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Boron removal from seawater by electro-chemical treatment as part of water desalination

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ABSTRACT

Significant decrease of boron concentration during seawater desalination is one of the more difficult, consuming and expensive tasks. Average boron concentration in the Mediterranean Sea is 4 mg/l, and due to heavy use of wastewater in irrigation the Israeli Water Authority (Ministry of Health) demands boron reduction to 0.4 mg/l maximum. The current boron removal procedure is based on two-pass reverse osmosis (RO) membrane treatment that requires pH adjustment to dissociate boric acid into borate ion. The operation is expensive, energy consuming and calls for cheaper and reliable alternatives. The current research was initiated to explore the abilities of electro-flocculation (EF) to remove boron from seawater. The EF experiments were performed under batch electro-chemical reactor conditions with iron electrodes. Settling time and pH of the solution were selected as two main independent parameters. The obtained results suggest that significant boron reduction can be achieved without membrane separation technologies. The obtained drop from 4.2 to 0.8 mg/l boron after 10 min EF and 60 min sedimentation suggests that RO can be applied as a polishing stage only, needed to achieve the goal of 90% B retention. At the same time, the average 80% boron retention achieved by EF/sedimentation is encouraging and can be viewed as a valuable alternative to currently applied RO-based technology. The studies were performed on seawater from the Palmachim beach (near Rishon-Le-Zion, Israel) and were an important step in detection of possible boron removal mechanisms.

Keywords: Boron; Seawater; Desalination; Chemical treatment; Electro-flocculation

1. Introduction

Boron is a unique nutrient that at low doses is required for plant metabolic activities and at high doses is toxic to the plants. The boron toxicity symptoms had been recently observed in chickpea [1], wheat [2,3], eucalyptus [4] and in stems of *Prunus rootstocks* [5]. The mechanism of B toxicity is still a matter of speculation. It is likely, though, that soluble B plays an important role in the occurrence of B toxicity [6]. According to a current model [7,8] high external supply of B could lead to an influx of boric acid into the cell, where it is partially converted into borate due to the higher internal pH and most likely forms complexes with a variety of putative legends in the symplasm. No boron effect is observed at concentration of 0.4 mg/l and below, and that concentration is therefore named the non-observed effect level (NOEL). However B concentration of 1 mg/l and higher are already considered toxic.

Boron concentration in seawater, boron concentration, range from non-detectable to approximately 7 mg/l. The

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current Israeli legislation requires reduction of B concentration to 0.4 mg/l. The relatively stringent demand is due to heavy use of treated wastewater in irrigation [9,10]. More than 90% of Israeli wastewater is treated for further use in irrigation [11], and measured B concentration is raising due to further addition of B from industries such as manufacturing of glass and porcelain wire drawing, production of leather, carpets, cosmetics and photographic chemicals; fireproofing fabrics; and weatherproofing wood. It is therefore the feed B concentration, in wastewater treatment plant, are usually near 1 mg/l. Boron is poorly removed by biological treatment, and therefore the secondary effluents with essentially initial B concentration are used in irrigation. The average B concentration of 0.42 and 0.37 mg/l in wastewater and secondary effluents of Beer-Sheva municipal wastewater treatment plant were reported, respectively [12]. The relatively low B concentration was explained by a separation of industrial and municipal wastewater streams in southern Negev. The average B concentration in effluents of three main Israeli wastewater treatment plants of Shafdan, Haifa and Jerusalem is between 0.7–0.8 mg/l.

