Boron removal by reverse osmosis membranes

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Abstract

While most of the chemicals present in water could be effectively rejected by reverse osmosis (RO) membranes, the removal of some trace elements such as boron is relatively low especially by RO membranes with a long service life. The interplay between pH and ionic strength is believed to be the key to understand the boron removal by RO membranes. Boron removal looks insignificant but is one of the challenging issues in membrane desalination industry especially to produce water for drinking or for irrigation of sensitive crops. Boron, with a pK_a value of 9.25, in water at low concentration is normally present in the form of boric acid, $B(OH)_3$, at around pH 7. It will then be dissociated into negatively charged form as borate, $B(OH)_4^-$, only at high pH. As a result, boron removal efficiency by RO membranes has typically been improved toward more than 99% through raising the pH to alkaline region and its removal mechanism has been suggested as either charge repulsion or size exclusion. However, boron removal by brackish water reverse osmosis (BWRO) membranes was reported to be 40 – 60% at neutral pH. Boron removal by BWRO membranes in this study was found to be 25 – 52% at pH 7.5.

It has been speculated that ionic strength of solution could alter the membrane surface characteristics, pK_a of boric acid, and transport of cation and anion between two sides of the membrane. Owing to several reports of lower pK_a value at higher salinity, one may expect to achieve better boron removal at higher salinity. Thus, there is a merit in investigating boron removal by various RO membranes at different salinities along with their respective zeta potentials. While the impact of salinity on zeta potential of RO membranes was similar, its impact on boron removal by BWRO membranes was different from that by SWC4+ and ESPAB membranes. RO membranes used in this

study showed negative zeta potential value at high pH. However, respective zeta potentials shifted towards positive values at higher salinity.

Even though pK_a value is lower at higher salinity for better boron removal, the result obtained in this study revealed that, at the same pH, boron removal at higher salinity was lower than that at lower salinity. Boron removal efficiency, at pH 10, for CPA2 membrane declined from 81% to 71% when NaCl concentration was increased from 500 mg/L to 15000 mg/L. At pH 9, the corresponding boron removal efficiency reduced more significantly from 61% to 45%. Boron removal by LFC1 and ESPA1 membranes also decreased with increasing salinity at pH 9. The shift of zeta potential towards positive value at higher salinity suggested that charge repulsion mechanism became less dominant.

Boron removal efficiency by ESPAB and SWC4+ decreased gradually when NaCl concentration increased towards 2000 mg/L at pH 9. However, removal efficiency improved again when NaCl concentration increased gradually beyond 2000 mg/L. This observation suggested that boron removal by these membranes at low salinity was partially contributed to charge repulsion mechanism. At higher salinity, size exclusion could be the dominant factor for boron removal by SWC4+ and ESPAB membranes.

This study also investigated the effects of salinity on zeta potential and boron removal by different RO membranes at pH 7. Impact of salinity on zeta potential of RO membranes was similar to that observed at pH 9. Zeta potential became positive at higher salinity. At pH 7, trends of boron removal by BWRO membranes were similar to those observed at pH 9. However, SWC4+ and ESPAB showed different boron removal trends at pH 7 from those observed at pH 9. Since there could only be negligible amount of borate ion formation at pH 7, lower boron removal by BWRO membranes at higher salinity might be attributed to enhanced diffusion. In contract, stable boron removal by SWC4+ and ESPAB observed across all salinities suggested size exclusion as the mechanism of boron removal by these two membranes. The results from this study and other reports suggested that it should be an effective strategy to improve boron removal at raised pH in second pass RO systems. BWRO membranes should be suitable choice as their boron removal efficiencies would be highest at lower salinity. High boron rejection membranes should be used as the first pass RO in a desalination system as high salinity present in seawater would not hamper boron rejection by such membranes.

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Nomenclature

BWRO	Brackish water reverse osmosis
c_w	Feed salt concentration at membrane surface (kg/m^3)
c''	Concentration of salt in permeate (kg/m^3)
C_{avg}	Bulk fluid interfacial concentration between feed & permeate (mol/m^3)
C_A, C_B	Concentration of permeate and feed adjacent to membrane (mol/m^3)
C_f, C_c and C_p	Concentration of solute in feed, concentrate and permeate (mol/m^3)
CA	Cellulose acetate
dU	streaming potential
dp	differential pressure
D_p	Hindered diffusion coefficient of solute through membrane (cm^2/s)
D_w	Real diffusion coefficient of solute in water (cm^2/s)
EKA	Electro kinetic analyzer
FO	Forward osmosis
FTIR	Fourier transform infrared spectroscopy
H	Partitioning coefficient (dimensionless)
HPLC	High performance liquid chromatography
ICP-OES	Inductively-coupled plasma optical emission spectrometry
J_w or J_v	Water flux (m^3/m^2-s)
J_s	Solute flux (mol/m^2-s)
K_w	Mass transfer coefficient of water (m^3/m^2-s-Pa)
K_s	Mass transfer coefficient of solute (mol/m^2-s)
L_p	Solvent permeability (m^3/m^2-s-Pa)

