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Boron removal and zeta potential of RO membranes: impact of pH and salinity

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ABSTRACT

Boron removal is a challenging task for any seawater desalination plant employing a single-pass reverse osmosis (RO) system. With a pK_a value of 9.25, more than 99% boron removal is normally achieved at pH >10.5. As pK_a value is theoretically lower at higher salinity, an increase of borate ion and a corresponding increase in boron removal could be expected as salinity increases. However, boron removals by CPA2 and SWC4+ membranes were found to decrease or, sometimes, unchanged at higher salinity where membrane zeta potentials shifted from negative values to positive values were observed at higher salinity at both pH 7 and 9. The decrease in boron removal by CPA2 membrane with increasing salinity at pH 9 could be attributed to the reduced charge repulsion mechanism. Similarly, boron removal by SWC4+ membrane decreased with increasing salinity. However, the removal efficiency reached its lowest value at 2000 mg/l of NaCl at pH 9. The subsequent increase in boron removal efficiency at salinity higher than 2000 mg/l could be attributed to size exclusion mechanism. At pH 7, the trend of boron removal by CPA2 membrane was similar to that observed at pH 9. However, the corresponding trend of SWC4+ membrane at pH 7 was different from that observed at pH 9. With a negligible amount of borate at pH 7, reduced boron removal by CPA2 membrane observed at higher salinity might be attributed to enhanced diffusion. In contrast, the relatively stable boron removal at pH 7 by SWC4+ membrane observed at all salinities suggested that size exclusion could be the dominant mechanism.

Keywords: Boron removal; Ionic strength; pH; RO membrane; Salinity; Zeta potential

1. Introduction

The presence of boron in seawater always imposes a challenge in meeting the product water boron concentration standards set by the authorities when a simple RO process is used for seawater desalination. Although the RO process has an inherent limitation in removing some trace elements such as boron, many such systems have been installed since the cellulose acetate asymmetric reverse osmosis (RO) membrane was introduced in 1970s for large-scale applications due to its process simplicity, flexibility and good performance characteristics [1]. Boron is an essential micro nutrient for living things. However, it becomes toxic to plants and harmful to human reproductive system at high concentration. In the 2004 edition of WHO guideline for drinking water quality, 0.5 mg/l was set as the limit for boron in drinking water [2]. This value is slightly higher than the 0.3 mg/l stipulated in its previous edition. The revision

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was attributed to limitations of most treatment technologies that were economically feasible at that juncture.

Although boron cannot be easily removed to a very low concentration by RO membranes at typical operating conditions, it can be reduced to almost zero level if the pH of the RO feed water is raised to the alkaline region. Many studies have been reported on the effect of pH on boron removal by RO membranes and the mechanism of boron removal has mainly been attributed to charge repulsion [3–9]. Boron removal by different methods, in combination or individually, has been extensively studied [10–18]. However, contribution of charge repulsion and size exclusion for boron removals by RO membrane are still not well understood. In addition, impact of other factors such as ionic strength in the solution on boron removal has not been taken into consideration in most studies.

As boron removal by RO membranes could partly be attributed to diffusion, it is necessary to understand the type and strength of ions that will interact with each other and with the charged membrane surface. There are studies that pointed out the importance of ionic type and its concentration on the performance of RO and NF membranes [19–21]. However, reference concerning the impact of salt concentration on the removal of trace element, such as boron is not readily available. Removal mechanism is rarely described too. In addition to ionic strength, membrane surface potential could also affect boron removal. Although membrane surface potential was studied at different pH, the effects of salt concentration have not been explored [22]. Owing to the findings of possible charge repulsion mechanism, there have been speculations that boron removal could be improved at higher ionic strength [3,7,15,23]. This is because pK_a value would be theoretically lower at higher salinity and hence it is possible to form more negatively charged borate ions that could be removed easier than boric acid [13,16,23]. However, these speculations are not supported by other experimental reports [24–26].

