



## Advanced treatment options to remove boron from seawater

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### ABSTRACT

Boron (B) is a unique nutrient essential for plant metabolic activities at low doses, while displaying toxic properties at high doses. The World Health Organization's recent guidelines recommend increasing the drinking water boron concentration limit to a maximum of 2.4 mg/L. The previous limit of 0.5 mg/L for drinking water sources (including seawater) was set by the agricultural sector seeking the unlimited irrigation of boron-sensitive crops. This review suggests a diverse view on the supply of desalinated tap water for irrigation purposes. Currently, there are no reports of B damage to humans at concentrations below 1.5 mg/L, routinely achieved on the first pass of a reverse osmosis (RO) membrane process. The proposed upper boron limit is evaluated based on technological advances and human health precautions, and can be especially useful for countries where desalinated water is directly used in irrigation. Further B reduction from 1.5 to 0.5 mg/L in irrigation water can be achieved not only by multistage RO, but also by electrocoagulation, electrodialysis, and adsorption-membrane filtration hybrid systems.

*Keywords:* Boric acid; Seawater desalination; High-pressure membrane; Distillation

### 1. Introduction

Conserving drinking water resources is a pressing issue worldwide. Due to increasing water demand, both for potable use and for irrigation, coupled with a decrease in suitable water sources, suppliers have to turn to alternative sources of water. Seawater desalination, as well as the treatment of highly saline wastewater, has become a standard. The use of these alternative methods has resulted in an increase in trace contaminants (such as boron) in the final product.

At low doses, boron is a nutrient necessary for plant metabolic activities. However, high doses of boron bring about toxic effects to plants. Boron toxicity symptoms had been observed in chickpeas [1], wheat [2,3], *Eucalyptus* [4], date palms [5], pomegranates [6], and stems of *Prunus* rootstocks [7]. Most

citrus species have a boron tolerance threshold of only 0.40–0.75 g/L [8]. The mechanism of boron toxicity is still a matter of speculation. It is likely, though, that soluble boron plays an important role in the occurrence of boron toxicity [9]. According to a current model [10,11], high external supply of boron could lead to an influx of boric acid into the cell, where it is partially converted into borate due to the higher internal pH. In this state, borate most likely forms complexes with a variety of putative ligands in the symplasm. Given that no boron effect is observed at a concentration equal to or less than 0.4 mg/L, it is deemed as the nonobserved effect level. However, a boron concentration of at least 1 mg/L is already considered toxic.

Consumptions of high boron doses can result in acute boron toxicity in humans. The toxicity symptoms include nausea, headache, diarrhea, kidney damage [12], fertility problems, and teratogenic effects

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[13]. Severe toxicity might result in death on account of circulatory collapse. On these grounds, the World Health Organization (WHO), for many years, recommended the drinking water limits for boron to be as low as 0.5 mg/L. The limit however, was rarely reached by conventional reverse osmosis (RO) desalination plants equipped with commercially available membranes [14]. In a recent meeting held on 9–13 November 2009, the Drinking-Water Quality Committee recommended revising the boron guideline value to 2.4 mg/L [15]. In this context, the Water Desalination Report (46(7), 15 February 2010) reported that:

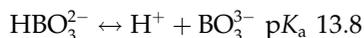
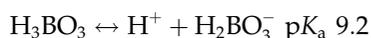
although a new guideline value is based on a human health perspective, some utilities may set seawater desalination plants product water limits as low as 0.5 mg/L to reflect agricultural related issues. These issues include boron's herbicidal effect on some plant species, which is a particular concern in areas of low rainfall.