LSMM	hydrophilic surface modifying macromolecule
l	Membrane thickness (m)
MF	Micro-filtration
NF	Nano-filtration
NMR	Nuclear magnetic resonance
NOM	Natural organic matter
O&M	Operation and maintenance
P_w	Water permeability (m^3/m^2-s-Pa)
P_s	Salt permeability (m/s)
pK_a	Dissociation constant
PES	Poly-ether-sulfone
ΔP	Pressure difference across the membrane (Pa)
Q_p	Permeate flow (m^3/s)
R	Gas constant (J-atm/K-mol)
RO	Reverse osmosis
SD	Standard deviation
SWRO	Seawater reverse osmosis
t	Time during the diffusion test period (s)
T	Absolute temperature (K)
TDS	Total dissolved solid (mg/L)
TFC	Thin film composite
UF	Ultra-filtration
UPW	Ultrapure water
V_A	Volume of the feed side of membrane (m^3)
V_B	Volume of the permeate side of the membrane (m^3)

WHO	World health organization
$\Delta\pi$	Osmotic pressure difference of feed & permeate at membrane surface (Pa)
ε	dielectric coefficient of water
ε_0	vacuum permittivity
η	viscosity
κ_B	electrolyte conductivity
ω	Solute permeability (mol/m^2-s-Pa)
σ	Molecular reflection coefficient (dimensionless)
ζ	Zeta potential (mV)

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Chapter 1 Introduction

Since the cellulose acetate (CA) asymmetric reverse osmosis membrane was developed and commercialized for large-scale applications (Sourirajan and Matsuura, 1985), many RO systems have been installed in different industries. Owing to process simplicity, flexibility and good performance characteristics, RO systems have been extensively used for seawater desalination and water reclamation since 1970s. Membrane materials and performance have been improved significantly over time. In the early stage of industrial applications, lower operating pressure, lower fouling and lower total dissolved solid (TDS) in RO permeate were the major considerations to design a membrane separation system for drinking water production. Subsequently, it was found that there would be a need to minimize other trace elements such as boron in RO product as well. For example, although boron is an essential micronutrient for plants and animals, it causes toxicity to plants and disturbs reproduction of animals at higher concentration. According to the third edition of WHO guideline for drinking water quality, boron concentration was set at 0.5 mg/L as the limit (WHO, 2004). It is slightly higher than the 0.3 mg/L stipulated in the previous edition of guideline. The revision made in the latter edition was attributed to limitations of most treatment technologies that were considered economically feasible at that juncture.

1.1 Background of the study

Membrane process such as ultra-filtration/micro-filtration (UF/MF) followed by nano-filtration (NF) or RO has been quickly becoming popular for wastewater treatment and water reclamation in recent decades. A study on the reuse of electroplating rinse water reported that high iron content in the solution could be the reason of enhanced boron removal by RO membranes (Qin *et al*., 2005). This phenomenon might be attributed to either co-precipitation, flocculation or complex formation reaction occurred before boron was removed by membrane. While boric acid may form hydrogen bond with iron oxide for co-precipitation, it is also possible that boric acid is linked with hydroxyl molecules to form a complex. Complex formation is similar to the working principle of boron-selective ion exchange resin where it could also be termed as chelating process. Generally, boric acid may undergo transformation into larger complex molecule for better removal by RO membrane.

However, the reported phenomenon could not be reproduced with synthetic solutions that contain only boron and specific metal salt. This observation might be attributed to iron being present in the other form of complex together with some organic compound such as glycol. Boron removal, likes the removal of other ions, by RO membrane is still unresolved whether it is by charge repulsion, size exclusion or enhanced diffusion under different conditions for different membranes. Thus, it is necessary to investigate and understand the mechanism of boron removal while taking into account of factors such as salt concentration and membrane characteristics. Although complex formation with diols has been reported to be a possible alternative for enhanced boron removal by RO membranes, the amount of chemical dosage needed to achieve good boron removal efficiency should be improved for practical application.

In the absence of complex formation, interaction of membrane surface characteristics and ionic strength of solution at different pH could be the factors that influence the boron removal mechanism by different types of RO membranes. Boron removal mechanism should be investigated together with solution chemistry and its interaction with membrane which can be changed under different operating conditions. In addition, it is necessary to look into boron removal under different situations and results obtained should be analyzed in relation to possible removal mechanism. With a better understanding of removal mechanism, it would enable one to select suitable membrane and optimize the operating conditions for seawater reverse osmosis (SWRO) plants. Removal of boron in the context of a large-scale system normally requires an optimal operating condition that could accommodate the effects of aging membrane and fluctuation of solution characteristics including temperature.

