Desalination and Water Treatment
www.deswater.com

doi: 10.5004/dwt.2019.23669

157 (2019) 274–280
July

Long-term boron rejection of thin-film nanocomposite membrane at Pembroke Desalination Plant in Malta: a case study

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Received 15 October 2018; Accepted 26 December 2018

ABSTRACT

Boron is one of the important regulatory constituents for drinking and irrigation water. For irrigational use, while boron in small quantities is essential for the plant growth, an excessive amount of boron is known to be toxic for some plants. Because of this, even though the World Health Organization (WHO) raised the maximum boron concentration for drinking water up to 2.4 ppm in 2009, there are still some countries that have much tighter regulation than the WHO guideline. For example, many countries in the Mediterranean Sea area have the drinking water guidelines stipulating the maximum boron concentration in the range of 0.3–1.0 ppm. Implementation of these stringent standards to the quality of water produced by reverse osmosis (RO) membranes creates a challenge to the seawater desalination industry. In early 2016, LG Chem's NanoH$_2$O seawater RO membranes manufactured with the patented thin-film nanocomposite technology were installed in Pembroke desalination plant in Malta. The most challenging requirement of this project was to ensure the boron concentration in the permeate stream to remain below 0.9 ppm after 5 y of operation. After more than 2 y of operation, the membranes maintain an excellent boron rejection performance without any further pH adjustment of the feed water which has relatively lower pH value around 6.7.

Keywords: Desalination; Reverse osmosis; Seawater; Membranes; Nanocomposite; Boron

1. Background

Boron is a vital element for organism growth, but excessive exposure to it can cause detrimental effects on plants, animals, and possibly humans [1]. Until 2008, the maximum acceptable level of boron in drinking water was set at 0.5 ppm by World Health Organization (WHO) [2]. In 2009, this level was increased up to 2.4 ppm [3].

Nowadays, despite of the new WHO drinking water regulation, many countries still require the maximum concentration for boron to be in the range of 0.3–1 ppm. Some examples are shown below:

- 1 ppm: Spain, Morocco, Algeria, Greece, Malta
- 0.5 ppm: Singapore
- 0.3 ppm: Israel

In agriculture, excessive boron concentration may cause damage to plants and crops. Although boron is vital as a trace element for plant growth, it can be detrimental at higher concentrations [4]. Among the more sensitive crops are citrus

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Presented at Desalination for the Environment: Clean Water and Energy, 3–6 September 2018, Athens, Greece.

trees, which show massive leaf damage at boron levels of more than 0.3 ppm in the irrigation water [5]. Excessive boron also reduces fruit yield and induces premature ripening of other species such as kiwi [6]. Below are examples of acceptable boron concentrations for certain plants and crops:

- <0.5 ppm: lemon, blackberry
- 0.5–0.75 ppm: avocado, orange, onion
- 0.75–1 ppm: garlic, wheat, sunflower
- 1–2 ppm: capsicum, potato, carrot
- 2–4 ppm: lettuce, cabbage, celery [7]

Manufacturers of seawater reverse osmosis (SWRO) membranes claim that their boron rejection varies from 88% to 95% [3].

2. Boron in Seawater

Boron in seawater has an average concentration of 4.5 ppm [8]. It is present in water in the form of two distinct species: boric acid ($B(OH)_3$) and borate ion ($B(OH)_4^-$). Boron is soluble in water as boric acid which can ionize into borate ions following the simplified dissociation equation [3]:

$$B(OH)_{3(aq)} + H_2O \leftrightarrow B(OH)_4^- + H^+$$

The equilibrium constant of the above equation depends on temperature and ionic strength. The ionic strength at the same time is function of salinity. This constant is in the range of 8.4–9.5 [1].

Due to the small size and lack of charge of the boric molecule, low boron rejection is typically observed with SWRO membranes. At elevated pH, the ionization rate of the boric species increases which improves rejection. The equilibrium between boric acid and borate ion shifts to lower pH values with increasing ionic strength of the solution [9]. Therefore, the rejection rate by SWRO membranes increases with higher pH and solution strength as it is shown in Fig. 1.