Many countries do not follow the WHO recommendations. For example, the European Union (EU) countries including the UK require 1 mg/L B in drinking water [16]. Regulations in the US vary based on the state, and fall in the range of 0.6–1 mg/L [17]. Significantly higher concentrations of 4 and 5 mg/L of boron can be found in Australian [18] and Canadian [19] regulations, respectively, explained by two important reasons. Firstly, an insufficient database exists for linking high B concentrations with human diseases [20], and secondly water-rich countries prefer to abstain from using wastewater for irrigation. Conversely, countries with limited water resources such as Israel and Saudi Arabia are following strict B regulations of 0.4 and 0.5 mg/L, respectively [21,17]. The relatively stringent demand is attributed to the heavy use of treated wastewater in irrigation [22,23]. For instance, more than 80% of Israeli wastewater is treated for further use in irrigation [24]. In addition, the measured boron concentration is rising due to the further addition of boron from industries such as those manufacturing glass, soaps, detergents, and fireproofing fabrics, or as a result of leaching from rocks and soils. Therefore, the feed boron concentrations in wastewater treatment plants are usually near 1 mg/L. Boron is poorly removed by conventional water (coagulation, flocculation, and filtration) and wastewater (activated sludge and trickling bed) treatment methods, and consequently the secondary effluents after biological treatment (which are later utilized for irrigation purposes) essentially have the same boron concentration as in the feed to the treatment methods. An average boron concentrations of 0.42 and 0.37 mg/L in

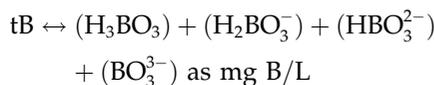
wastewater and the secondary effluents of the Beer-Sheva municipal wastewater treatment plant were reported [25,26]. The relatively low boron concentration was explained by the separation of industrial and municipal wastewater streams in the southern Negev. The average boron concentrations in effluents of three main Israeli wastewater treatment plants of Shafdan, Haifa, and Jerusalem were observed to be between 0.7 to 0.8 mg/L [27].

## 2. Boron chemistry

Boron is comprised of a mixture of  $^{10}\text{B}$  (19.78%) and  $^{11}\text{B}$  (80.22%) isotopes [28]. In water, boron mainly exists as undissociated boric acid,  $\text{H}_3\text{BO}_3$ . Boric acid is a very weak acid, with a  $\text{p}K_a$  of 9.2, and therefore at neutral pH values, boric acid  $[\text{B}(\text{OH})_3]$  is the predominant form. At a pH value greater than 11, the borate anion  $\text{B}(\text{OH})_4^-$  becomes the main species in solution. Between these two pH values, boric acid deprotonates into a hydrogen and monoborate anions, as shown below:



In addition to monoborate anions, a variety of polynuclear boron species such as  $\text{B}_2\text{O}(\text{OH})_6^{2-}$  or those incorporating  $\text{B}_3\text{O}_3$  rings such as  $[\text{B}_3\text{O}_3(\text{OH})_4]^-$ ,  $[\text{B}_4\text{O}_5(\text{OH})_4]^{2-}$ , and  $[\text{B}_5\text{O}_6(\text{OH})_4]^-$  are also formed [29]. According to Su and Suarez [30], those polynuclear ions are negligible at concentrations below 290 mg/L. Given that the boron concentration in seawater ranges from nondetectable to approximately 7 mg/L, dissolved boron is mainly found as the mononuclear boron species,  $\text{B}(\text{OH})_3$  and  $\text{B}(\text{OH})_4^-$ . The total boron (tB) in water is therefore a sum of all boron species expressed as the molecular weight of boron atom



The  $\text{p}K_a$  values of boric acid depend on ionic strength, pressure, and temperature [31]. Elevating the temperature from 285 K to 320 K decreased the  $\text{p}K_a$  value from 9.4 to 9.1. Furthermore, increase in hydrostatic pressure from 0 to 6 kbars [32] increased the  $\text{p}K_a$  value from 9.2 to 11. The latter observation however

is of little relevance to boron removal technologies, given that it is uncommon to operate at extremely high pressures [31]. The effect of salinity on B retention was found to be membrane-dependent [33–37]. Although boric acid is easily dissociated as temperature and salinity increase [33–35], Oo and Song [36,37] continuously report lower B retention at higher salinity levels. This trend is explained by a shift to neutral or possibly positive zeta potential values at higher ionic strengths. The shift depresses the charge repulsion and powers size exclusion as the predominant B retention mechanism.