1.2 Boron removal by RO membranes and other processes

Boron removal by a single-pass RO process for seawater desalination is generally not sufficient to produce drinking water that satisfies water quality standard in terms of boron. Generally, boron content in seawater is about 5 mg/L but it may vary within the range of 4 – 15 mg/L depending on locations around the world. While boron removal by new generation seawater RO membranes reported by some manufacturers was approximately 91 – 93% (Taniguchi *et al.,* 2001 and 2004; Toray, 2008) at nominal test condition, maximum removal efficiency achieved by conventional brackish water RO membranes has been in the range of 40 – 60% (Pastor *et al*., 2001; Prats *et al*., 2000). Thus, boron removal has always been one of key challenges for desalination industry especially to produce drinking water or water for irrigation of sensitive crops. In practice, salt rejection efficiency normally decreases as membranes become old. Therefore, even with the highest rejection RO membranes, it has not been able to ensure that a single-pass RO system can produce drinking water that meets the boron level stipulated in WHO guideline (WHO, 2004) over the entire service life of membrane. As a result, additional steps or processes have been required during the installation of overall desalination plant. In fact, different methods for boron removal (Choi and Chen, 1979; Okay *et al.,* 1985), in combination or individually, were studied extensively in the past. These include adsorption (Karen and Bingham, 1985; Keren and Gast, 1983; Polat *et al.,* 2004), ion exchange (Simonnot *et al.,* 2000; Nadav, 1999), electrodialysis (Melnik *et al.*, 1999; Zalska *et al.*, 2009), reverse osmosis (Taniguchi *et al.,* 2001 and 2004; Pastor *et al.*, 2001; Prats *et al.*, 2000; Glueckstern *et al.*, 2003; Magara *et al.*, 1998; Oo and Song, 2009; Oo and Ong, 2010), electrocoagulation (Yilmaz *et al.*, 2005), co-precipitation (Sanyal *et al.,* 2000), membrane distillation (Hou *et al.*, 2010), adsorption with magnetic particles (Liu *et al.*, 2009) hybrid membrane process (Bryjak *et al.*, 2008) and facilitated transport (Pierus *et al.*, 2004). Table 1.1 summarizes the respective applications of each process and their pros and cons. Most of the studies on boron removal by RO membranes overlooked the impact of salinity.

Table 1.1 Pros and cons of different boron removal processes

Process	Applications	Boron level	Advantages	Disadvantages
Reverse osmosis	Desalination, and reclamation.	1–35 mg/L	Flexible to run. Good removal at high pH.	Need high pH for good removal. Risk of short membrane life.
Ion exchange	Desalination, reclamation, and ultra-pure water.	2–500 mg/L	>99% removal. Selectively remove boron.	Need chemicals for regeneration and disposal of chemical.
Adsorption	Wastewater	100 mg/L	Low initial cost. Can handle high concentration.	Long contact time, and unable to attain low level of boron in product water.
Precipitation	Wastewater	5 mg/L	Low initial cost. Can handle high concentration.	Long contact time, and unable to attain low level of boron in product water.
Electro-dialysis	Pure water	4.5 mg/L	>99% removal.	Require high energy input.
Hybrid membrane	SWRO permeate	5 mg/L	>99% removal.	Need chemicals. Resin abrasion.

For desalination industry, second pass RO at raised pH could be the best option to achieve the low level of boron in product water. However, ion exchange process might be included for reduction or optimization of total operation cost where it is acceptable for partially compromised product salinity. This is because salinity of product water from second pass RO will be lower than that treated partially or fully by boron-selective ion exchange process. Other processes such as adsorption and precipitation are more suitable for wastewater with high boron concentration. For ultra-pure water production, ion exchange resin is mainly used for removing trace level of boron. More details of reported studies in terms of test capacity, operating cost and references are tabulated in Appendix 1.

Influence of solution chemistry, process material, unit process and operating conditions of different methods were widely explored in the past. While solution chemistry such as pH, concentration and temperature are normally adjusted to optimize the performance of respective processes, operating conditions such as percent recovery, operating pressure and hydraulic pattern in RO system also affect the rejection efficiency while treating the boron containing water. Generally, higher flux, higher operating pressure and faster cross-flow velocity will improve the salt rejection of RO membrane. In addition to these factors, performance of RO membranes also depends on other factors such as membrane characteristics, charge density, ionic strength of the solution, and interactions among them. It has also been noted that negatively charged membrane could improve rejection of anions and higher charge density could enhance the diffusion of ions across membrane. In the past, boron removal by RO membranes was studied typically at different pH and separately from conventional methods such as coagulation due to the potential of severe fouling on membrane. Although there have been some studies of concentration impact on removal of major ions, very limited studies can be found regarding the impact of salinity on trace element removal by RO membranes. On the other hand, membrane surface characteristics in terms of zeta potential was normally measured at different pH in the study of RO membrane fouling (Elimelech and Childress, 1996; Gerard *et al*., 1998). Other studies on the relation of zeta potential and pressure gradient or salt rejection measured the membrane surface potential at different pH, too (Deshmukh and Childress, 2001; Ernst *et al*., 2000; Matsumoto *et al*., 2007). Thus far, there has been a lack of study on changes of membrane surface potential at different salt concentrations and implication of those changes on trace element removal.

Owing to the stringent water quality requirement and discharge standard, researchers have been exploring different approaches to improve boron removal. Taniguchi *et al.* (2001) conducted a study on new generation of SWRO membranes and found that boron rejection on Asian seawater desalination could achieve a level greater than 90% under standard test conditions (in a solution of NaCl 32000 mg/L and operates at 800 psi for 10% recovery at 25 °C) with a new membrane. From the study, it was concluded that SWRO followed by BWRO at high pH for the first pass permeate and the boron-selective resin for the BWRO concentrate was the most cost-effective process to achieve a low boron concentration in the product water. Their study did not elaborate further on boron removal mechanism and importance of inter play between pH and salt concentration on boron removal. Although removal mechanism was briefly speculated as size exclusion, there was no in-depth discussion or other attempt to support their assumption. As the type of membrane tested was limited to SWRO, there has been a lack of suggestion to adopt a suitable type of RO membrane for boron removal under different situations. Thus, it is necessary to find a better way to support the assumption on removal mechanism and to extend the investigation to different type of RO membranes too.

