Desalination 310 (2013) 18–24

Contents lists available at SciVerse ScienceDirect

Desalination

journal homepage: www.elsevier.com/locate/desal

Methods for boron removal from aqueous solutions — A review

Joanna Wolska *, Marek Bryjak

Division of Polymer and Carbonaceous Materials, Wroclaw University of Technology, Wyb. Wyspianskiego 27, 50-370 Wroclaw, Poland

HIGHLIGHTS

► Updated review on boron problem
► Presentation of methods for boron removal
► Comparative studies on technologies for water deboronation

ARTICLE INFO

Article history:
Received 13 May 2012
Received in revised form 30 July 2012
Accepted 1 August 2012
Available online 30 August 2012

Keywords:
Boron
Removal technologies
Materials
Hybrid systems
Polymer microspheres

ABSTRACT

The manuscript gathers knowledge on boron — its properties, sources, presence in the environment, effects on plants and animals and methods for its removal. It is shown that so far used recovery technologies should be developed and there is still a room for new separation methods. It seems that introduction of new sorption materials as well as the use of sorption–membrane filtration hybrid, combining sorption on fine B-sensitive sorbent with membrane separation, can offer promising features for technological approach. The intention of this review is to update the information on methods for boron removal and to show the direction of its development.

Contents

1. Introduction

Boron is semimetal, situated in Block P (group 13) of the periodic table. In its own properties it is located somewhere between aluminum and carbon. The stable isotopes of boron are of mass 10 and 11 with

* Corresponding author. Tel./fax: +48 713202987.
E-mail address: joanna.wolska@pwr.wroc.pl (J. Wolska).

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http://dx.doi.org/10.1016/j.desal.2012.08.003

estimated 20:80% ratio [1]. Elemental boron has a high melting point, good hardness and is a rather poor conductor of electricity. Boron has various oxidation states in compounds but the most significant and common is +3. It appears in lower oxidation states +1, 0 or less than 0, but these states are found in compounds such as e.g. higher borates only [1,2].

Boron is a ubiquitous element in rocks, soil and water, and although it is widely distributed in nature, it occurs in nature only in low and very low concentrations [3]. The average content of boron in the earth crust is 10 mg/L [4]. In soils its average concentration is in the range of 10–20 mg/L. There are large areas of the world suffering for deficiency of this element. The content of boron in rocks is 5 mg/L in basalts to 100 mg/L in sedimentary shale. Seawater contains an average of 4.6 mg/L boron with variation of concentration from 0.5 to 9.6 mg/L. The concentration of boron in fresh water is usually from less than 0.01 mg/L to 1.5 mg/L and increases significantly in areas where soils are boron enriched — the western part of the U.S., and a ground stretching from the Mediterranean Sea to Kazakhstan [5]. In nature it is found mostly in the form of over 200 minerals with different amounts of calcium, sodium or magnesium. Among them the most popular are: borax, tincal, colemanite, ulexite and kernite [6]. Boron can occur in nature in the form of: undissociated orthoboric acid, partially dissociated borate anions in the form of polyborates, complexes of transition metals and fluoroborate complexes [7]. These forms are present in surface waters mostly — the boron in surface waters in Europe varies from less than 10 mg B/L to greater than 1000 mg B/L [8]. It is also found in ground water, brackish water or hot springs, especially at geothermal or tectonic areas [4,7,9]. In general, the amount of boron in fresh water depends on such factors as the geochemical nature of the drainage area, proximity to marine coastal regions and imputes from industrial and municipal effluents [10].

2. Chemistry of boron in aqueous solutions

Boron appears predominantly in the form of boric acid in aquatic environment. Boric acid is a solid substance soluble in the water — with solubility of 55 g/L at 25 °C. As boron is an electron deficient element, boric acid acts as a weak acid. Its pK_a value can be determined at relatively low concentrations, particularly below 22 mg/L [1], when mononuclear species $B(OH)_3$ and $B(OH)_4^-$ present only. In Fig. 1 the fraction of boric acid and borate as a function of pH is presented [11]. When pH is increased above pK_a value, most borate anions can be found. Polyborates appear at higher than 1000 mg/L concentration of boron [12].