### 3. Boron removal methods and process description

Conventional water treatment coagulation, sedimentation, and filtration does not significantly remove boron, and blending of high- with low-boron water may be the only economical method to reduce boron concentrations. If blending is not an option, alternative methods must be used, such as state-of-the-art technologies incorporating the retention of boron in the form of a borate anion [38]. For this process, the pH of the entire solution is raised above the first deprotonation pH of 9.2, and subsequently lowered to acceptable levels once the borate anion is retained. Although extremely costly, highly efficient (and sensitive) RO and ion exchange processes have also been implemented for seawater purification. Alternatively, electrocoagulation (EC), electrodialysis (ED), and adsorption-membrane filtration (AMF) are more economically affordable. However, these technologies are less efficient and not as prevalent in the industrial market. Nevertheless, these methods are less sensitive to the presence of impurities in raw water and can therefore be implemented for wastewater purification. Retention of boron as boric acid can be performed by complexation to polyol compounds [39] as well as by constructed wetlands. However, the retention ratios and final boron concentrations are far from satisfactory. An average of 30% of B removal was reported [40–42]. In addition, Del-Campo and Oron [43] found that this method can be effective only when the initial boron concentration was below 2 mg/L. Therefore, a further detailed discussion of the method applied in boron retention will be limited to advanced technologies that are also sufficiently described in scientific literature and practiced around the world.

#### 3.1. RO membranes

RO is the leading desalination technology widely used to reduce the boron concentration, pertaining not

only to seawater. RO is a physical process in which contaminants are removed by supplying pressure on the feed water to direct it through a semipermeable membrane. Size exclusion, electrostatic, and hydrophobic interactions are the three fundamental phenomena governing solute rejection by RO membrane processes. Size exclusion is usually used to describe the rejection of neutral solutes, whereas electrostatic interaction is commonly used to explain the rejection of charged solutes [31]. Significant advantages of the RO technology include its ability to reject nearly all contaminant ions and most dissolved nonions, immediate operation, minimal space requirements, modular type construction, and ease of scale [8]. The high power demand, expensive maintenance, and frequent monitoring are inherent drawbacks of RO desalination.

Rejection of nonionized boric acid by RO is low, due to its smaller size and lack of electric charge. The dissociated form, on the other hand, will be fully hydrated, resulting in a larger radius and an appearance of a negative ionic charge. This, in turn, results in a higher rejection, both by size exclusion and charge repulsion of the negatively charged membrane [44]. In good agreement with these observations, Dydo et al. [45] investigated the boron removal from landfill leachate initially with a boron content of approximately 25 mg/L, and found that boron rejection was low at a pH of less than 8.5, but remarkably increased as the pH of the solution rose above 9.5. A maximum value of approximately 99% was reached at the pH of 11. However, the reported rejection rates vary and are membrane dependent. For example, Prats et al. [46] reported 40–60% boric acid rejection at pH ranges of 5.5–9.5. According to Glueckstern and Priel [47], currently available RO membranes for seawater have the ability to remove boron (boric acid and borate ions) from 85 to 90% at standard test conditions (set by the manufacturers). Koseoglu et al. [48] reported 90% boron removal at normal operation conditions (pH 8.2, 55.2 bar, 25 °C) with high boron rejection membranes. About 80% boron removal with modified for low B passage membranes was reported by Bernstein et al. [49]. The rejection depends considerably on the membrane itself and might differ between 99.6 and 86.4% for two spiral wound FilmTec membranes [50]. Huertas et al. [51] reported a 45% decline in the retention of 5.5 mg B/L by RO membranes due to biofouling. According to Redondo et al. [52], the desalination costs directly depend on the B concentration requirements. A typical 0.38–0.50 US\$ cost of 1 m<sup>3</sup> desalinated water increases by 10 cents when the required final B concentration is 0.3–0.5 mg/L. An additional

5–7 cents/m<sup>3</sup> of desalinated water is expected when a B content below 0.4 mg/L is required.