In view of the above, the objective of this study was to investigate the effects of salinity and pH on boron removal by different types of RO membrane. Zeta potential of membranes at different salinity and pH was also studied and possible boron removal mechanisms were discussed.

2. Materials and methods

RO membranes used in this study were CPA2 and SWC4+ of Hydranautics (Oceanside, CA, USA). Boron removal at desalination plant is normally achieved at second pass RO where brackish water reverse osmosis (BWRO) membrane is selected due to the low salt concentration. CPA2 is a BWRO type membrane and thus it was selected in this study. SWC4+ membrane was included due to its common application as seawater reverse osmosis (SWRO) membrane and of its higher boron removal efficiency. Zeta potential of membranes used in this study can be generally described as positive at low pH and negative at high pH [22,25]. Salt rejections of CPA2 and SWC4+ membranes are 99.5% and 99.8%, respectively, based on the manufacturer's standard testing conditions. Boron rejection of SWC4+ membrane is 93% at the standard testing conditions. Zeta potentials of CPA2 and SWC4+ membranes are −20 mV and −13 mV at pH 7 and 0% salinity [25].

Reagent grade boric acid, sodium chloride, hydrochloric acid and caustic soda from Merck (Damsdalt, Germany) were used in the experiments. Dried boric acid and sodium chloride were dissolved directly into DI water according to its respective testing concentration (5 mg/l as boron with 500–15000 mg/l of NaCl solutions). 0.1 M HCl and 0.1 M NaOH were prepared for pH adjustment during the experiments. The flat sheet RO testing unit and procedures adopted were presented in a previous study [24]. In general, a rectangular flat sheet membrane with an effective area of 155 cm^2 was used for the experiment. Owing to small area of membrane sheet, percent recovery of permeate was maintained at 1%. Operating pressure was adjusted to maintain a stable flux for testing at different salinities. The cross flow velocity of feed stream was approximately 0.3 m/s and temperature of feed solution was maintained at 23.5–25.5°C. Boron was analyzed by ion-coupled plasma optical emission spectrometry (ICP-OES) model Optima 3000DV of Perkin Elmer (Waltham, MA, USA). For each sample, analysis of boron was conducted twice at replicated mode with a variation of results of less than ±5%. Other parameters such as pH and temperature were measured by portable meters (Oakton pH10 and Oakton Temp5 from Singapore). Membrane performance in terms of percent removal of a particular component was defined as follow:

$$\text{Removal} = \left(1 - C_p/C_f\right) \times 100\%$$

where C_f and C_p are the component concentrations in the feed and permeate, respectively.

Anton Paar Electro Kinetic Analyzer (EKA) was used to measure zeta potential of RO membranes. Details of EKA operation can be found elsewhere [25].

3. Results and discussion

3.1. Boron removal at different pH

As pK_a of boric acid is 9.25, boron at low concentration and neutral pH will normally be present in the

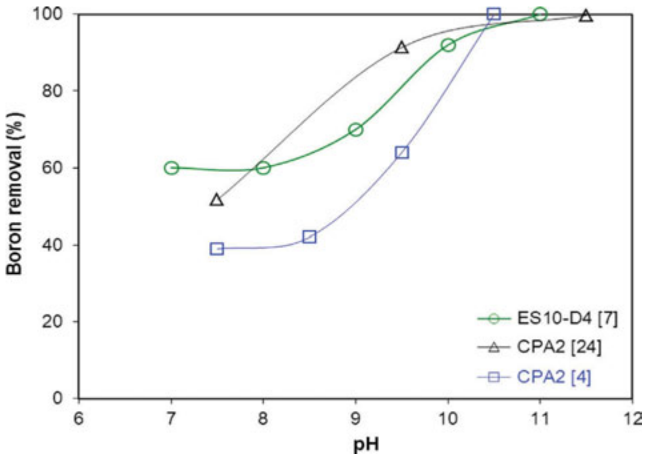

Fig. 1. Effect of pH on boron removal by BWRO membranes [4,7,24].