Pastor *et al*. (2001) analyzed the impact of pH on boron removal by RO membranes and projected the extra cost needed for boron removal. It was suggested that treating the first pass RO permeate at a pH of 9.5 would cost an extra € 0.06 per m^3 of product water. Other researchers also explored the influence of recovery and pH on boron removal and concluded that the process could be further improved at pH higher than 9.5 (Prats *et al.*, 2000). Glueckstern *et al*. (2003) conducted a field test to validate the optimization of boron removal in old and new SWRO systems. One of the studies on boron removal even proposed to raise pH at second or third pass to avoid potential scaling on membranes (Magara *et al*., 1998). Although raising the pH of second pass RO feed is a possible option to improve boron removal, long-term performance of RO membrane at such aggressive condition is still not well understood. Suggestion by Magara *et al.* (1998) to raise pH at third pass seems to be impractical too. Understanding of boron removal mechanism under different conditions and selection of suitable RO membranes for different steps in desalination or water reclamation RO system should be further investigated to achieve better boron removal. Magara *et al.* (1998) also reported that boron rejection did not depend on feed boron concentration when it was lower than 35 mg/L. In most of the studies on boron removal by RO membranes, better boron removal at higher pH was linked to the transformation of the negatively charged borate ion and negative membrane surface potential. The phenomenon of better boron removal by RO membranes at high pH seems to be attributed mainly to the charge repulsion mechanism as described in most of the studies. Impact of salinity was generally ignored.

Studies on boron removal have typically been focusing on one or two membranes and suggesting the removal mechanism based on observed data of boron removal. Although some researchers attempted to propose removal mechanism, there has been a lack of supporting data such as measured membrane surface characteristics under respective testing conditions in their studies. It should also be noted that when pH is raised to achieve better boron removal by SWRO, percent removal increases from 90+ % to 99+ %. When higher pH of up to 11 is applied to BWRO membranes, boron removal efficiency also improves from 40 – 60 % to 99+ %. This observation suggested that charge repulsion effect could be more pronounced in BWRO for solute rejection. However, it might only be correct at certain salt concentration which is normally below 1500 mg/L and for specific type of RO membranes. Salt passage or rejection by RO membrane depends on salt concentration too. Generally, salt passage improves towards higher salt concentration up to 1500 mg/L and starts to decline at higher concentration for typical BWRO membranes (Bartels et al., 2005). Thus, it would be interesting to further investigate the impact of higher salt concentration and pH on membrane surface characteristics and boron removal by different types of RO membranes.

On the other hand, the study by Schäfer *et al.* (2004) highlighted the importance of ionic type and concentration which may cause Donnan effect, in affecting the solute transport across membranes. With a higher concentration of divalent ion, rejection of monovalent ion by NF membrane could become negative. It has also been reported that transport of trace elements such as chromate, arsenate and perchlorate through membranes could be faster at higher ionic strength (Yoon *et al.,* 2005). Although their study did not address boron removal, impact of ionic strength should be considered in the study of removal for other trace elements such as boron by RO membrane. They reported that solute permeability decreased with increased pH and decreased conductivity. One of the studies analyzed the effect of feed water concentration on salt passage in RO membranes (Bartels *et al*., 2005). Their results indicated that percent salt passage increased almost double if the feed NaCl concentration was increased from 1000 mg/L to 10000 mg/L. However, higher salt passage at higher feed salinity may not be universal for all membranes and therefore needs further analysis. According to technical information of Hydranautics, permeate salinity in terms of TDS seems to increase linearly with feed TDS from 500 to 6000 mg/L. Yezek *et al.* (2005) reported that variation of ionic strength allowed evaluation of Donnan partitioning and diffusion of metal ions through charged thin film and their approach might explain the diffusion of trace elements at high ionic strength and neutral pH. Impact of ionic strength on salt rejection does not seem to be universal and may also act differently for boron removal. Thus, there is a need to study the interplay of pH, salinity and membrane surface potential on RO performance.

Effect of solution pH to improve boron removal by RO membranes has been reported extensively in the past and the importance of the charge repulsion between borate ion and negatively charged membrane surface has been suggested repeatedly (Glueckstern *et al*., 2003; Magara *et al*., 1998; Pastor *et al.,* 2001; Prats *et al.,* 2000). However, contributions of charge repulsion and size exclusion on boron removal by RO membranes have not yet been well understood. In addition, impacts of other factors such as ionic strength of the solution on boron removal has not been taken into consideration in most cases. In other words, not much research work has been conducted on impacts of ionic strength on changes of mass transfer of minor ions, membrane surface potential, complex formation and ultimately boron removal. In fact, some of the studies (Geffin *et al*., 2006; Wilf, 2007) literally suggested that a better boron removal could be expected at higher ionic strength of the solution. This postulation requires further investigation and verification for different types of membranes. Otherwise, it could be misleading to select suitable membrane and to design an optimal membrane system. There is a need to support the proposed mechanism practically with experimental results and relevant transport principles. The other review of boron removal for seawater desalination also indicated similar postulation (Kabay *et al*., 2010). They simply stated that handling higher salinity seawater understandably lead to better boron rejection than handling brackish or geothermal water. In fact, it is most likely that structure of membrane to handle seawater should be tighter than that of brackish water RO membrane. Although higher salinity could lead to formation of more borate ion, enhanced boron removal by RO membrane needs to be verified. Higher salinity could affect not only the shift of pK_a value but also the membrane surface characteristics. Study on transport of major ions at different ionic strength is also very limited.