The influence of ionic strength on boron rejection by RO membranes is a complex phenomenon. On the one hand, it was reported that the rejection of negatively charged organics would increase as the ionic strength of the solution decreases [31]. This is attributed to a thicker membrane electrical double layer existing at low ionic strength conditions. The thicker electric double layer limits the transport of the charged solute, whereas water transport is not affected by the thicker double layer. Consequently, the overall rejection increases. On the other hand, increasing the ionic strength may decrease the zeta potential of the membranes, which would reduce the electrostatic interaction between borate and the membrane surface, and hence boron rejection. In addition, an increase in ionic strength may lead to a decrease in the dissociation constant ( $pK_a$ ) of boric acid (see above). A decrease in the dissociation constant can be directly translated to changes in the speciation of the boric acid compound, resulting in a higher fraction of negatively charged borate species at a given pH. This observation can therefore lead to an increase in the overall rejection of boron as the solution ionic strength increases. However, this is solely applicable to a pH range below 11. At higher pH values, boric acid is fully deprotonated and the ionic strength does not affect the retention. An increase in the temperature of the solution might decrease the  $pK_a$  value of boric acid. In other words, a higher temperature of the feed solution would result in a higher fraction of the negatively charged borate and hence lead to a higher boron rejection level at a given pH (it is also prudent at a pH range of 7–11). Similar conclusions were drawn by Sagiv and Semiat [53].

Today, single-stage seawater reverse osmosis (SWRO) membranes are able to reduce boron concentration from approximately 6 mg/L to approximately 0.9–1.8 mg/L [65]. It is insufficient to reduce the boron concentrations to the 0.5 mg/L demand level in the Middle East and North Africa (MENA) countries. The low B concentration is achieved through several design concepts that had been developed by original equipment manufacturers, engineering companies, process consultants, and end users (plant operators). The concepts are evaluated by their ability to achieve efficient and safe boron removal at competitive costs. Glueckstern and Priel [47] optimized eight different design concepts to minimize boron removal costs. It was reported that 2–3 cents/m<sup>3</sup> of cost reduction can be expected with the implementation of more advanced RO membranes, as well as with the operation at elevated permeate flux pH values of the feed

water. A superior performance of cascade design over a two pass system was reported by Faigon and Hefer [54]. The cascade design was used to retrofit the SWRO plant in Eilat (southern Israel). Nadav et al. [55] reported that the retrofit was successful and that the boron concentration in the permeate is now kept at 0.39 mg/L. Some of the most common multistage membrane process options for B retention are summarized below. Further detail on numerous options can be found in a comprehensive review by Hilal et al. [15].

### 3.1.1. Two passes with increased pH

This concept, shown in Fig. 1, has been widely proposed for systems where the product boron requirement is between 0.4 and 0.5 mg/L, and the boron concentration of the seawater feed ranges between 4.0 and 6.3 mg/L [52]. As explained above, high B retention is achieved at a pH higher than 9.5. However, the raise at the first pass increases the membrane scaling with calcium carbonate and magnesium hydroxide. The first pass is therefore commonly equipped with high-pressure seawater RO membranes and operates at a pH below 8.2. Alternatively, operation of the first stage at an elevated pH requires suitable antiscalants [56–59]. After significant reduction in the ion concentration at the first pass, the second pass is constructed from low-pressure brackish water RO membranes and operated at a pH of 11 (required for complete B dissociation) [31]. Some of the first-pass permeate is by-passed to keep some minerals in the water, as well as for mixing with the second-pass permeate in order to reduce the pH in the product water. With a feed boron concentration of 6.3 mg/L, a temperature of 34°C, and recoveries of 45% in the first and 85% in the second pass, the boron concentration of the permeate was expected to be in the range of 0.2 mg/L, provided the pH of the feed was adjusted [52]. A constant boron concentration below 0.3 mg/L at a pH > 10 and at temperature > 30°C was observed following 6 months of full scale operation at the Ashkelon Desalination Plant [60].