water as charge neutral boric acid. However, it will fully transform into negatively charged borate ion, which possesses larger molecular dimension, at pH 11.5 or higher. Thus, boron removal will be improved at higher pH and most studies on boron removal by RO membranes were therefore conducted at different pH [3–7]. An example of reported findings is shown in Fig. 1 where boron removal efficiencies using CPA2 membrane and at pH 7.5, are reported at 40% and 52% by Prats et al. and Oo et al., respectively [4,7,24]. Boron removal efficiency was noted to improve almost linearly as pH increases. When the pH was increased to 10.5 and 11.5, more than 99% of boron was removed. This is because the boric acid in the solution becomes largely dissociated into borate form. In the study of Magara et al., 99% boron removal was observed at pH 11 [7].

There were also studies reporting that ionic strength could influence the shift of pK_a value [19–21]. It was reported that pK_a of boric acid is 9.25 at 0% salinity and it reduces to 8.5 at 30% salinity. Salinity is one of the useful measures to indicate ionic strength that is a function of concentration and charge of ions in a given solution. Ionic strength equals to $\frac{1}{2}\sum_{i=1}^{n} c_i z_i^2$, where c_i and z_i are concentration and charge of ith ion in the solution, respectively. Ionic strength increases with salinity. Change of pK_a to a lower value, due to the changes in activity of borate ion resulted from an increase in ionic strength of solution, indicated an enhanced dissociation of boric acid into borate ion occurred at higher salinity. At pH 9.0, negatively charged borate accounts for about 36% of the total boron present in the solution at 0% salinity and it will increase to approximately 76% at 30% salinity [24]. It is also noted that difference of borate compositions at different salinities is more significant at pH around the region of 9. The difference in borate compositions is negligible when pH is less than 7 or more than 11.

3.2. *Zeta potential of RO membranes at different salinities and pH*

As membrane surface charge or zeta potential could play a major role in the removal of boron by RO membranes, it is useful to investigate the zeta potential of RO membranes. Zeta potential of RO membranes at different pH were investigated in the past [22]. However, change in zeta potential at different salinities was rarely reported despite it could affect the boron removal by RO membranes. In addition to boron removal at higher salinity, this study also investigated zeta potential of RO membranes at different salinities and pH. Figs. 2 and 3 show the zeta potential of CPA2 and SWC4+ membranes at different salinities and pH. Those values at pH 9 were adapted from a previous study [25].

Although zeta potential of RO membranes tends to be negative at high pH, it was observed that zeta potential would shift towards positive region at higher salinity at both pH 7 and 9. As shown in Fig. 2, at pH 9, zeta potential of CPA2 membrane shifted from −16 mV to +36 mV when NaCl concentration was increased from 500 mg/l to 10000 mg/l. Similarly, at pH 7, zeta potentials were −15 mV and +37 mV at 500 mg/l and 10000 mg/l of NaCl, respectively.

For SWC4+ membrane, changes of zeta potential were narrower than those of CPA2 membrane. As shown in Fig. 3, at pH 9, zeta potential of SWC4+ membrane shifted from −15 mV to +18 mV when NaCl concentration was increased from 500 mg/l to 10000 mg/l. The corresponding values were −9 mV and +25 mV, respectively, at pH 7. The phenomenon of shifting zeta potential from negative to positive value could be attributed to a stern layer that was densely shielded by positive ions explained in the other report [25].

