

REMOVAL OF BORON BY DESALINATION PROCESS – A REVIEW

MAHESWARI P AND POORNIMA

ABSTRACT

Boron is a vital nutrient for humans, plants and animals. It is also known as a micro - nutrient for metabolic activity. On the other hand, it might cause negative effects for some plants when its concentration exceeds the permissible limits in irrigation water, such as plant decay and in humans lead to health problems like Headache, Kidney damage, Diarrhea. Boron concentration must be reduced from sea water to match the final user specifications and environmental restrictions. In seawater, boron exists almost exclusively in the form of boric acid. Due to a severe water shortage and increasing salinity of natural sources, in many countries currently, they are undergoing seawater reverse osmosis desalination plant construction and desalination of a number of wells. In this review, disparate approaches were accessible for the operation of seawater RO desalination plants in which the boron concentration in the product water should not exceed 0.5 mg / L.

The objective is to explore the performances of disparate methods of boron removal from reverse osmosis (RO) permeate. The studies included in this review highlight the potential for further process to enhance the removal of boron in salinated water using desalination applications. The proposed approaches were to be both technically feasible and cost effective, as compared with conventional boron removal alternatives. This work focus at overcoming the limitation, and presenting an extension to our previously developed approach that enables the extraction of optimal RO configurations whilst accounting for boron removal.

Keywords: Boron; Desalination; Membrane; Reverse Osmosis; Hollow fiber membranes, ultrafiltration, Nanofiltration.



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1 INTRODUCTION

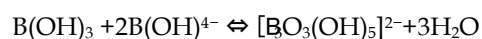
Many countries, currently in the world are suffering from a shortage of fresh water, mainly due to a large expansion in industrial activities, increased population as well as the increasing salinity of natural sources. Over the last several decades, seawater has become an important source of fresh water because it is one of the most abundant resources on earth. Traditional desalination plants have evolved into reliable and established processes. They are undergoing an intensive programme of both large seawater reverse osmosis (SWRO) desalination plant construction. Removal of boron species (B) from desalinated water is a significant component in the process design of many seawater reverse osmosis (SWRO) desalination plants. At concentrations above 1.0 mg B/L, boric acid is known to damage various agricultural crops and plant species used in municipal gardening. For example, crops such as avocado and most citrus types are sensitive to Boron in the concentration range 0.5–0.75 mg B/l.

Boron is widely distributed in both the hydrosphere and lithosphere of the earth. Boron it is an element, which is available in the environment and an important micronutrient for metabolic activity in all living organisms. Boron acts as one of the most important micronutrients for plants, and is essential for normal growth of most crops. In water, it is in the form of Boric acid. Generally, boron in aqueous environment, which is found in the form of boric acid and partial borate salts (Xu and Jiang et.al., 2008).

boron chemistry

A. General

Boron is a metalloid of group 13 in the periodic table. Boric acid is a waxy solid and soluble in water (55 g/L at 25°C). Being the only non-metallic element in group 13 of the periodic table, the chemistry of boron and its compound boric acid is unique. At relatively low concentrations ($\leq 0.02\text{M}$ or 22mg/L as B), only the mononuclear species $\text{B}(\text{OH})_3$ and $\text{B}(\text{OH})_4^-$ are present. However, at higher concentrations and with increasing pH, especially above pH 10, poly-nuclear ions such as $[\text{B}_3\text{O}_3(\text{OH})_5]^{2-}$ and $[\text{B}_4\text{O}_5(\text{OH})_4]^{2-}$ would be formed. The formation of these rings is attributed to the interaction of boric acid molecules and borate ions in solution:



However, there is a narrow range between its deficiency and toxicity; boron is beneficial to plants only in small quantities and excessive amounts are injured and even lethal (Parks and Edwards, 2005).

Long-term exposure to water with increased boron content can result in malfunctioning of cardiovascular, nervous, alimentary, and sexual systems of humans and animals [Melnyk et.al. ;2005, sof.w.; 2000, Shwartz., 1994).

The World Health Organization (WHO) once set a guideline limit of 0.5 mg/L for boron in drinking water and the value is revised to 2.4 mg/L recently. Although this new change seems more relaxed for drinking water, the requirement of 0.5 mg/L is still kept for irrigation water since boron demonstrates a herbicidal effect (Wei et.al; 2011). In seawater, the average boron concentration is approximately 4.6 mg/L. The Boron concentration in confined ocean bodies can deviate substantially from this average value. For example, the boron concentration in the Mediterranean Sea can be as high as 9.6 mg/L. The concentration of boron in seawater together with the recent growth in seawater desalination using reverse osmosis technology has reinstated boron as a major contaminant of concern in the water supply.