3. Typical methods to improve boron rejection

In the water industry, to improve the boron rejection by SWRO membranes, the following methods are widely used: single-pass system with pH adjustment, dual-pass system, and dual-pass system with pH adjustment.

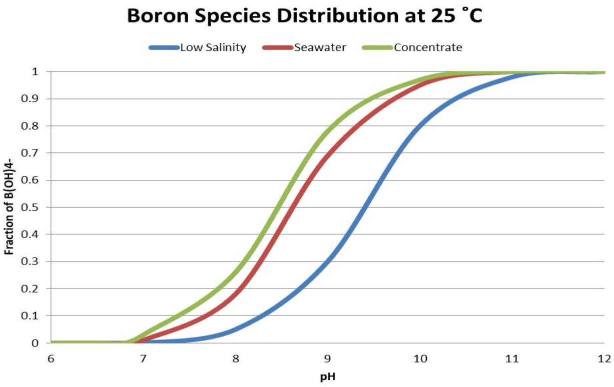


Fig. 1. Boron species distribution as a function of pH and ionic strength [9].

3.1. Single-pass system with pH adjustment (Fig. 2)

As described previously, higher pH helps to improve boron rejection as the ionization rate of boric species becomes higher. However, use of pH adjustment leads to process cost increase.

3.1.1. Capital cost

Capital cost increases since a new dosing system is required. This includes new dosing pumps, dosing lines, valves, chemical tanks, and related instrumentation.

3.1.2. Operational cost

Operational cost related to consumables would also increase because of using additional chemicals such as caustic soda to raise pH and antiscalant to avoid scaling at higher pH.

3.1.3. Energy cost

To capitalize on the improved boron rejection at higher pH, higher flux membranes can be used to reduce process energy and thus partially offset the higher capital and operational expenses caused by pH dosing.

3.2. Dual-pass system (Fig. 3)

Implementation of a second pass requires an increase in the production of the first pass in order to meet the production requirements. If a system was designed hypothetically to achieve 90% recovery at second pass, the production of the first pass would need to be 11% higher compared with a single-pass configuration. It is obvious that the addition of second pass leads to a cost increase.

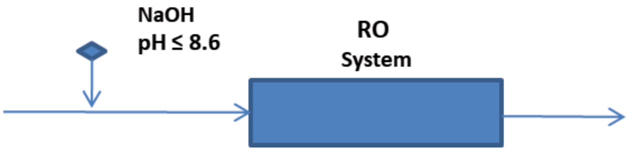


Fig. 2. Single-pass system with pH adjustment.

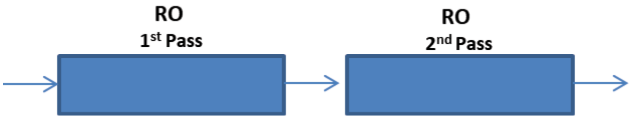


Fig. 3. Dual-pass system.

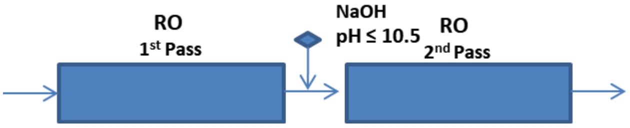


Fig. 4. Dual-pass system with pH adjustment.

3.2.1. Capital cost

The need of higher production in the first pass would imply a larger system to be able to meet new production requirement. This includes larger pretreatment, pipework diameter, valves, and pumps of 1st pass RO. In addition, capital cost increases due to capital cost of a second pass, which also requires pipework, pumps, valves, instrumentation, pressure vessels, and RO membranes.

3.2.2. Operational cost

Operational cost due to new amount of consumables also increases. A higher capacity of first pass would require higher chemical consumption to maintain the same dosages. This includes higher amount of coagulant, antiscalant, sodium metal bilsulfite, or hypochlorite.

