



## Boron removal from seawater: State-of-the-art review



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### HIGHLIGHTS

- Boron may have negative effects on some plants.
- Hybrid methods are highly efficient for boron removal from seawater.
- Combination of ion exchange with easiness of membrane separations has advantages.

### ARTICLE INFO

#### Article history:

Received 15 September 2014  
Received in revised form 5 October 2014  
Accepted 8 October 2014  
Available online 23 October 2014

#### Keywords:

Boron  
Desalination  
Electrodialysis  
Ion exchange  
Hybrid process  
Membrane process  
Nanofiltration (NF)  
Reverse osmosis (RO)  
Seawater

### ABSTRACT

Boron is a vital nutrient for humans, plants and animals. On the other hand, it might cause negative effects for some plants when its concentration exceeds the permissible limits in irrigation water. Seawater is an essential water source for life in which boron concentration should be reduced to match the final user specifications and environmental restrictions. Boron removal from seawater is challenging as it can not be achieved by conventional treatment methods. This paper provides a state-of-the-art review on technologies employed most recently, including ion-exchange, membrane processes, hybrid systems and other methods to remove boron from seawater efficiently.

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## 1. Introduction

### 1.1. Boron in seawater and its chemistry

Due to increasing demand of safe potable water and irrigation water, a decrease in suitable water sources, water suppliers have to turn to alternative water resources. For this purpose, desalination of seawater or treatment of highly saline water, even contaminated surface waters, has become potential methods to obtain clean water sources. By using those alternative sources, some trace contaminants could appear in the product water. Boron is one of them.

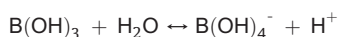
Boron is found in any natural water resource. Typical boron concentration in seawater by far exceeds required value and can be as high as 7 mg/L in the Arabian Gulf and usually is in the range of 4.5–5.0 mg/L [1].

There are two predominant reasons for limiting boron in water:

- The WHO set a limit of 0.3 mg/L for Boron in drinking water for many years but this value was revised as 2.4 mg/L in 2011 due to the positive effects of boron for human health. On the other hand, EU still suggests maximum boron concentration in drinking water as 1.0 mg/L [2].
- A major limiting factor is the possible damage of excess boron to some plants and crops. Although boron is vital as a trace element for plant growth and is supplied in fertilizer, it can be detrimental at higher concentrations. Among the most sensitive crops are citrus trees, which show massive leaf damage at boron levels of more than 0.3 mg/L in irrigation water. Boron at relatively higher levels also reduces fruit yield and induces premature ripening on the other species such as kiwi [1,3].

The problem of high boron concentration was observed for the first time in Israel after installing a seawater reverse osmosis (SWRO) plant in Eilat, Israel, in 1997. Farmers using post-treated product water for irrigation noticed poisoning of crops and partly discolored leaves. Later, boron was identified as the toxic element responsible for these effects. Since then, several post-treatment methods have been investigated for boron removal in SWRO desalination [4].

In seawater, boron is usually present as boric acid ( $B(OH)_3$ ) and the following equilibrium reaction takes place, which leads to a pH-dependent distribution of boron containing species, with a pKa value around 9.3 [5]:



At lower pH, the major species of boron is boric acid in molecular form. Due to the absence of ionic charges in aqueous media, the hydration of the boric acid molecule is less pronounced. This results in a smaller size and less rejection of the molecule by a membrane. The dissociated form, on the other hand, will be fully hydrated, resulting in formation of an ion with a negative charge and a larger radius. This, in turn, results in higher rejection, both by size exclusion and charge repulsion by negatively charged membrane [5].

## 2. Boron removal processes from seawater

### 2.1. Removal of boron by ion exchange

Ion exchange is an alternative method to remove boron from seawater. Ion exchange processes are usually involved in simple operational requirements. This technique can be used in diluted water streams as well as seawater streams, but mostly efficient at low salt concentrations. Dissociation of boron salts in aqueous solutions requires the use of a strong basic ion-exchanger and all anions of the solutions will be retained resulting in an inefficient removal performance. Therefore, boron specific ion exchange resins are needed for effective separation. Indeed, the use of boron selective chelating ion exchange resins is one of the most widely studied methods for removal of boron from water.