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 started using post-treated as a product water for irrigation purpose. In a short duration of time, they noticed poisoning of crops and partly discolored leaves. Later, it was identified that Boron as the toxic element responsible for these effects. Since then, several post-treatment methods have been investigated for boron removal in SWRO desalination. So far, we can see that the use of ion exchange resins and composite reverse osmosis (RO) membrane systems, as well as their combination with or without increasing the pH, are the only used technologies considered effective for the removal of boron. It was found that the Boron rejection is largely depends on operating conditions and water quality parameters such as pH. It is also generally known that the type of membrane used and the operating conditions, which is having a strong influence on the boron rejection of sea water reverse osmosis system. This extends the list of possible factors to the following: Feed water characteristics such as pH, temperature, TDS, Elements of Membrane such as membrane chemistry, element efficiency, and in system design and operation such as an average permeate flux (APF), system recovery, concentration polarization, cleanings.

2 LITERATURE REVIEW

Sah and Brown;1997 had investigated the four flat-sheet fully aromatic polyamide RO membranes (SG from Osmonics and UTC80, UTC80A and UTC80S from Toray Industries) using cross-flow cell. On boron rejection, the UTC-series membranes from Toray had better performances than SG membrane. UTC-series membranes provided boron rejections in the range of 48–70%, whereas SG membranes could achieve only 12–30%.

Dydo et.al ;2005 had investigated the boron rejection by NF and RO membranes in the presence of glycerol, mannitol and sorbitol and obtained significant boron removal. Especially NF membranes exhibited higher boron removal in the presence of polyols than RO membranes that could achieve without the polyols.

Although RO membranes had better capabilities to retain the plain boron, NF membrane showed an apparent boron removal from polyol containing media. Besides that, the presence of polyols, it did not cause any observable membrane fouling issue.

Koseoglu et al. ; 2008 reported that the boron rejections from two different salinity feed waters – seawater and diluted water were almost the same as pH 10.5. The authors had argued that there were negative effects of concentration polarization at high ionic strength are compensated by the more ionized species produced at high pH.

Geffen et al. 2006 had employed the complexation reaction between boric acid and mannitol (a polyol compound) to enhance boron rejection using a NF, a brackish water and a seawater RO membranes. Significant improvement in the boron rejections by NF-200 membrane and BW-30 membrane were reported. The authors also reported that the boron rejections by these two membranes were strongly affected by the concentration of mannitol or the molar ratio of mannitol over boron. Boron rejection by the seawater RO SW-30 membrane in the presence of mannitol was also considerably higher than that under baseline condition (without mannitol). The reported increase in boron rejection has been attributed to the formation of borate complexes which is not only bigger in molecular size but also negatively charged. It has a significant potential to enhance boron removal in membrane desalination applications. Indeed, an enhanced boron rejection can be obtained at a relatively low feed solution pH, thus reducing the risk of membrane scaling. It may be possible to apply this technique to the first pass, allowing for the elimination of the second pass.

Güler. et al ;2011 had reported a report of two different types of polyamide thin film composite SWRO membranes for comparative study for boron removal from seawater. The viability of a new Film Tec SWRO membrane, so called XUS SW30XHR-2540, to use it as a membrane for high rejection of boron and salt were checked. A conventional membrane (SW30-2540) was also checked simultaneously in order to make a comparison between the performances of the membranes. In this study, quantity such as salt and boron and quality of product water so-called permeate were investigated by using measurements such as electrical conductivity (EC), pH, total dissolved solid (TDS) salinity, and B-concentration. Azomethine-H method was performed in order to determine boron concentration. This comparison was made via an investigation of the effects of feed seawater temperature (10–16 °C), operating pressure (55, 60 and 62 bar), and pH adjustment on the feed side (pH 7.0–7.5). XUS SW30XHR-2540 membrane showed a comparatively higher flux and recovery values than conventional SW30-2540 membrane. Besides, this membrane showed the highest

values of salt and boron rejections as 99.6% and 86.4%, respectively. Although pH of the feed water did not exceed 8.3, it was possible to see the enhancement of boron rejection when compared with the situation of acid adjustment. At natural pH values, boron rejection was as high as 89% for the high rejection membrane.

Turek. et al; 2007 had investigated the Tarnowskie Gory landfill leachate ,which contains excessive amounts of heavy metals, such as Zn, Cd, Mn, Pb, Sr, Ni, and Cr. It consisted of a relatively high boron content (about 75 mg/L). They had attempted to identify the suitable solid boron-rich concentrates obtainment method and proposed an integrated RO system that matches the requirement. In this system, at high feed-water pH levels were being applied to obtain a permeate that matches wastewater quality requirements (<1 mg of B/L). The RO retentate containing 300 mg of B/L were being used as a feed-water for the adsorption/ co-precipitation step. The supernatant from the above step, containing 95 mg of B/L, were then recycled to the RO step. When they analyzed the metal hydroxide type and feed water boron content influence on the boron adsorption/co-precipitation efficiency, they found that nickel, aluminum and iron hydroxides were the most efficient and thus, suitable for boron removal. The authors had supposed that the boron uptake during alkaline precipitation might be the result of both mechanisms, since the chosen ions were supposed to form either insoluble hydroxides of high specific area or insoluble borates under the conditions applied. The influence of the initial boron content and metal ion load of boron removal efficiency and hydroxide adsorption capacity were examined. It was also shown that the adsorption/co-precipitation step should be operated at a high boron content in order to avoid large precipitant load and resulting high RO feed-water salinity. However, due to its relatively high supernatant concentration, the use of nickel might be questionable. It was also shown that the adsorption/co-precipitation step should be operated at a high boron content in order to avoid large precipitant load and resulting high RO feed-water salinity.