3.2.3. Energy cost

The energy consumption would also go up due to larger pumps required to transfer higher volumes in a first pass and operation of a second pass. On the other hand, a second pass would make possible to use membranes with higher permeability as boron rejection would be increased with an additional pass. Membranes with higher permeability would require less energy consumption in a first pass.

3.3. Dual-pass system with pH adjustment (Fig. 4)

A dual-pass system with pH adjustment would have the same expenses associated with a two-pass system as described above. In addition, there is an additional cost of a new dosing system to adjust pH in a second pass, which would be similar to the cost shown for a single-pass configuration.

All the solutions to improve boron rejection incur additional overall cost for a project. Therefore, improved membrane boron rejection has always been targeted as a very important membrane asset by all membrane manufacturers.

4. Pembroke desalination plant

Malta is an archipelago of three islands situated in the Mediterranean Sea. There are no rivers of any significance on the islands, and the sparse annual rainfall is only about 500 mm. Due to the lack of fresh water, the Government decided to invest in RO desalination capacity. In 1983, the first SWRO facility in Ghar Lapsi became operational. This was followed by a second plant at Cirkewwa in 1988 and a third plant at Pembroke in 1994 [10]. The Water Service Corporation is the public institution in Malta responsible for the supply of water to the population [11] and therefore responsible for the operation of the desalination plants.

Pembroke desalination plant is located in the main island. The plant has the capacity to produce 54,000 m^3/d of water on 12 single-pass trains at 45% [10]. The levels of boron and conductivity of the water produced are very restrictive: boron must be below 0.9 ppm and conductivity below 400 μS/cm. LG Chem was selected in 2015 to partially retrofit the membranes for the three different desalination plants including Pembroke where the membranes from 8 trains were replaced. The specifications of the plant are shown in the following Table 1:

The plant diagram can be found in Fig. 5:

Table 1
Pembroke desalination plant specifications

Client	Water services corporation
Start-up date	2016
Feed water intake	Sea water
Application	Potable water
Plant configuration	8 trains (currently 6 in operation), 45 pressure vessels each, 7 elements per pressure vessel
Recovery	42%
Project capacity	36,000 m^3/d (9.5 MGD)
Feed temperature range	20°C–22°C (68°F–72°F)
LG Chem NanoH$_2$O™ membrane model	LG SW 440 GR, LG SW 440 SR
Total number of LG Chem NanoH$_2$O™ elements	2,520 (1,890 installed)
Feed pressure range	65–67 bar (943–972 psi)
Permeate boron	0.45–0.63 ppm

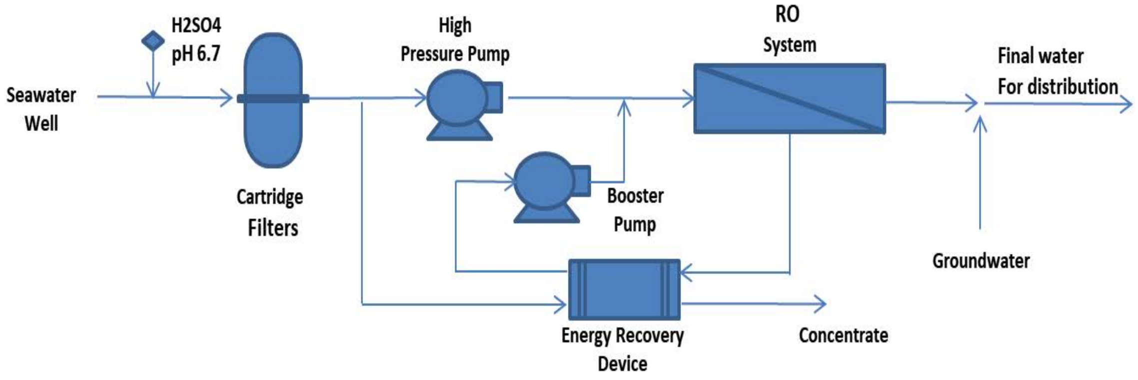


Fig. 5. Pembroke desalination plant diagram.