One of the recent studies (Geffin *et al.,* 2006) revisited the use of mannitol to form boron-diol complex for enhanced boron removal by SWRO. The need of mannitol to boron molar ratio at 5 – 10 was notably very high and it would not be practical or economical to dose such a large amount of chemical in large-scale RO plants. Theoretically, molar ratio of 0.33 – 0.66 should be sufficient to form boron mannitol complex. Requirement of a high dosage of mannitol could be due to the fact that diol in suspension has limited opportunity to be in contact with boron to form a complex which can easily be removed by the membrane. Therefore, it would also be interesting to explore other chemicals for enhanced boron removal by RO membranes. Since membrane surface charge plays an important role in salt rejection, alteration of membrane surface to be more negatively charged by adding anionic surfactant, without causing membrane fouling, could also be an alternative to enhance boron removal by RO membrane. In general, limited work has been published to explain the transport of trace ions through RO membranes under the influence of high salinity and different pH on different types of RO membranes.

1.3 Objective of the study

The main objective of this study is to investigate the suitable approach for optimized boron removal and better understanding of different boron removal mechanisms by respective RO membranes. This study further investigated the effects of pH, salinity, interplay between them and respective surface potentials on boron removal mechanisms by different types of RO membranes. In addition, research work has been extended to the verification of potential complex-forming agents to enhance boron removal. Attempt was also made to propose the contribution of size exclusion and that of charge repulsion under different situations on boron removal by RO membranes.

In order to achieve the objective, following scopes of work were explored.

a) Verification of membrane surface potential at different ionic strength.

b) Effects of ionic strength, pH and flux on boron removal.

c) Effects of other components on enhanced boron removal.

1.4 Overview of the dissertation

This dissertation is organized into 5 chapters. Chapter 1 contains an introduction of background, current state of study and objectives of this study. Literature review of other studies on boron removal and research needs are presented and discussed more details in Chapter 2. Chapter 3 describes the materials and methods used in this study and Chapter 4 presents the results obtained and discussions on boron removal under different test conditions. Finally, Chapter 5 provides the conclusion of this study and some recommendations for future work.

Chapter 2 Literature Review

2.1 Studies of boron removal in the past

Taniguchi *et al*. (2001 and 2004) developed a procedure to estimate boron in the RO permeate in relation to measured salt permeability. Their analysis was based on concentration polarization model developed by Kimura (1995). Firstly, membrane transport parameters such as salt permeability and mass transfer coefficient were calculated from water flux and salt rejection data. The permeate quality was then estimated under various operating conditions such as different pressures and temperatures. However, changes of membrane characteristics and performance under different salt concentrations were not considered and included in their estimation. Taniguchi *et al.* (2001) did not directly estimate the boron level from transport parameters of target membrane. In fact, they used the flux and rejection results from the experiments to indirectly estimate the respective salt and boron permeability using the model of Kimura. They then established a correlation to estimate the boron concentration from the measured salt concentration. Boron permeability was approximated at 94.3 times of the salt permeability. Since it was conducted for specific membrane, UTC-80, and salt concentration of 35000 mg/L, it will be necessary to establish a correlation for each application with different membranes.

Result presented in the study of Prats *et al*. (2000) could be a good example of the necessity to establish relation of boron concentration and TDS in permeate of each membrane. In their study, membrane-1 with the lowest salt rejection performed better than membrane-3 in terms of boron removal. Although the data is not applicable to all applications and different membranes, it could be a good idea for membrane systems that have on-line data of RO permeate TDS or conductivity to establish a relation for estimating the boron level in the product water. Estimation of boron in the field would require data collection for a range of water quality, operating conditions and seasonal effect. In addition, calibration would be required from time to time because performance of membrane would be different along its service life.

Taniguchi *et al*. (2001) also used the chemically degraded membranes to relate experimental data for forecasting the concentration of boron in RO permeate. Chemical degradation of RO membrane was performed at 10, 20 and 40 mg/L of NaOCl. Although boron removal was suggested via molecular size, they indicated that further study is necessary to determine the mechanism of boron removal which may include contribution of electrical charge of both membrane and ions. When boron in the feed was 4.0 mg/L, boron in permeates of new and chemically degraded SWRO membranes were found to be 0.2 and 1.0 mg/L, respectively. The results fall well within the typical range of SWRO performances. In addition, they proposed a chlorine degradation mechanism of aromatic polyamide membrane and suggested that mechanical degradation would not affect boron rejection as much as salt rejection. From the results, they proposed that boron removal could be mainly related to molecular size but did not rule out charge repulsion too. Thus, it is necessary to further investigate the mechanism of boron rejection by RO and to find out the effects of membrane pores and electrical charges under different operating conditions. Type of membrane, solution chemistry and their interaction might also play different roles in boron removal. More recently, Taniguchi *et al*. (2004) conducted another study on new generation SWRO membranes and found that boron rejection on Asian seawater desalination could achieve as high as 95%. Besides, they concluded that SWRO followed by BWRO at high pH and boron-selective resin treating some of BWRO concentrate could be the most cost-effective process to achieve a low boron concentration in the product water. Further investigation on boron removal mechanism by different types of membranes could enable process designer to better select the suitable type of membrane.