There is no easy method for removing boron from aqueous solution. As was mentioned above, sedimentation and biological treatment have a minor effect on B removal [13]. Other widely reported techniques for removing boron from solution, namely evaporation crystallization and solvent extraction processes, are effective in high concentration streams and are geared more to the production of boric acid rather than to its removal from waters. The adsorption of boron by ion-exchange resins, clays, soils and other minerals has been extensively studied in lab but no clear recommendation has been obtained yet. The procedure developed and currently implemented at desalination plant includes two stages usually called second and third membrane passes [14,15]. At second pass, the seawater pH is raised to the levels of 9.5 where boric acid is turned into borate ion following the dissociation reaction [Eq. (1), Ka = 6.10^{-10}, pKa 9.1].

$$B(OH)_3(aq) + H_2O \leftrightarrow B(OH_4)(aq)^- + H(aq)^+ \quad (1)$$

The pH alteration increases B rejection from 55% at pH 8 to more than 90% at pH 9.5 [16]. At the second stage or third RO pass the pH is reduced back to neutral values. The cost of NaOH only used for pH adjustment at second pass is estimated at 5 cents per m^3 of feed water [8]. Needless to say that the entire operation is costly, provides one of the obstacles in further reduction of desalination cost.

It has been offered to partially reduce the boron concentration using the flocculation with water soluble inorganic salts such as alum [17] and ferric chloride. Comparison of chemical and electrochemical aluminum coagulation for retention of B from boron-reached surface water was previously reported by Yilmaz et al. [18]. It was suggested to perform the current study with ferric ions to complete the puzzle and to be able to compare the retention trends observed after application of two different coagulants. The ferric hydroxides were generated by the electrolytic oxidation of iron anode [19] at typical pH 8 of the seawater. According to Letterman et al. [20], addition of ferric ions at this pH causes sweep coagulation where the ferric hydroxide particles are forming a mesh able to either entrap or adsorb impurities from a solution. The performed study aimed at evaluating ability of EF to remove B from seawater. Specifically, the proposed study will address two research topics which are of fundamental interest:

- How the shift in of the coagulation conditions (pH-value and current density) influence the electroflocculation process.
- How the high ionic strength and presence of colloidal material influences boron removal. That point is not obvious and both positive and negative influence can be expected [18,21]. The negative effect is that part of the coagulant will be spent on colloidal material. The probable positive effect is dual: 1) the colloids can absorb boron; and 2) colloids can help to create stronger flocks less breakable during flocculation and sedimentation.

2. Materials and methods

Schematics of Palmachim desalination plant including sampling points are depicted in Fig. 1.

The facility supplies some 30 million m^3 of water per year since May 2007, using a 4-pass reverse osmosis technology. Three sampling ports were chosen: raw seawater after pretreatment and before the first pass (sampling 1). RO permeate after first pass (sampling 2) and RO permeate after second pass (sampling 3). The water was collected into 10 L jars and transported to the laboratory of environment biotechnology at Ben Gurion University (Beer Sheva, Israel). The experiment with seawater were supplemented with experiments with synthetic boron solution prepared with tap water that was purified with 50-micron poly-aramid filter UF-PA 50H and ion exchange column made from a mixture of Emberlite IR 120 and IRA400. For synthetic solutions, 459.1 mg $Na_2B_4O_7$ (99.99%, Merck) were dried at 105°C and dissolved in 1 L of the purified tap water. The same operation was repeated for the solution with boron concentration of 500 and 1000 mg/L with different $Na_2B_4O_7$ weights. Ferric chloride $FeCl_3.6H_2O$ (Merck, 99% purity) was used in chemical coagulation experiments. The pH adjustments to the values pH 8, 9 and 10 were performed with NaOH and sodium carbonate. The latter was used as a buffer. The previously reported chemical jar-test protocol [22] was followed. Briefly, the calibrated water and additives were mixed in conventional jar-test apparatus at 100 rpm for 1 min. Paddle speed was adjusted thereafter to 30 rpm for the next 20 min. The slow mixing was stopped and the suspension was allowed to settle for 30 min. After settling,