The water intake is coming from beach wells with a silt density index below 1. pH is adjusted with sulfuric acid down to 6.7 in order to protect the pipework further downstream. After pH adjustment, cartridge filters are installed upstream the RO unit. There is energy recovery device installed in parallel with the high-pressure pump. The final permeate water is blended with groundwater before being distributed to the network. The temperature range is very stable between 19°C and 22°C. The cleaning in place (CIP) frequency varies between 6 and 10 months depending on the train condition and time of operation.

A membrane hybrid configuration was selected for the installation. The models of LG Chem membranes installed are shown in Table 2:

The first trains with thin-film nanocomposite (TFN) membranes started operating in March 2016.

4.1. Operational and normalized data

The operational and normalized data for 5 out of 8 trains currently installed with LG Chem membranes are shown in Fig. 6. The membranes were installed progressively, and at present, 8 trains have been retrofitted.

From the data in Fig. 6, it can be observed that the permeate conductivity was maintained stable and below 200 µS/cm, significantly lower than the maximum admissible limit of 400 µS/cm. The feed water conductivity and temperature are stable averaging around 60,000 µS/cm and 20°C–21°C, respectively. Feed pressure is also stable varying between 65 and 67 bar since the start-up. This is well aligned with the data obtained with Q+ Projection Software from LG Chem as shown in Fig. 7.

In Fig. 8, the normalized data shows a stable normalized permeate flow with a gradual decline as the membranes were

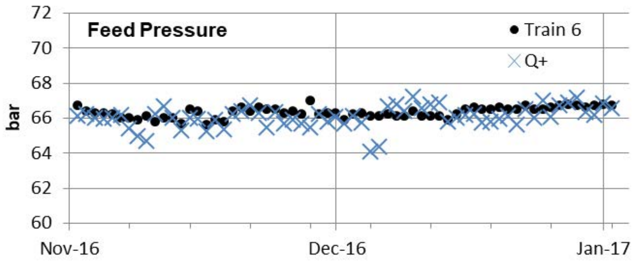


Fig. 7. Q+ Projection Software feed pressure vs site readings.

Table 2
Membrane models installed

Model	Surface (ft²)	Flow (gpd)	Salt rejection (%)	Boron rejection (%)	Feed spacer (mil)
LG SW 440 SR	440	6,600	99.85	93	28
LG SW 440 GR	440	8,250	99.85	93	28