Magara *et al*. (1998) proposed the use of raised pH at third stage (pass) to avoid potential scaling. They noted that boron rejection does not depend on concentration when it is lower than 35 mg/L. Better boron removal at higher pH has been attributed to the charge repulsion between borate ion and membrane surface. No other factor was included in the examination of different boron removal at varying pH. Contributions of size exclusion and charge repulsion at different pH and salt concentrations on boron removal require further investigation. Effect of recovery on removal in the study of Magara *et al.* (1998) was calculated from overall recovery without any detailed explanation. If the permeate was withdrawn from the lead element side of pressure vessel, effect of recovery to improve product quality could be more significant at elevated pressure. This is because the lead element contributes higher percentage on overall product recovery at higher operating pressure. More water is produced at elevated pressure while salt diffusion rate through membrane might not be as fast as the water permeability. Thus, arrangement of membrane should be clearly described in their study. Although the use of a 2-pass system seemed to be logical, the merit of using a 3-pass system needs further investigation. Analyzing the results of permeate quality for a 3-pass system with and without pH adjustment did not clearly show the advantage of this system compared to that of a 2-

pass system. $Mg(OH)_2$ precipitation was described as the reason to raise the pH at third pass but there was no indication of Mg concentration to support the suggestion.

Similar to other studies which reported a reduction of boron in permeate below 0.5 mg/L by raising the pH of second pass RO feed, Magara *et al.* (1998) achieved a boron concentration of less than 0.2 mg/L by raising the pH to 10.3 at the second stage (pass) of a 2-pass system. However, it may not be practical to design such a system because membrane life span could be shortened at high pH and may even need to operate at pH > 10.3 when membrane aged. In addition, the effect of salinity on boron removal was not included and no indication of selecting suitable RO membrane was mentioned in their study. It is therefore necessary to investigate the performance of different membranes under different conditions for better understanding on boron removal and selection of suitable membrane for different stages of an RO system.

Study of Sagiv and Semiat (2004) is a good example of investigating the effects of RO operating parameters on boron rejection via numerical analysis. They noted that boron removal could be improved theoretically by lowering the operating temperature, increasing the applied pressure and raising pH of RO feed. Although it is theoretically possible to enhance boron removal by above factors, a better understanding on boron removal mechanism is required to improve surface characteristics of new RO membrane and selection of a suitable RO membrane for different feed water qualities. Their attempt to explain the boron removal mechanism is similar to the explanation by Pastor *et al.* (2001). Their explanation of poor boron removal at neutral pH was that uncharged boric acid diffused through the membrane, forming hydrogen bridges with the active groups of membranes. At higher pH, they suggested that borate ions were hydrated by dipolar water molecules that lead to an increased molecular size which in turn enhanced the rejection by RO membrane. These are the common assumptions which should be supported by different scenarios and measurements by analytical instruments on changes of solutions chemistry and membrane surface characteristics. Their numerical analysis was based on a single membrane and solution strength. In addition, they assumed that membrane surface characteristics would be the same under different operating conditions such as temperature, pressure, salinity and pH. The implications of these simplifications need to be further investigated.

Pastor *et al.* (2001) also claimed that their model could be a basis for cost analysis on improving boron removal by RO membrane. However, transport parameters are intrinsic properties of each type of RO membranes and thus may require adjustment. This could be done by introducing correction factors into their model to account for different applications, membrane types and ionic strength of the solutions. Their suggestion to optimize the boron concentration in permeate by splitting the permeate stream from lead and tail sides of RO vessel looks tedious but might be useful for some of the stringent applications. It was also reported that boron level could be lowest if the permeate is split at about the middle of RO vessel.

Pastor *et al*. (2001) analyzed the influence of pH on boron removal by RO membranes and the cost associated with RO systems. It was noted that treating the RO permeate with a raised pH of 9.5 or higher would cost an extra amount of € 0.06 per m^3 of product water. They tried to correlate the boron dissociation with membrane surface chemistry to explain low boron rejection by RO membrane at neutral pH. It was noted that boric acid at pH around 7 could form hydrogen-bridge (bond) with active group (amide in their example) of membrane material. Thus, boric acid could diffuse easily in a similar way as that of carbonic acid and water. When pH was adjusted to 9.5, rejection of boron removal by SWRO membranes became >99%. They pointed out that enhanced boron removal was due to the formation of more negatively charged borate at higher pH. According to pK_a value of boric acid, boric acid will still be about 30% of the total boron in solution at pH 9.5 and yet boron removal could reach >99% by SWRO.

