



Review

Boron removal from water: needs, challenges and perspectives

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ABSTRACT

Boron is often present in water streams to be treated to match final user specifications or environmental restrictions. It can not be removed by conventional water treatments and its separation still remains an issue. An overview on this topic is provided. Needs are identified considering information regarding boron level effect on environment, human health and activities. Challenges are described envisaging boron main physical–chemical properties and current approaches for its removal. Perspectives are sketched pointing to possible technology improvements.

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1. Introduction

Less than 3% of water on our planet exists in a readily usable form for human activities (US Geological Survey's, 2012). According to that, it is not surprising that a tremendous effort has been performed towards development of technologies able to get freshwater from streams not exploitable as such (e.g., seawater, brackish water or even wastewater) (Macedonio et al., 2012). Furthermore, use of renewable energy sources in water treatment processes has recently drawn attention in order to reduce their environmental impact (Amores et al., 2013). In this context, oil and gas industry could play a key role: produced water is by far the largest volume waste stream associated with oil and gas exploration and production (Ahmadun et al., 2009). It is water trapped in underground formations, brought to surface along with hydrocarbons. Main produced water pollutants are oil and grease, chemical additives used in drilling and exploitation activities, natural compounds (both organic and inorganic) and naturally occurring radioactive materials. Just to have an idea of the amount to be considered, approximately 9,000,000 m³/d of produced water are generated in USA from nearly a million wells. About 86% of this wastewater is managed by subsurface reinjection while the rest undergo surface discharge (US Department of Energy, 2012). Additional sources of

concern have to be expected from water streams connected with intensive shale gas exploitation (e.g., backflow after rock hydraulic fracturing) (Gaudlip et al., 2008). Impressive volumes involved makes production water not only an environmental care but also a potential freshwater resource, once provided efficient and cost-effective treatment methods (it has to be recalled that many oil and gas producers are water-stressed countries, as well).

Boron is often present in water streams to be treated to match final user specifications or environmental restrictions. In particular, its concentration in produced water may be huge, heavily affecting its exploitability by means of technologies presently available on the market. It can not be removed by conventional wastewater and drinking water treatments and its separation still remains a challenging task. Within this framework, present review has two main purposes: i) to sketch present status of knowledge concerning impact of boron level on environment, human health and activities; ii) to survey available approaches for the treatment of boron-rich water streams. Status of knowledge updating has been done taking advantage both from reference papers and from recent ones pointing to emerging technologies.

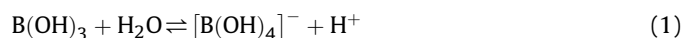
2. Boron in the environment

Boron is the most electronegative element in group IIIA of the periodic table. Its behaviour is intermediate between metals and non-metals and for some aspects it is similar to neighbours aluminium, carbon and silicon. According to its electron structure,

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boron usually forms three bonds. At the same time, it shows very strong tendency for fourth bond to be formed in order to complete octet of valency electrons. In nature boron has never found in its elemental state. Conversely, it mainly occurs in the form of boric acid ($B(OH)_3$ or H_3BO_3) and its salts (borates) or as boro-silicate (Parks and Edwards, 2005). Boric acid can be easily dissolved in water (solubility of 55 g/L at 298 K) where it performs as very weak Lewis acid (pK_A of 9.2 at temperature of 298 K), accepting electrons according to Reaction (1):

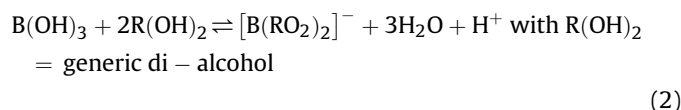


The anionic form is predominant at solution pH higher than 9.2 while at lower values the neutral form prevails.

Boric acid pK_A actual value is strongly influenced by solution ionic strength. In practice, borate formation is more favoured in presence of strong electrolytes (Choi and Chen, 1979). This behaviour has important implications in boron removal operations (Section 3).

At concentrations below 216 mg/L (20 mmol/L) as boron only the mononuclear species $B(OH)_3$ and $[B(OH)_4]^-$ are present, while poly-nuclear anions or ringed structures have been observed at higher concentrations (Power and Woods, 1997).

Tendency to form stable esters with poly-hydroxylated organics (e.g., poly-alcohols, saccharides) is also known and exploited for boron separation. Specifically, strong complexes are formed when poly-alcohols used involves the hydroxyl groups oriented in such a way that they accurately match the structural parameters required by tetrahedrally-coordinated boron (Fig. 1). It has to be stressed that complexation causes proton release in solution (Reaction 2). According to that, pH buffering is needed to avoid ester hydrolysis due to acidic environment (Power and Woods, 1997).