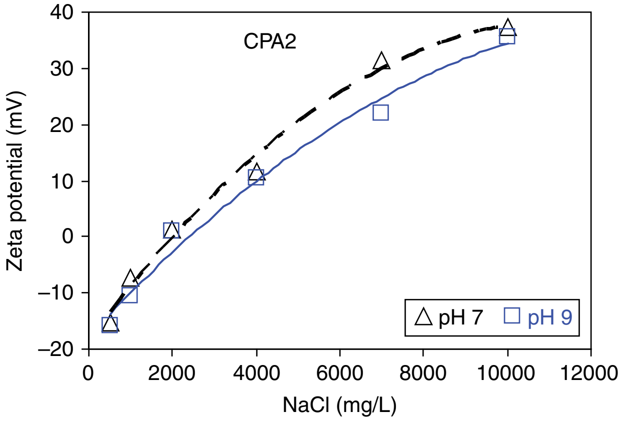

Fig. 2. Zeta potential of CPA2 membrane at different salinities and pH.

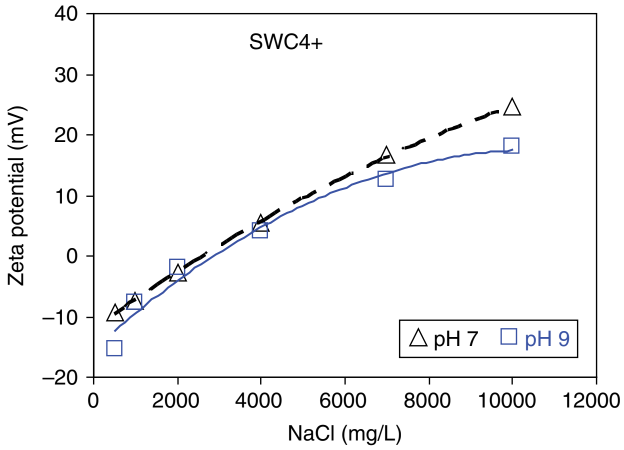

Fig. 3. Zeta potential of SWC4+ membrane at different salinities and pH.

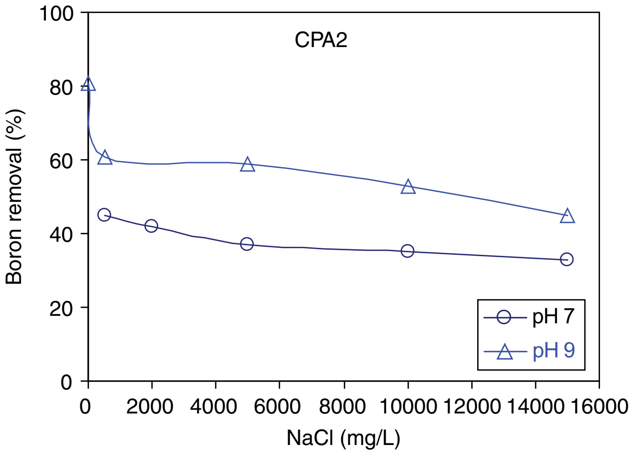

Fig. 4. Effect of salinity on boron removal by CPA2 membrane at different pH.

3.3. Boron removal by RO membranes at different salinities and pH

As it is possible to expect conversion of more boric acid to borate at higher salinity at a given pH, as discussed in Section 3.1, experiments on boron removal were conducted at different salinities with the expectation of achieving better boron removal at higher salinity. As the proportion of borate at different ionic strengths changes significantly at pH 9, this value was selected for initial tests to assess the effect of salinity on boron removal. Subsequently, experiments were extended to pH 7 where the percentage of borate composition could not be distinguished clearly between low and high salinities. Results of boron removal by CPA2 and SWC4+ membranes at different salinities and pH are shown in Figs. 4 and 5. The values at pH 9 were adapted from a previous study [25].

As shown in Fig. 4, boron removal by CPA2 membrane at pH 9 decreased from 61% at 500 mg/l of NaCl to 59%, 53% and 45% at 5000, 10000 and 15000 mg/l of NaCl, respectively. The trend of lower boron removal observed at higher salinity was similar to that observed at pH 7. That is, boron removal by CPA2 membrane was 45% at 500 mg/l of NaCl and it reduced to 37% and 33% at 5000 and 15000 mg/l of NaCl, respectively.