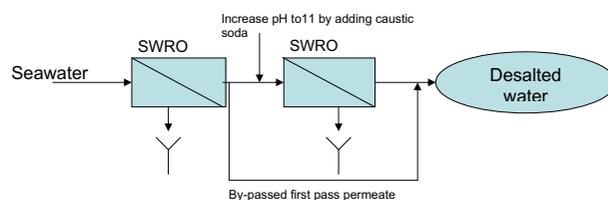


Fig. 1. Two pass desalination with increased pH.

### 3.1.2. Two RO passes combined with boron-selective ion-exchange resins

The concept of using a sea water desalination pass followed by treatment with a boron-selective resin is especially attractive in plants that have not been designed for boron removal and want to achieve a more stringent boron limit without a major redesign. Also, in situations where the observed or projected boron permeate concentration is very close to the target boron concentration, the addition of a small ion-exchange system is suitable [13]. Depending on the designer approach and feed water conditions, various ways of designing a system with a boron-selective resin can be implemented. The most efficient option is to completely avoid the operation of a second membrane pass. In cases where the required removal levels are significantly lower than 0.4 mg/L, or when special safety considerations are taken into account, it is possible to use a partial second pass and a partial stream to the ion-exchange resin [13]. The concept of combining a second membrane pass with a boron-selective resin has been proposed for seawaters containing 4.5–6.0 mg/L of boron. The seawater were also required to achieve a boron concentration below 0.4 mg/L in the final blend of the streams from the first-pass RO system, second-pass RO systems, and from the boron selective ion exchange resin. The partial second pass contributed between 50 and 60% to the final blend, resulting in a boron concentration between 0.2 and 0.35 mg/L. The boron-selective resin flux with 0.1 mg/L B contributed between 10 and 25% of the total mix. The mix, comprised of 40% of the first-pass permeate, with an average B concentration of 1 g/L resulted in a final solution that contains 0.5–0.6 mg/L of boron. The concentration of boron depends on both the pH values and temperatures of the feed. The blend can be adjusted to have a boron concentration of less than 0.4 mg/L at all times [61]. Blending of brackish water with desalted seawater has also been suggested as an alternative approach to brackish water desalination [62–64].

### 3.2. Removal of boron by EC

Coagulation is one of the most implemented physical–chemical treatments of water. Essentially, coagulation is carried out by the addition of ions with an opposing charge to that of solutes. The goal of coagulation is to reduce the net surface charge to a point where the solutes, previously stabilized by electrostatic repulsion, can approach closely enough for van der Waals forces to hold them together and allow aggregation [65]. While the coagulation is performed by the

addition of inorganic salts, in EC, the coagulant is generated *in situ* by the electrolytic oxidation of an appropriate anode material [66]. In its simplest form, an EC reactor is made up of an electrolytic cell with one anode and one cathode. When connected to an external power source, the anode material will electrochemically corrode due to oxidation, while the cathode will be subjected to passivation. Consumable metal plates, such as iron or aluminum, are usually used as sacrificial electrodes to continuously produce ions in water. The released ions neutralize particle charges and thereby initiate coagulation [67,68]. They also remove undesirable contaminants either by chemical reaction and precipitation, or by causing the colloidal materials to coalesce. In the latter case, removal by flotation is practiced. The flotation of the aluminum and iron ions is attributed to the presence of hydrogen gas bubbles generated on the cathode surfaces.