Pastor *et al.* (2001) used a Toray membrane and reported 40% boron removal at pH lower than 8 and total boron removal was achieved at pH 9.5. If the membrane is SWRO, reported boron removal at low pH seems to be relatively low. On the other hand, typical BWRO membrane could not readily achieve >99% boron removal at pH 9.5. Their explanation of boric acid permeation at pH less than 8 is not consistent with that of total boron removal achieved at pH 9.5. At pH 9.5, boric acid still contributes about 30% of the total boron and membrane therefore should not be able to achieve 99% removal of boron. If there is diffusion or permeation of boric acid through the membrane for low boron removal at pH less than 8, boron removal could not possibly reach >99% at pH 9.5. Relationship between boron concentrations in permeate and boric acid percentage at different pH was not clearly established. It has not been clearly explained or proven that enhanced removal was achieved whether via charge repulsion alone or via charge repulsion plus size exclusion. In fact, there could also be a shifting of membrane surface potential at different salinities. It is also necessary to differentiate the contribution on enhanced boron removal due to charge repulsion. While boron in permeate was 60% and boric acid was 100% of total boron at pH 7.8, their respective percentage became 30% and 50% at pH 9.2. Finally, boron in permeate suddenly headed to 0% at pH 9.4 – 9.6. At pH 9.5, boric acid percentage just gradually reduced to 30% and reached 0% only at pH around 11.5. Later, they suggested that reason of total boron removal at pH 9.5 while boric acid contributes 30% of boron might be due to changes of membrane surface potential or characteristics. Thus, it is necessary and will be useful to investigate membrane surface characteristics such as zeta potential during the study of boron removal by RO membrane at different conditions. It is also necessary to look into the possibility that non-ionic and smaller boric acid could partly diffuse through membrane. If diffusion or incomplete size exclusion of boric acid is considered linear for SWRO membrane which can remove 80% of boron at neutral pH, boron passage due to boric acid should be around 20%, 6%, 2% and 1% at pH 7.5, 9.5, 10.0 and 10.5, respectively. It is because percentage of boric acid is calculated to be 100%, 30%, 10% and 5% of total boron in solution at the respective pH. In other words, at pH 7.5, boric acid contributes 100% of total boron and 20% of boric acid will pass through the membrane at 80% removal. At pH 9.5, boric acid contributes 30% of total boron and 80% of boric acid, which is 24% of total boron, should be removed. At the same time, borate ion contributes 70% of total boron. If 100% removal of borate ion is assumed, total boron removal should be 94% (24% from boric acid removal and 70% from borate ion) at pH 9.5. And, it is not clearly explained why the boron removal suddenly reached 99% at pH 9.5 when boron removal was only 40% at pH lower than 8 in the study of Pastor *et al*. (2001).

Prats *et al*. (2000) investigated the effects of pH and recovery rate on boron removal by different RO membranes. Their study was conducted using a 7.2 m^3/d plant with BWRO membranes from Hydranautics and Toray. Boron removal was 40 – 60% at pH 5.5 – 8.5 and it increased to >94% at pH 10.5. When permeate recovery was increased from 10 to 40%, boron removal improved from 33 – 44% to 50 – 59%. That is, 4 times higher in recovery could only increase boron rejection by 1.5 – 2 times. On the other hand, stretching the permeate recovery to 40% might be workable only for short-term study purpose. This is because membrane manufacturers normally do not recommend operating at more than 30% recovery for the two RO elements used in their study. While boron removal by membranes-1 and membrane-3 used in their study increased sharply after pH 8.5, the increase of boron removal by membrane-2 appeared only after pH 9.5. It will also be interesting to investigate the reason of slow response of membrane-2 to pH till 9.5 before boron removal improved. It might be typical characteristics of high boron rejection RO membranes. There was no further investigation of boron removal mechanism or other changes of membrane surface characteristics.

Generally, the results of enhanced boron removal observed in the study of Prats et al. (2000) were similar to those reported in other studies (Magara *et al*., 1998; Oo and Song, 2009; Pastor *et al*., 2001; Taniguchi *et al*., 2001). They also reported that boron removal improved when pH is higher than the pK_a value of boric acid. With a relatively short period of studies conducted, there is still a lack of information about long-term membrane performance at raised pH and explanation about the effects of potential changes in membrane and solution chemistry on boron removal. In addition to pH, salinity could also have impacts on membrane surface characteristics and boron removal.

Glueckstern *et al*. (2003) conducted a field test to compare the optimization of boron removal in old and new SWRO systems. They noted that additional operation and maintenance (O&M) costs would be 5 – 7 cents per m^3 of product water for old plant to reduce boron concentration from 5.3 to 0.4 mg/L at large SWRO systems (30 – 100 million m^3 per year) and 4.2 – 4.8 cents per m^3 for new plant. Power cost, chemical cost and water loss in their estimations are set at 4.5 cents/kWh, 1.8 cents/m^3 and 8%, respectively. Their cost estimations assumed that boron rejection by old plant is 88% whereas new SWRO plant could achieve 93% boron rejection. Variation of cost was due to the split ratio of permeate, percentage of permeate treated by second pass RO or ion exchange process. With more percentage of permeate treated by boron-selective ion exchange resin, it could be more economical but TDS of product water would be higher too. With the improvement of feed quality by better pretreatment and higher membrane permeability, additional O&M cost could be reduced to 2.0 – 2.5 cents per m^3 in the future.

With the introduction of feasible idea on splitting the permeate to optimize the capacity of second pass RO, their study could be used as an indicative guideline when boron removal is the main concern for both old and new desalination plants. Sample illustration of splitting the SWRO permeate was adapted and shown in Table 2.1. If SWRO product is to be treated 100% by BWRO membranes at raised pH indicated as optional system "A" in Table 2.1, SWRO system initially needs to produce 108% of final product water quantity. If SWRO product is to be split and further treated partially by both boron selective ion exchange (IX) resin and BWRO membranes, SWRO system will require to produce only 105% of final product. When SWRO product is treated 100% by BWRO membranes, Cl^- concentration of final product would be lower at 20 mg/L compared to 110 mg/L of optional system "B" in Table 2.1. Boron concentration of both systems will be same at 0.4 mg/L. However, it is necessary to adjust site specific operational and economic parameters on a case by case basis. In addition, it will be useful to conduct a pilot-scale study for 6 – 12 months in each application. It is also noted in their report that pK_a of boric acid could be shifted from 9.5 in zero salinity environment to 8.5 in seawater. While the trend of shifting pK_a to a lower value in their report is similar to other publications (Choi and Chen, 1979; Wilf, 2007), the pK_a value of 8.5 for boric acid could only be found in much higher salinity according to the literature (Adams, 1965).