It should be noted that at pH 9, the positive impact of salinity due to lower pK_a value was overshadowed by the negative impact of salinity that changed the membrane surface potential from negative to a positive value. One of the past studies suggested that membrane surface charge could be altered at high salinity and this phenomenon might have caused a faster diffusion of ions through membrane at higher ionic strength [21]. This phenomenon could explain the reduced boron removal noted at higher salinity and pH 7.

Although the effects of salinity on boron removal by CPA2 membrane at different pH exhibited a similar trend, the corresponding effects associated with SWC4+ membrane were different. As shown in Fig. 5, boron removal by SWC4+ membrane at pH 9 decreased from 95% at 500 mg/l of NaCl to 87% at 2000 mg/l of NaCl. However, boron removal recovered again towards 91% and 89% at higher salinity of 10000 mg/l and 15000 mg/l NaCl, respectively. The corresponding removal profile at pH 7 showed a relatively stable trend across all salinities. As shown in Fig. 5, boron removal by SWC4+ membrane was found to be stable at around 75% at pH 7.

When surface potential was negative at 500 mg/l NaCl concentration and pH 9, boron removal by SWC4+ membrane was most efficient. With certain percentage of borate formation, boron removal at low salinity could be attributed to both size exclusion and charge repulsion

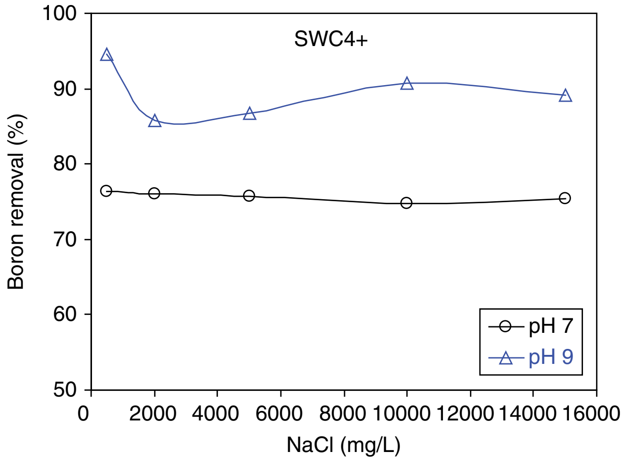

Fig. 5. Effect of salinity on boron removal by SWC4+ membrane at different pH.

mechanisms. When salinity was higher than 2000 mg/l, the positive impact of salinity to lower the pK_a value outweighed the negative impact of less charge repulsion. That is, size exclusion mechanism should be the dominant factor of boron removal at higher salinity. The relatively stable boron removal by SWC4+ membrane at all salinities observed at pH 7 also suggested that boron was removed mainly by size exclusion mechanism.

4. Conclusions

The lower pK_a value at higher salinity theoretically implies an increase of borate ion at certain pH that in turn would enhance boron removal by RO membrane. However, boron removal by CPA2 and SWC4+ membranes was found in this study to decrease or sometimes, unchanged at higher salinity where zeta potentials of both membranes shifted from negative values to positive values at higher salinity at both pH 7 and 9.

Boron removal by CPA2 membrane decreased at higher salinity for both pH 7 and 9. With significant amount of borate ion at pH 9, boron removal could be attributed mainly to charge repulsion mechanism and it would reduce when zeta potential of membrane turned positive at higher salinity. With negligible amount of borate ion at pH 7, size exclusion should be the boron removal mechanism while enhanced diffusion should be the cause of lower boron removal at higher salinity.

Boron removal by SWC4+ membrane was relatively stable at higher salinity for pH 7. However, removal trend exhibited a V-shape at different salinities for pH 9 where lowest boron removal was observed at 2000 mg/l of NaCl. Better removal at lower salinity could, to a certain extent, be attributed to charge repulsion mechanism and that at higher salinity could be due to the impact of lower pK_a, i.e., increased fraction of borate. In general, size exclusion should be the dominant factor for boron removal by SWC4+ membrane.

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