EC strongly depends on process duration and current density. The removal efficiency increases with the process time and current density. A process time of 20 to 30 min and a current density of 20 mA/cm<sup>2</sup> were sufficient for 90% B removal from 2.5 g/L of boron solution [69]. In these experiments, the initial B concentration was significantly higher than in natural waters. Yilmaz et al. [70] conducted research to compare the efficiency of boron removal by EC and chemical coagulation. Although all operational parameters were the same, boron removal efficiencies between each treatment process were quite different. The boron removal efficiency by EC was significantly greater than by chemical coagulation, which is 94 and 24%, respectively. Unfortunately, no sound explanation was provided. The highest boron, at pH value of 8, falls into the sweep when boron was present as boric acid. This trend was partly explained by the fact that boron at a pH value of 8 falls into sweep coagulation region [71]. According to the coagulation theory, added aluminum ions form hydroxide precipitates that are able to either enmesh or adsorb other particles and molecules. The obtained flocs have a higher sedimentation ability due to their increased hydrodynamic radii. However, at a pH value of 8, most of the boron in water remains in the form of boric acid, an unionized compound that is adsorbed or enmeshed inefficiently [27]. Also, research has indicated that the boron removal efficiency decreased with increasing boron concentration for each treatment process. The same amount of coagulant was utilized for the increased concentration of boron; however the amount of the coagulant added should be increased proportionally to increase the coagulant concentration.

Xu and Jiang [12] reported that EC with Alum anodes can remove 15–20% more boron than chemical

Alum coagulation. The operating cost for 75% boron removal by EC was 6.2 times more economically favorable than by chemical coagulation. The price difference was explained by low chemical shipping and waste removal costs.

Ofir et al. [27] evaluated the ability of electroflocculation (EF) to remove boron from seawater as a function of pH. Chemical jar-test experiments were performed at a pH value of 8. An average 20–30% boron retention (from 4.2 to 3.5 mg/L) was obtained with 150 mg/L of ferric chloride and 35 min of sedimentation time. EF experiments with 3 A current and 30 V for 5 min were performed at a pH of 8, and were followed by NaOH addition (required to raise the pH to 10). The EF samples were then allowed to settle for a total of 18 h. At a pH of 8, EF was only partially successful in boron retention. However, at a pH of 10, boron concentration in seawater dropped by 54% during the first 5 min of EF, and continuous sedimentation (18 h) resulted in 78% boron rejection (from 3.7 to 0.8 mg/L). This study demonstrated the potential advantage in using EF systems for efficient B retention. In addition, the use of iron as the sacrificial electrode material for this purpose was found to be pH dependent [27].

Local deionization near high surface-area activated carbon fiber (ACF) was recently reported by Avraham et al. [72]. The researchers were able to dissociate boric acid into borate ions near the surface of ACF electrodes and demonstrated that electro-adsorption of ions onto the positive electrode in capacitive de-ionization cells reduced the B concentration by 30%.

### 3.3. Boron removal by ED and electrodialysis reversal

ED is an electrochemical process in which ions migrate through ion-selective semipermeable membranes as a result of their attraction to two electrically charged electrodes. ED differs from pressure-driven membrane processes by utilizing an electric current as the main driving force of matter separation [8,73]. A typical ED system includes a membrane stack with a number of cell pairs, each consisting of a cation transfer membrane, a demineralized flow spacer, an anion transfer membrane, and a concentrate flow spacer. Compartments for the electrodes are placed at opposite [8].

