isotopes, the mass of which is 10 and 11 respectively with a ratio of 20:80. The isotope boron-10 is crucially used in the nuclear industry, which can control the nuclear reaction rate in order to avoid explosion [17].

Nowadays, the concentration of boron increases obviously in ground water because of both natural and anthropogenic reasons. During the use of these boron products, boron waste becomes a serious problem. This element has high volatility, when it is discharged to the environment. It may volatilize and form acid rainfall back to the ground, and be deposited in soil, and absorbed by plants. Eventually, it pollutes the drinking water sources, and leads to a series of environment and health problems.

The standard of boron is established throughout the word in drinking water, irrigation water, and waste water, but the level of boron content is diverse in different regions. The recommended content of WHO guideline in drinking water is 0.5 ppm set in 1998, which is revised to 2.4 ppm in 2011. However, only a few countries follow it. In fact, the value of 2.4 ppm is below human tolerant level, but exceeds the required concentration of several types of crops, which are sensitive to boron. Therefore, many countries still implement their own standard. The recommended content of boron is 1.0 mg/L in the European Union, UK, South Korea Singapore and Japan. Instead of federal regulations in USA, the boron content level depends on the state in the range of 0.6 ppm to 1.0 ppm. In New Zealand and Israel, the concentration is 1.4 ppm and 1.5 ppm respectively. The maximum boron concentration in Canada and Australia is higher than WHO guideline as 5 ppm and 4 ppm. Saudi Arabia is the only country complying with the guidelines [2].

1.3. Chemistry of boron in aqueous solutions

Boron dissolves in aqueous solutions as various species on the basis of concentration. In high boron concentration aqueous, several boron species are found, such as $B_2O(OH)_6{}^{2-}$, B_3O_3 rings including $B_3O_3(OH)_4{}^{-}$, $B_4O_5(OH)_4{}^{2-}$, and $B_5O_6(OH)_4{}^{-}$ [18]. As the boron concentration is below 290 mg/L, these ions are negligible. While the boron concentration is below 216 mg/L, $B(OH)_3$ and $B(OH)_4{}^{-}$ are mainly found as boron species. Boron exists dominantly in the form of $B(OH)_3$ and $B(OH)_4$ in nature. In sea water, they are the only boron species, as the concentration is around 4.8 mg/L [19].

In acidic and neutral aqueous solutions, boric acid is the dominant specie of boron. Boric acid is a kind of solid, which could be solved in water with a solubility of 55 g/L at 25 °C. As the pK_a is below 9.24 in aqueous solutions, boron acid is a weak Lewis acid, which accepts a hydroxide ion and releases a proton. In alkali aqueous solutions, boric acid transform to monoborate anion. When the pK_a increases to above 9.24, the mainly boron specie is monoborate anion [20].

2. Adsorption process for boron removal

The most effective method to remove boron from aqueous solutions is adsorption technique, because the process requirements are simple and can be used in aqueous media with low concentration of boron. Boron adsorption can be conducted on various sorbents, e.g. chelating resins, polysaccharides, oxides, synthesized clay and fly ash.

2.1. Chelating resin mechanism

Chelating resins are the most important sorbents in boron adsorption technique. Most of them have at least three hydroxyl