Simonnot et al.;2000. had reviewed the methods of boron removal from drinking water. Among them, it has been pointed out that the use of boron selective sorbents based on macroporous polystyrene matrices with N-methyl glucamine ligand is still the most efficient one for boron removal.

Kabay. et al.;2006 had reported a comparable performance of adsorption-membrane filtration (AMF) system for the boron removal from natural and as well as artificial sea water to RO methods. With their integration of the sorption process were with the membrane separation via a non-hazardous binding agent. That can be easily regenerated and reused in the process. The combination of the advanced coupling agents with their separation in

membranes revealed many advantages compared to other conventionally used systems. The main benefit of the adsorption membrane filtration (AMF) hybrid process was higher efficiency and lower costs of the process as compared to the classical fixed bed column sorption. It was also observed that the sorbents can be used as very fine particles which reported that the suggested method as the interface area and results in the enhancement of the process rate considerably.

Park. et al., 2011 had investigated on gas hydrate-based desalination for removal of dissolved minerals (Na^+ , Mg^{2+} , Ca^{2+} , K^+ , B^{3+}) and their characteristics. It was observed that the equipment continuously produces and pellets CO_2 hydrates by a squeezing operation of a dual cylinder unit, which we're able to extract hydrate pellets from the reactor containing hydrate slurries. Removal efficiencies for each dissolved mineral from seawater samples was also tested by Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES) analysis. It showed that ion rejection of the hydration process strongly depends on the ionic size and charge and they had also method and apparatus may solve the separation difficulty between hydrate crystals and concentrated brine solutions, thus it can be applied for more effective desalination processes.

Redondo et al. 2003. had confirmed some results to Koseoglu et al., who investigated B rejection with different high B rejection membranes and reported 85–90% rejection at natural-pH seawater. It was found that approaches seemed to be impractical not only for reducing B to below 0.3 milligram Boron per litre, but even for attaining 0.75 milligram Boron per litre in the product water, because of instabilities associated with variations in temperature and seawater B concentration. Moreover, the latter authors had reported a maximum of 30% recovery, while the practical higher recovery values are bound to reduce the total B rejection. Rejection of over 99% could be achieved by adjusting pH to 10.5. However, flux reduction due to chemical scaling occurred in their experiments after an operation time of merely 14 hour.

Tagle. et al. 2011, theoretically examined the potential for single-pass B removal of small desalination plants. They had considered 14 commercial membranes and observation for the membranes were noted. They concluded that with the most up-to-date high B rejection membranes, a high B removal ($[\text{B}] < 0.5$ milligram per litre in the product water) can be achieved at the expense of a 12% increase in energy consumption.

Odednir et al. 2012, reported a new approach for B removal, applying a single SWRO pass, were suggested and evaluated. The process was aimed at separating boron species to attain B concentration < 0.3 milligram Boron per litre in the product water, by using low-energy SWRO

membranes. The ideas were to elevate pH to beyond pH 9, and at the same time avoid the risk of chemical fouling. It was found that the cost of the suggested process significantly lower than the 2nd pass BWRO alternative, and comparable to the BSR method for B removal. It is also reported that the SWRO designs, membrane selection for the 1st RO stage is compromised for medium flux (6000–9000 GPD) – high boron rejection membranes, because of the use of higher flux membranes (10,000–12,000 GPD) under normal seawater conditions (pH 8.0–8.2) results in higher B concentration in the 1st pass permeate, leading to more expensive post-treatment B removal step.

Busch. et al. 2005, to compare the cost of B removal by a 2nd BWRO pass and by ion exchange, using B selective resins (BSR). For the purpose of comparing these alternatives to the one suggested in Oded Nir. et al., The same assumptions about energy prices and operational conditions which were used in the cost assessments. When additional data were needed, it was taken from other sources or approximated by the authors. The operational expenses (OPEX) of the suggested process were calculated considering desalinated water production of 76,000 m³ per day (20 MGD) and 45% recovery. Strong acid consumption was the main cost item in the current approach. Accordingly, the H_2SO_4 price was obtained from a variety of sources and found to be $\square 100$ \$/ton. This cost was used in the presented assessment, instead of 90 \$/ton, the 2005-based price. The cost of NaOH, as 230 \$/ton, was updated to 400 \$/ton.

3 CONCLUSION

This review highlights the potential for further process optimization to enhance the removal of boron in seawater desalination applications. The discussions provided, however, also emphasize the need for more fundamental research to improve the scientific understanding of boron rejection by NF/RO membranes. A bench scale experimental study conducted with five different RO membranes with varying operating conditions suggested that boron rejection is substantially affected by pH due to dissociation of boric acid to negatively charged borate ions. It has been observed that using of the Sodium Lauryl Sulfate recipe as a surface modifier of TFC RO membrane results in the improvement of the membrane performances. Different experimental analysis proves that Sodium Lauryl Sulfate is the best on the active poly amide layer. And D-Mannitol is best in the complexation.

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