It is commonly known that ED is subject to membrane fouling because its liquid process streams must be free of both particles and high organic content. For this purpose, electrodialysis reversal (EDR) is a possible solution. EDR is similar to ED, aside from the fact that the polarity of the electrodes is regularly reversed, thereby freeing accumulated ions on the

membrane surface. This process minimizes the effect of inorganic scaling and fouling by converting product streams into waste streams. Therefore, it is possible to prolong the ED operation without stopping and cleaning the equipment. EDR systems are fully automated and require little operator attention, with the exception of data collection and routine maintenance (i.e. changing cartridge filters, and calibrating and maintaining instruments). Additional advantages of ED and EDR systems include the absence of chemicals, low Transmembrane Pressure requirements, easily operated in remote settings, and lowered scaling (based on the automatic cleaning of electrodes with acid formed during anodic operation). The disadvantages include high capital and operational costs, large quantities of pretreatment required, and frequent electrode replacement.

Melnik et al. [74] studied ED of boron solutions using heterogeneous (cation-exchange membrane MK-40 and anion-exchange MA-40), homogeneous (cation-exchange MK-100 and anion-exchange MA-100), and ionic (CR67-HMR and anion-204-8XZL-366(5188C)) membranes. The experiments indicated that boron removal depends on the type of the membrane and on the pH of the solution. ED of model water resembled those of the Sea of Asov and the Black Sea with typical 1.5 and 2.3 mg B/L, respectively, and ocean water (4.7 mg B/L) with MK-40 and MA-40 resulted in 0.2–0.5 mg/L B in dialyzate. Maximum of 86–92% B removal was achieved at a pH level greater than 10. The ionic membranes reduced the boron concentration from 4.0 to 1.0 mg B/L.

Kabay et al. [75] studied the effect of pH and initial boron concentrations on the boron removal by ED in batch experiments performed with 25, 50, 75, and 100 mg B/L boric acid solutions. The pH values of the solutions were regulated between 8.5 and 10.5. The research indicated that boron removal increased from 20% at pH 9.0 to 80% at pH 10.5. The higher initial boron concentration resulted in an increased relative removal and higher total process time.

Oren et al. [76] demonstrated that the inverse position of the cation and anion spacers, where the former is in contact with anion-exchange membrane and the latter with cation-exchange membrane, improves the retention from 60 to 80%. However, the increase in boron removal efficiency was accompanied with a decrease in the overall efficiency of the ED process. Another drawback for the removal of boron to the desired levels involves the removal of salt to extremely low levels. This result is usually not essential when treating drinking water or water for irrigation purposes, leading to unfavorable energy consumption.

### 3.4. Boron removal by Ion-exchange resins (IX)

IX are used to remove the undesirable ions such as arsine and boron. The exchange medium consists of a solid phase of naturally occurring minerals or synthetic resins having a mobile ion attached to an immobile functional acid or base group. In the exchange process, the mobile ions are exchanged with solute ions having a stronger affinity for the functional immobile group [8]. Applications based on flying ashes, natural sorbents, inorganic adsorbents [44], and macroporous polystyrene matrices with N-methyl glucamine ligand [77] for boron removal had been reported. Simonnot et al. [78] indicated that boron-selective resins can reduce B concentration from 100 to 0.1 mg/L, and therefore illustrating that resins are the most efficient method for B removal.

The two most important parameters for a boron-selective resin are the operating capacity and the kinetic capability. The operating capacity will determine the frequency of regeneration and the chemical consumption, while the kinetic capability will have a major influence on the flow velocity and hence on the size and cost of the ion-exchange unit. Busch et al. [13] described the boron-selective resin DOW Developmental Resin XUS 43594 and illustrated a higher boron resin capacity of 1.75 gB/L with XUS 43594 compared to 1.45 gB/L with competitive membrane for a 0.1 mgB/L set point. It was also suggested to split the feed water into two parts and blend it at the end of the treatment to achieve the required B concentration. Simonnot et al. [78] reported a 1.87 g B/bed capacity of Amberlite IRA743 with the feed concentration of 20 mg B/L. Ozturk and Kose [79] reported that the amount of boron absorbed by Dowex  $2 \times 8$  anion-exchange resin increased from 5 to 15.5 mgB/g as the concentration of boron in the solution rose. Demircivi and Nasun-Saygili [77] performed experiments with Amberlite IRA743 with the feed concentration of 20 mg B/L. Ozturk and Kose [79] reported that the amount of boron absorbed by Dowex  $2 \times 8$  anion-exchange resin increased from 5 to 15.5 mgB/g as the concentration of boron in the solution rose. Demircivi and Nasun-Saygili [77] performed experiments with Amberlite IRA 743 and demonstrated that the removal efficiency increased with increased amounts of adsorbent and decreased with higher B concentration. The maximum 98.9% efficiency was achieved with lower B rate at a pH greater than 10.5, probably due to the deprotonation of boric acid and predomination of borate ion. The optimum B removal was achieved at a pH of 9.5 [79–82]. Kabay et al. [75] reported that the decrease of resin particle size increased B reten-