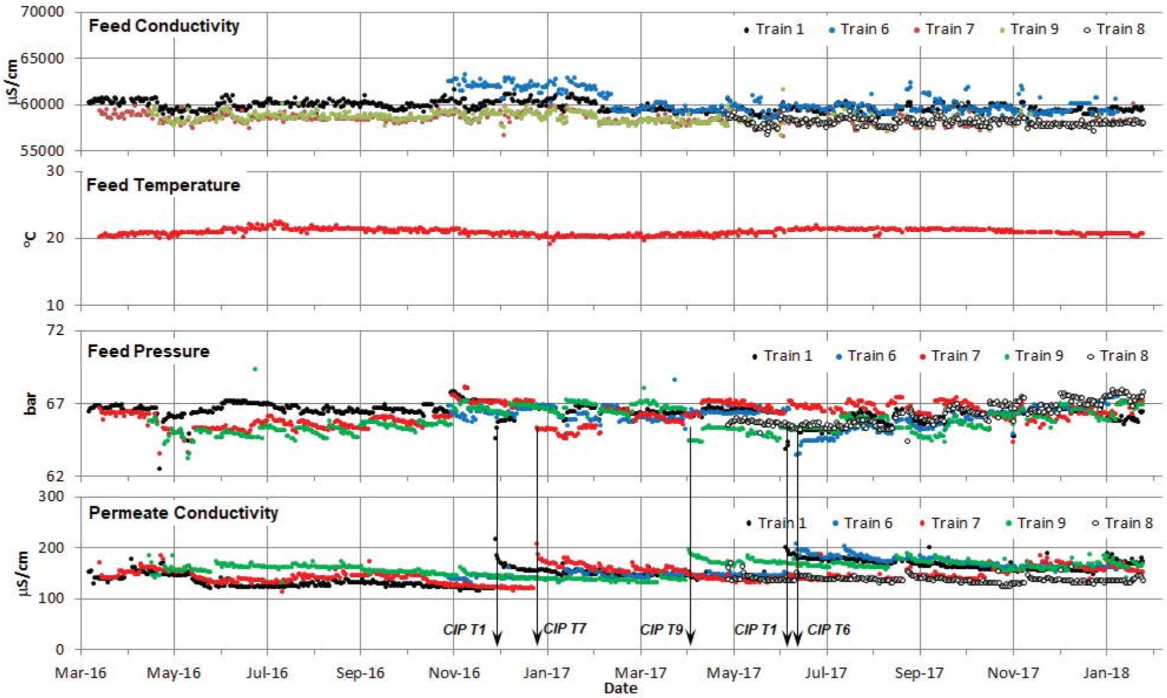


Fig. 6. Operational data.

getting fouled. The flow recovered well after performing CIP. Normalized salt rejection averaged around 99.8%, a value more commonly expected from a single element.

The data shown in Fig. 8 was obtained from QSee Normalization Software from LG Chem.

4.2. Boron rejection

The boron requirement for the permeate water in this project is 0.9 ppm. The feed pH due to the adjustment in the pretreatment is 6.7 before entering the RO system. As explained previously, the boron rejection is improved with higher pH as the ionization rate of boric species becomes higher, increasing the presence of borate which is well rejected by RO membranes.

Fig. 9 shows the evolution of the boron concentration in the permeate water from the different trains.

The results displayed in Fig. 9 show a boron feed concentration between 4.72 and 4.89 ppm. The permeate boron concentration from all trains is around 0.5 ppm with three trains being in operation for over 2 y.

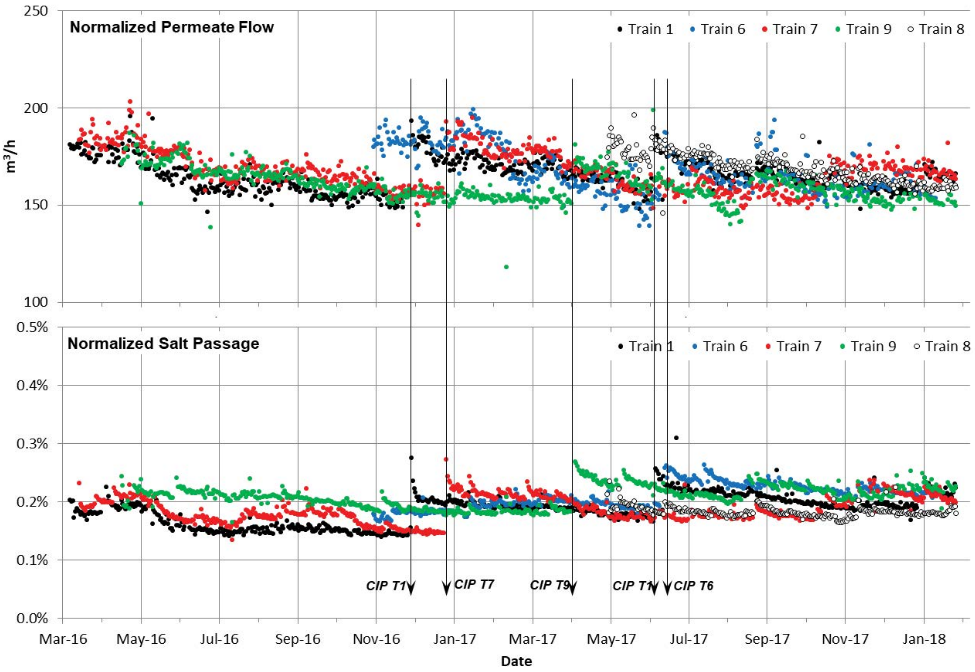


Fig. 8. Normalized data.