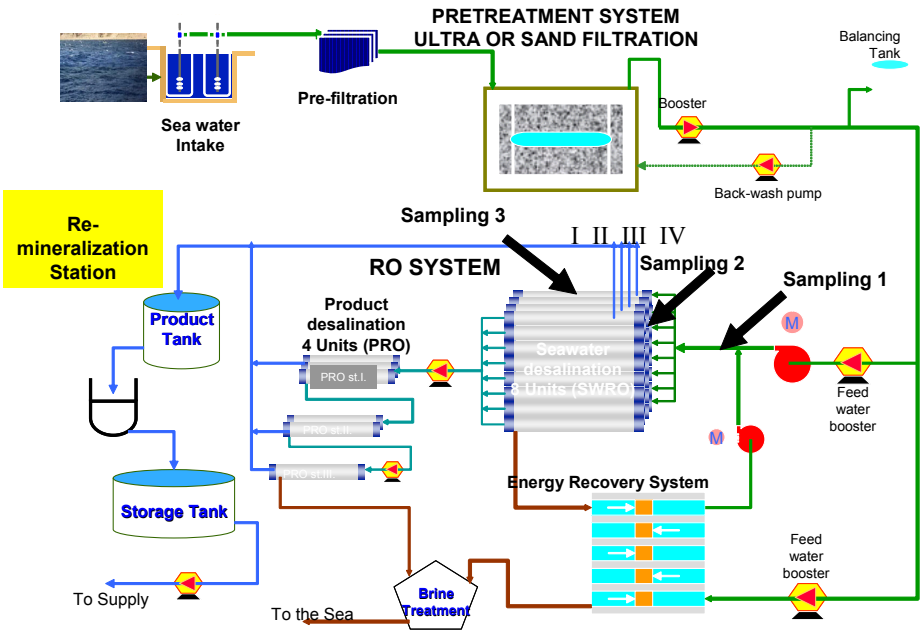

Fig. 1. Palmachim desalination plant — operation scheme.

samples were drawn from 4 cm below water level and checked for boron concentration.

For EF experiments, the jar-test was modified [23]. Two SAE1020 steel electrodes were added to each of six jars. The electrodes were connected to a DC power generator and fitted in a way that allowed the paddle to rotate freely [24]. The DC power supply provided current and voltage over the ranges of 0–5 A and 0–30 V, respectively. Sodium nitrate was used to adjust the suspension conductivity.

Boron concentration was measured with DR 2800 portable spectrophotometer (Hach, Loveland, CO, USA) that allows measurements in a rather large B spectrum between 0.02 and 14.0 mg/l. The results were compared by additional B measurements performed with ICP Optical Emission Spectrometer Varian 720-ES.

3. Results and discussion

Weekly sampling of seawater near Palmachim was performed for 5 months. The collected samples were analyzed in the lab in order to obtain the average boron concentrations in seawater. The results are presented in Fig. 2. The average B concentration in seawater near Palmachim site was 3.55±0.92 mg/l.

Results of chemical jar test experiment performed on raw seawater, synthetic water and water after the 3rd pass at pH 8 with addition of 150 mg/l ferric chloride are depicted in Fig. 3.

The experiments were performed with rather different initial boron concentration that varied between 4.2 mg/l in seawater, 1.5 mg/l synthetic water and 0.2 mg/l RO water. At the same time, the similar trend was observed.

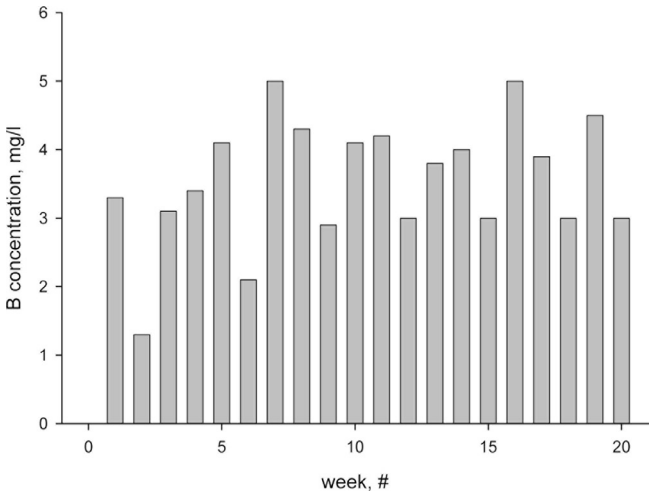

Fig. 2. Boron concentration in seawater near Palmachim site (Rishon Le Zion, Israel).