tion. High levels of boron retention on coal and fly ash as adsorbents (alternative to IX resins) were reported by Polat et al. [81]. The researchers showed that the B rejection ratio can reach 95% of its initial content under certain optimal conditions (e.g. pH=9, liquid/solid ratio=1/10, reaction time>6 h).

Bick and Oron [8] indicated that the advantages of IX resins include simplicity of operation, minimum contact time, and simple control for the desired boron concentration (due to the presence of a modulating valve). Nadav [82] estimated the cost of 4–6 US cents per cubic meter of permeate, depending on the cost of resin, chemicals, operation, and maintenance. Storage of strong acids and bases needed for regeneration, batch mode operation, production of concentrated corrosive wastes, and high resin and operational costs were marked as possible drawbacks of this technology.

### 3.5. AMF hybrid process

The AMF hybrid process can be an attractive alternative to a fixed bed technology. In the AMF process, boron is adsorbed onto a microparticle adsorbent, resulting in the separation of formed complexes on microfiltration membrane. The integrated system includes two separation loops. In the first loop, the boron is bound on a specific sorbent S, which is subsequently followed by the separation of the BS complex from an RO permeate (by means of microfiltration membrane). Here, water-free boron is a main product, whereas the complex passes to the second stage of separation. In the second loop, splitting of BS complex on the free sorbent and boron occurs, followed by membrane separation. This step allows for sorbent regeneration and concentrated brine production.

Kabay et al. [44] reported that the submerged adsorption-microfiltration hybrid system, with a capillary microfiltration module, was operated for 24 h from an RO permeate with 1.3 mg/L B. The process efficiency of this system was evaluated for the machine-ground Dowex XUS 43594.00 resin (average particle diameter 20  $\mu\text{m}$ ) using polypropylene hollow fiber microfiltration membrane module. It was found that boron concentration reached zero in the first hour of the process and kept constant until the experiment was terminated.

## 4. Conclusion

Boron is a unique compound that can simultaneously be vital and harmful. There is a demand to reduce B concentration to a certain limit, most recently set by WHO to 2.4 mg/L. The reduction can be

achieved by many advanced technologies including a multistage RO that is capable of reducing B concentrations in drinking water to below 0.5 mg/L. This extremely low concentration was demanded by a strong agricultural lobby seeking the unlimited irrigation of boron-sensitive crops (using all sources of drinking water including the seawater).

The current water supply situation should be reevaluated given that there are no reports of B damage to humans at concentrations of 1.5 mg/L. Hasson et al. [83] recently showed that concentration at present can be achieved after the first RO pass. The regulations are therefore set to over treat the water for use in agriculture in every region, despite recent reports that suggest irrigation with desalinated water is not a preferable solution in locations experiencing water shortages [84]. A wiser water policy should opt to raise the B concentration in drinking water of MENA countries to 1.5 mg/L, and perform further reductions only in irrigation water. Comparative full-scale trials should be conducted to evaluate B reduction in irrigation water from 1.5 to 0.5 mg/L by multistage RO, EC, ED, and AFM.

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