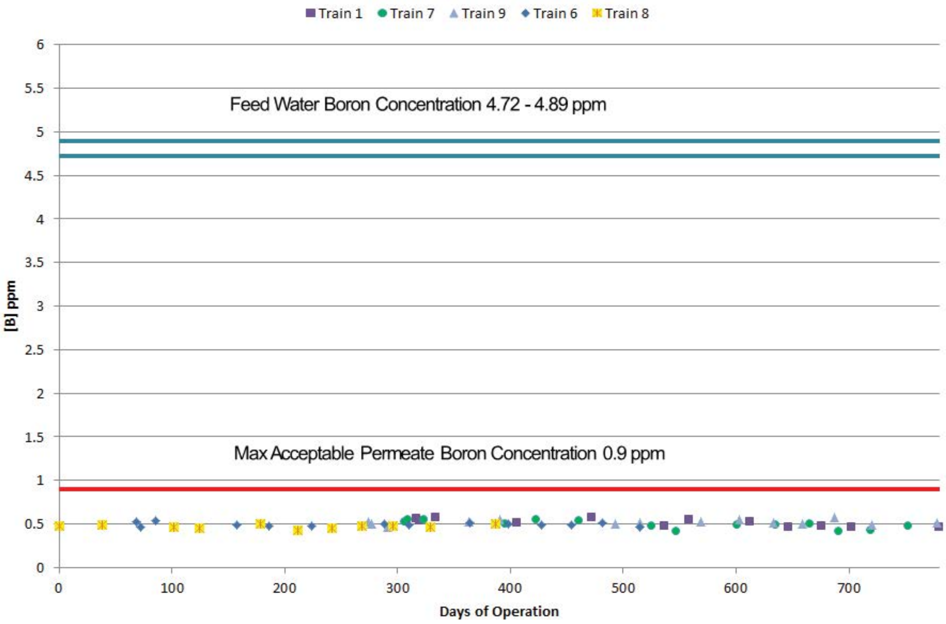
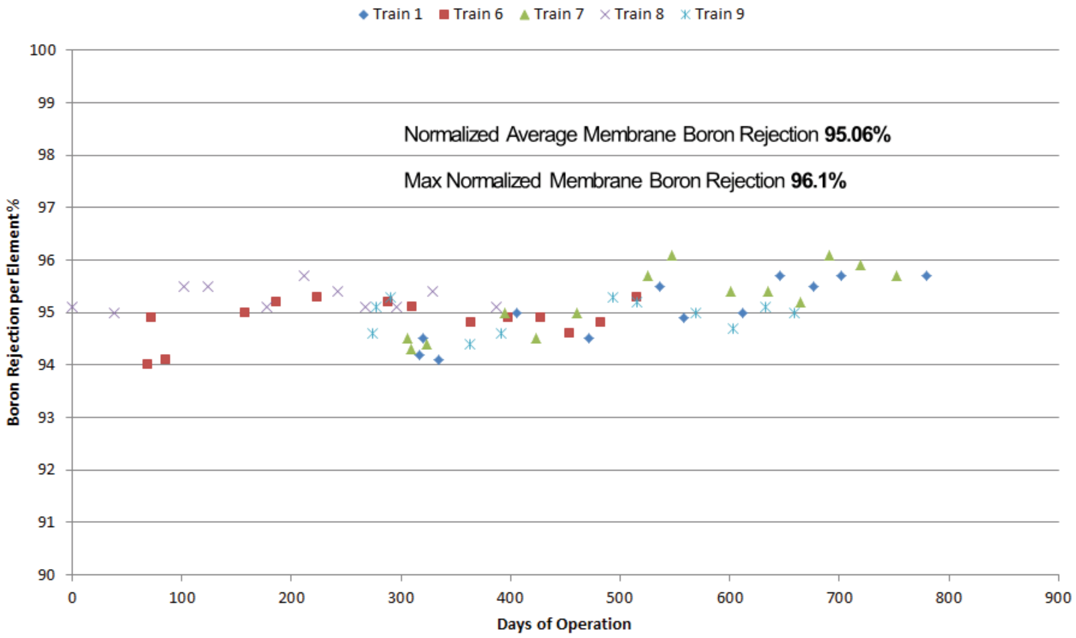