The B concentration in suspension slightly decreased as a function of settling time. The B concentration in seawater decreased from 4.2 to 3.5 mg/l after 35 min of sedimentation. Reduction from 1.5 to 1.1 mg/l in B concentration in synthetic water and from 0.2 to 0.15 mg/l in RO water was observed. As a result, average 20–30% B retention after chemical flocculation with 150 mg/l ferric chloride and 35 min of sedimentation was observed.

Regarding the coagulation mechanism, the pH of 8 belongs to the sweep coagulation region [20]. According to the coagulation theory the added iron forms ferric hydroxide precipitates that are able to either enmesh or

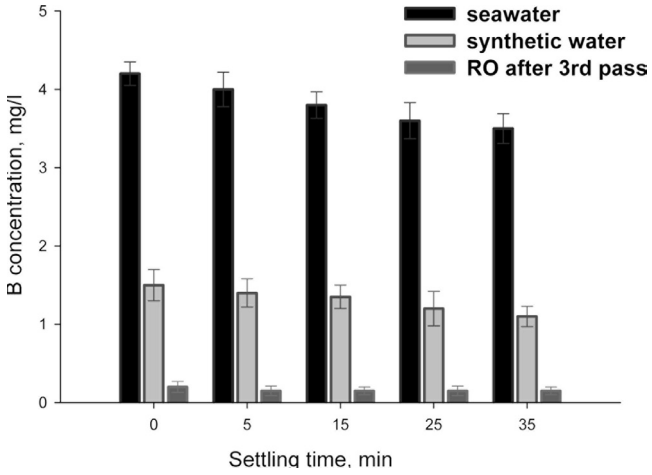

Fig. 3. Changes in boron concentration as a function of settling time.

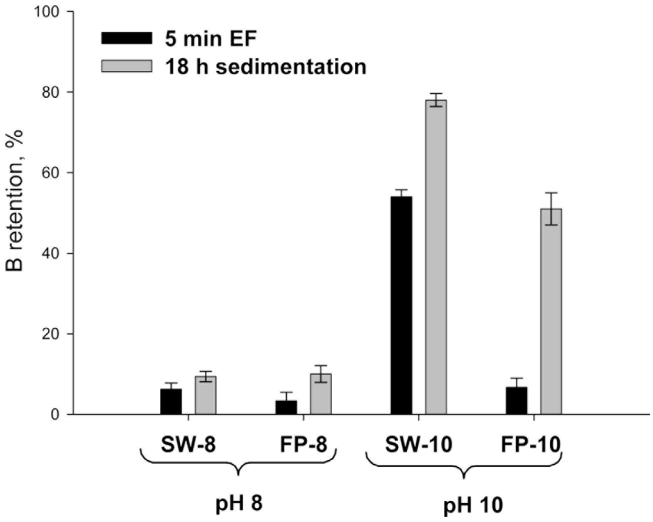

Fig. 4. Boron retention as a function of pH.

adsorb other particles and molecules. The obtained flock has higher sedimentation ability due to its increased hydrodynamic radii. However at pH 8 most of the B in water is still in a form of boric acid $B(OH)_3$, unionized compound that is not efficiently adsorbed or enmeshed.

EF experiments were performed with 3 A current and 30 V for 5 min. The experiments were performed at natural seawater pH 8 and with addition of NaOH needed to raise pH level to pH 10. After EF, samples of seawater and RO permeate were left to settle for 18 h. The results are depicted in Fig. 4 as a percentage of boron retention after the EF alone and EF followed by sedimentation. In accordance with the previous experiment, EF performed at pH 8 was only partially successful in B retention. Boron concentration decreased by 6% after EF and 9% after EF and 18 h of sedimentation. However, addition of NaOH that resulted in pH raise to pH 10 revealed to be much more powerful treatment option. Boron concentration in seawater dropped by 54% during the first 5 min of EF, and continuous sedimentation resulted in 78% B retention from 3.7 to 0.8 mg/l. Interesting though that the experiment performed on the first path RO permeate was less successful and pointed at almost no retention after flocculation and 51% retention after 18 h settling. The success in coagulation at pH 10 can be attributed to the dissociation of boric acid and formation of borate $B(OH)_4^-$.