3. Boron related problems

In the recent years a significant increase in the concentration of boron in surface waters has been observed. The increase as well as concentration fluctuations at different areas are caused by many natural and anthropogenic factors. For the natural source one can count weathering of rocks and leaching of salt deposits. The deposits of natural boron appear on the shoreline mostly. Because of the high volatility of this element, boron is found in the rainfall at coastal areas. The same component can be found in the "acid rain" also resulted from industrial activities [7]. The industrial activities are the next reason in increase of boron amount in surface waters as well. Boric acid and boron salts are widely used in many branches of industry and used as a preservative [4–7,9]. Recently, some boron compounds are used in manufacturing of high-energy fuels, coolants and catalysts [6]. Because of all these factors, the concentration of boron in surface water at industrial and urban areas still increases. Therefore, the problem of removing boron from water is not only related to the countries with natural deposits of this element but it has also become the critical issue for highly developed countries.

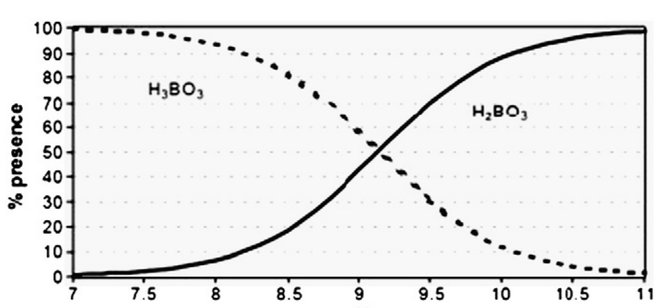

Fig. 1. Fraction of H_3BO_3 and $[B(OH)_4]^-$ as a function of pH of seawater. Adapted from [13].

4. Effect of boron on plants

The essential role of boron in plants was first described in the 20s of the XX century [14]. Boron is a micronutrient essential for growing fruits and vegetables [9]. This is the element of special attention as its deficiency and excess are harmful for many plants, and the gap between both these levels is very narrow [4,15,16]. Boron plays an important role in the normal growth and functioning of plants [14,16] while its deficiency inhibits growth of meristematic tissue, disrupts normal cell formation and delays enzymatic reactions. The visible effects can be seen in the interruption of root and leaf growth, leaf thickening, bark cracking, poor budding, excessive branching and reduction of germination [16–18]. When boron amount is higher than required, there are signs of toxic effects: yellow tips of leaves, defoliation, spots on fruits, decay and fall of unripe fruit [9,15,16,19–21]. These effects result in dwarfing or death of plants, in some extent.

Boron can run on almost all cultivations, but its concentration in irrigation water should not exceed 0.3–4 mg B/L depending on the crop type and soil characteristic. In agricultural production, boron toxicity is more difficult to manage than boron deficiency which can be avoided by proper fertilization [14]. Different plants can tolerate boron on a different level. Some plants are more and some less sensitive to the excess of boron compounds [1,20]. Tu et al. [1] collected dates about the tolerable doses of boron for many agriculture crops, and divided them into three groups [1]: *Sensitive*, with the B tolerance: <1.0 ppm, *Semi-sensitive*, with the B tolerance: 1.0–2.0 ppm and *Tolerant*, with the B tolerance: above 2.0 ppm.

5. Effect of boron on animals and humans

According to the medical and biological research, boron compounds are among the second group of toxic substances [9]. Since 1981 there have been many studies on the different species of animals [5] that showed the effect of boron deficiency on the composition and functioning of many parts of an animal's body [5]. This element has a positive effect on the metabolism of several other nutrients such as calcium, copper or nitrogen [22]. It was noted that boron deficiency reduced absorption of calcium, magnesium and phosphorus [5]. Boron is also an important element in the humans' diet, but its function is not so unequivocal as for plants [5] and its essence of action is not fully understood. The mammalian organisms need boron only in very small amounts. World Health Organization has defined 1–13 mg/day dose of boron as safe and adequate for a healthy individual [23]. Boron has a positive effect on functioning of many organs but long-term consumption of water and food with increased boron content results in creation of problems with cardiovascular, coronary, nervous and reproductive systems [23,24]. Moreover, it causes changes in blood composition, neurological effects, physical disorders and intellectual development of children. Excess of boron can be particularly