Fig. 9. Feed and permeate boron concentration.



* Boron rejection normalized using LG NanoH2O's Q+ software under the standard SWRO test condition: 800 psi, 32,000 ppm NaCl, 5 ppm Boron, 8% recovery, pH 8, and 25 C

Fig. 10. Normalized boron concentration at the standard SWRO test conditions.

Using Q+ Projection Software v2.4, a study was performed to estimate the average normalized boron rejection of the membrane configuration used in this project at the standard SWRO test conditions (800 psi, 32,000 ppm NaCl, 5 ppm of boron, 8% recovery, pH 8, 25°C). The results obtained are shown in Fig. 10.

Fig. 10 shows an average normalized boron rejection of 95.06% with a maximum normalized boron rejection value of 96.1%.

5. TFN membranes and potential mechanism for boron rejection

TFN membranes differ from the conventional thin -film composite membranes by the presence of special nanomaterial in the active layer. The presence of nanomaterials in the polyamide layer renders RO membranes more permeable for water without a significant increase in salt passage. The resulting membranes possess an average salt rejection up to 99.85%.

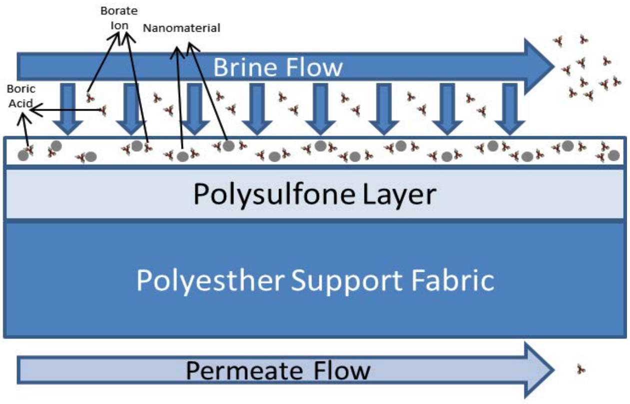


Fig. 11. Potential boron rejection mechanism.

This study suggests that the presence of the nanomaterial in TFN membranes has also a beneficial effect on their boron rejection. It is speculated that the nanomaterial has a high selectivity to boron through a binding mechanism by capturing boron species through a covalent attachment and forming internal coordination complexes that are stable over a wide range of pH. This proposed mechanism is shown in Fig. 11 and it needs to be experimentally verified in further studies.

6. Conclusions

- Boron removal in water desalination is still a challenge in many countries mainly due to its use for irrigation purposes.
- Boron rejection by reverse osmosis (RO) membranes is strongly influenced by feed temperature, pH, and ionic strength of the solution.
- Commonly used methods to further improve boron rejection through RO systems result in higher capital and operational costs.
- TFN membranes show very good boron rejection performance during long-term operation in Pembroke desalination plant at low pH (6.7).
- Normalized membrane boron rejection at the standard test conditions for seawater for the membrane configuration used at Pembroke desalination plant is 95.05% on average with maximum peaks recorded up to 96.1%.

- Possible boron rejection mechanism with TFN membranes suggests that boron species bind with the nanomaterial in the active layer over a broad range of pH.
- Future work is needed to prove the hypothetical mechanism of boron rejection by TFN membranes.

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