The experiment was repeated with prolonged 10 min EF at 3 A current and much shorter settling times of 20 and 60 min. The results were compared with those achieved with 1080 min settling time. Once again, pH was raised to 10 with NaOH. The results are depicted in Fig. 5. In general, the obtained results are well correlated with the previous experiments. The better retention is achieved with seawater, and as the water is moving aside

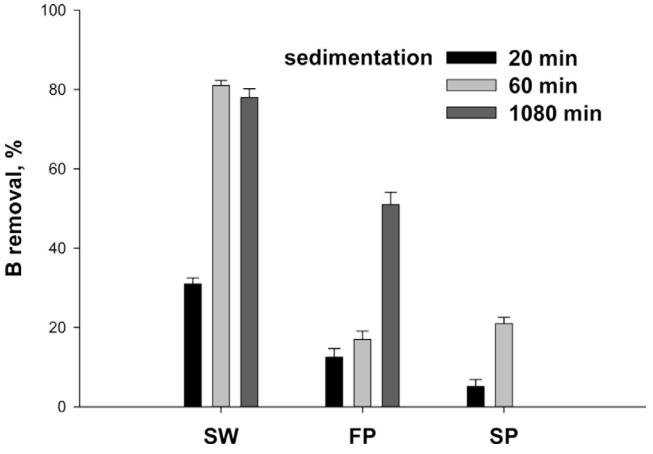

Fig. 5. Boron retention as a function of sedimentation time.

of the RO desalination chain, boron retention decreases. Prolonged EF step is probably less critical in obtaining good B removal.

Also, 18 h sedimentation does not provide a real gain in comparison with 60 min settling. At the same time, the 20 min settling is a small time period to achieve good sedimentation. Comparing the results with chemical flocculation described in a discussion to Fig. 5, it can be assumed that the flocculation is satisfactory when the key to good boron removal is the sedimentation step. Slightly higher B retention after 60 min sedimentation, comparing to the 1080 min settling, was explained by higher initial boron concentration of 4.2 mg/l, when the experiment with 1080 min sedimentation was performed at 3.7 mg/l initial boron concentration.

4. Conclusion

This study has shown the possibility to use EF for efficient retention of boron from seawater. The EF was significantly more effective than chemical coagulation performed with ferric chloride. The use of iron as sacrificial electrode material in the treatment of boron-containing seawater was found to be pH dependent. The most effective removal was achieved at pH 10. EC was found to be more effective to raw sea water than for permeates of RO stages. The treatment rate was seen to increase with increasing the current density. The highest current density gave the quickest treatment for boron removal from synthetically prepared waters.

The performed study suggests that boron can be effectively removed without membrane technologies. Still, the key for effective retention is pH raise and ionization of boric acid $B(OH)_3$ to borate $B(OH)_4^-$. However, the borate can be effectively neutralized by flocculation or EF process followed by sedimentation and filtration (that is used anyway as a preliminary treatment stage before the RO). An alternative membrane filtration (ultrafiltration) can also be considered as a preliminary treatment stage in place of granular filtration to increase B removal and to protect of RO system. The obtained average 80% retention at pH 10 suggests that the RO can be applied as a polishing stage needed to achieve the 0.4 mg/l goal in B concentration. (i.e. 90% retention) At the same time, the drop from 4.2 to 0.8 mg/l boron after 10 min EF and 60 min sedimentation/filtration is encouraging and can drawn attention to EF followed by sedimentation as a valuable alternative to currently applied RO-based technology.

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