Boron is the 10th most abundant element in oceanic salts, varying in concentration in seawater from 0.52 mg/L in the Baltic Sea to as much as 9.6 mg/L peaks in the Mediterranean Sea (Wolska and Brijak, 2013). The global average, however, is approximately 4.6 mg/L (Argust, 1998). Naturally occurring boron is present in groundwater primarily as a result of leaching from rocks and soils. It has been suggested that for most groundwater, concentration values vary from 0.017 to 1.9 mg/L, although huge variability has been ascribed to location intrinsic characteristics (e.g., proximity to sea, geothermal activity, presence of boron-rich minerals or sewage sludges) (Argust, 1998). Peaks of about 100 mg/L have been reported from a survey on produced water streams. Saline content frequently of the order of magnitude of 100,000 mg/L together with dissolved and dispersed organics, further complicate produced water treatment, making its exploitation in most cases unfeasible (Ahmadun et al., 2009). Main anthropogenic sources of water-soluble boron are agrochemicals (e.g., pesticides, fertilisers) and detergents. However, employment of boron peroxides as bleaching

agents has decreased significantly and levels of boron in municipal wastewater continue to fall.

Behaviour of boron and its environmental fate remains in many respects obscure and can be only roughly explained through boric acid chemistry. In particular, little is known about boron speciation in soils, natural water streams and sediments (Kot, 2009). Data on physiological functions of boron are fragmentary and often contradictory. Boron is recognised to be an essential micronutrient both for animals and plants with narrow range between its deficiency and excess. Endemic symptoms and diseases among humans and cattle are supposedly triggered by boron abundance in the environment. Interestingly, bacteria involved in wastewater treatment by activated sewage seem not to be affected by presence of boron up to 20 mg/L (Parks and Edwards, 2005). Globally, published data are scarce and vague and consequently regulations on boron limits in water are quite variable, depending on the reference institution. Just to provide an idea of the messy situation, boron limits in drinking water have been established to 0.5, 1, 4 and 5 mg/L respectively by Saudi Arabia, EU, Australia and Canada. Concerning USA, each state has set up specific regulations (Hilal et al., 2011).

Drinking water quality guideline value of 2.4 mg/L has been recently suggested by World Health Organisation. Noteworthy, this value has been decided exclusively extrapolating possible effects on human health. On the contrary, a reasonable arrangement among health remarks and performance of available water treatment technology was assumed as criteria in the past. Curiously, previous guideline value was 0.5 mg/L, thus by far lower than current one (World Health Organisation, 2012).

On the other hand, boron content has to be reduced till 0.3 mg/L in water streams used to irrigate sensitive plants (e.g., citrus trees) and actions against boron accumulation in soil have to be put into practice (Gupta et al., 1985). These issues are sources of concern especially in arid regions affected by low soil leaching (due to lack of rainfalls) and in case of extensive use of desalted seawater or wastewater (e.g., produced water, sewage sludge) in agriculture (Nable et al., 1997). In this context, Australia, Middle East and North Africa can be cited among the most critical areas (Tu et al., 2010).

3. Technology options

Dissolved boron has been effectively removed to nearly-zero concentration by thermal desalination based on *multi-stage flash* (MSF) or *multi-effect distillation* (MED) (Van der Bruggen and Vandecasteele, 2002). However, in the last decades this technology has lost favour because of its high energy intensity, in spite of the considerable savings due to technology improvements (Table 1, Fig. 2) (Ghaffour et al., 2013).

Several alternative approaches, each at different level of performance and implementation (from academic laboratory to commercial processes) have been proposed. They can be grouped into two wide categories: i) separation by *sorption* on solids (Section 3.1); ii) separation by *membrane filtration* (Section 3.2). Separation by combination of sorption on solids and membrane filtration (*hybrid processes*) can be traced, as well (Kabay et al., 2010).

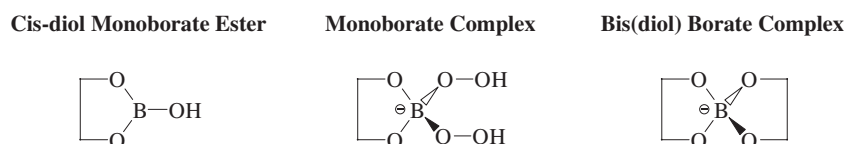


Fig. 1. Schematic drawings of borate esters and complexes. Diol structure has been simplified for the sake of clarity (Tu et al., 2010).

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