Three or more hydroxyl groups as ligands, located in the cis position, the so-called “vis-diols”, are usually engaged in the synthesis of chelating resins. They show a high selectivity to boron while these groups are not reactive to ordinary metals and other elements. The presence of tertiary amine group attached to the polymer matrix is essential for boron chelating. It functions as neutralization agent of protons during complexing of borate by hydroxyl functionalities [6].

Chelating type of boron selective resins is often synthesized by using macroporous crosslinked polystyrenic resins and functionalized with N-methyl-D-glucamine (1-amino-1-deoxy-D-glucitol; NMDG) group as illustrated in Fig. 1 [7].

According to the binding mechanism given in Fig. 2, the NMDG groups capture boron through a covalent attachment and formation of an internal coordination complex [7]. Over a wide range of pH, this relatively stable cis-diol borate ester complex can be formed.

The NMDG group can also be integrated in amine-based components by chemical grafting to form composite structures. Commercially available boron selective chelating ion exchange resins are generally prepared from macroporous poly(styrene-co-divinylbenzene) by functionalization with NMDG group [7]. These ion exchange resins were effectively employed for boron removal from wastewaters of geothermal power plant [8–13]. Novel boron selective resins with higher ion exchange capacity, higher selectivity, and faster sorption kinetics are still required for removal of boron from water and wastewater. Boron selective small particles (25  $\mu$ m) were synthesized by attaching NMDG group to styrene–vinylbenzylchloride–divinylbenzene monomer mixture by membrane emulsification method followed by polymerization. The resulted chelating resins showed a good performance in sorption–membrane filtration hybrid system used for removal of boron from water [14,15]. Elsewhere, the monodisperse porous particles with dextran based molecular brushes attached to the particles were synthesized via click chemistry and direct coupling. These particles were efficient in boron removal from aqueous solution [16]. The poly(glycidyl methacrylate-co-ethylene methacrylate) based monodisperse porous particles carrying NMDG functionality were reported to have a potential as boron selective resins [17]. These resins were used for removal of boron from geothermal water and its reverse osmosis permeate also [18]. The monodisperse-porous poly(vinylbenzyl chloride-co-divinylbenzene) beads with a 8.5  $\mu$ m in size were synthesized by a new “modified seeded polymerization” technique. The beads were derivatized by a simple, direct reaction with a boron-selective ligand NMDG by using their chloromethyl functionality [19].

Recently, a novel boron adsorbent was synthesized by grafting NMDG onto the hydrophilic silica–polyallylamine composites (SPC). It has a high loading capacity, chemical affinity and physical adsorption. It gave a highly effective removal for boron from aqueous solution and synthetic seawater containing high concentration of other ions [6]. Moreover, the authors suggested the possible use of this material at elevated temperature due to its high physical and chemical stability.

Thakur et al. [20] developed NMDG functionalized poly(propylene) sheet sorbent for selective extraction and determination of boron from various aqueous streams. As a result, it was found to be chemically stable and effective for the removal of boron from aqueous solutions over a

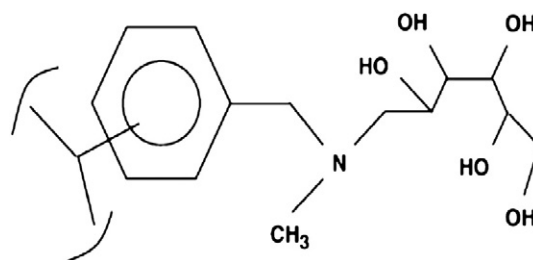


Fig. 1. The structure of boron selective chelating resin containing NMDG group. Source: [Reproduced from Ref. [7] with the permission of M.Busch].

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