Table 2.1 Alternative systems for optimal boron reduction (Glueckstern *et al.*, 2003)

ID of optional system	**Fraction of system product (%)**									
	SWRO system %		**Split %**		**BWRO system %**		**IX system %**		**Final product %**	
	Cl (mg/L)	B (mg/L)	Cl (mg/L)	B (mg/L)	Cl (mg/L)	B (mg/L)	Cl (mg/L)	B (mg/L)	Cl (mg/L)	B (mg/L)
A	**108%**		**NA**		**100%**		**NA**		**100%**	
	340	2.0	NA	NA	20	0.4	NA	NA	20	0.4
B	**105%**		**20%**		**60%**		**20%**		**100%**	
	340	1.42	70	0.74	25	0.4	400	0.1	110	0.4

***A**: option without split and IX treatment, 100% treated by BWRO.*
***B**: option with 20% split, 60% BWRO and 20% IX treatments.*
Note: Feed boron 5.3 mg/L, 88% boron rejection, pH 7.0.

Glueckstern *et al.* (2003) highlighted the difference of actual and nominal boron rejection by RO membranes. While membrane manufacturers normally indicate nominal rejection of 85 – 90% in their membrane specification sheets, actual rejections in commercial systems typically fall within the range of 78 – 80%. For advanced SWRO, nominal and actual rejections could be estimated at 92 – 94% and 85 – 87%, respectively. However, pilot tests in their study could obtain only 82 – 85% boron removal under field operating conditions. Thus, it is necessary to consider a safely margin for boron removal in designing a desalination system. If time and budget are permitted, a pilot study with a testing period of about 6 months in the field should always be conducted before finalizing the design of a large-scale desalination plant. System installation at a place with high energy cost should also consider the merit of incorporating ion exchange process for boron removal and to achieve maximum water production rate at the expense of a slight increase in product salinity. However, ion exchange process is not environmentally friendly as it requires the use of significant amount of chemicals to regenerate the exhausted resins. Boron-selective resin would not improve the product salinity, too. Sustainability of operating a RO system at very high pH is still a questionable debate for most membrane practitioners.

Kabay *et al.* (2010) revisited the boron removal studies for seawater and conducted a review on three methods; namely reverse osmosis, ion exchange and adsorption-membrane filtration. Although the 2004 edition of WHO drinking water standard set boron level at 0.5 mg/L as its limit, this value has recently been raised to 2.4 mg/L (WHO, 2011). This revision could be due to the fact that there have been no substantial evidences of boron toxicity on human health. However, most of the players in desalination industry still maintain 0.5 mg/L as the boron limit especially when the product water is intended to be used for sensitive crops for agriculture and for drinking. In the study of Kabay *et al.* (2010), it was stated that boron removal not only depends on pH but also on other factors such as temperature and salt concentration. However, no further information was given on results or trends of boron removal at different salt concentrations. Thus, it is necessary to look into the effects of salt concentration on boron removal and further investigate the mechanism behind boron removal by different types of RO membranes. They also referred to other reports and stated that higher boron rejection of seawater compared to brackish and geothermal water was due to higher salinity, which leads to a lower dissociation constant pK_a and more formation of borate ion. Actually, lower pK_a at higher salinity of seawater alone could not be the reason of better boron removal. The implication of this phenomenon will be further discussed in Section 4.2.2.

The review of Kabay *et al.* (2010) on function of ion exchange resin leads to the impression that boron-selective resins work on chelating of boron through a covalent attachment and formation of an internal coordination complex. Those resins are classified as macro-porous cross-linked poly-styrenic resins, functionalized with N-methyl-D-glucamine (NMG). While fixed bed ion exchange systems are still more practical, there are studies on using resin in suspension followed by micro- or ultra-filtration. These arrangements are referred to as adsorption-membrane filtration (AMF) hybrid process. Their advantages are stated as better sorbent capacity and lower power consumption. However, the studies are still at lab-scale testing and needs to be validated at larger and longer scale. Besides, resins in suspension could be exposed to enhanced abrasion and breakthrough of those resin power could endanger the quality of product water after microfiltration process.

The boron removal from seawater by NF and RO membranes was also investigated by Sarp *et al.* (2008). They indicated that boron removal increased with higher salt concentration for RO membranes but decreased with higher salt concentration for NF membranes. However, they did not explain clearly whether pH of different solutions was maintained at the same level. In addition, results of boron removal with BWRO membrane in their study reported at around 22 – 37% at different salt concentrations, namely (i) DI water spiked with boric acid, (ii) solution prepared from sea salt, and (iii) actual seawater. They have also measured the zeta potential of the membranes tested at different pH. However, it would be more useful to measure zeta potential at different salt concentrations and related the results to boron removal. Their study also extended to the effect of boron toxicities on cell protein. According to their results, production of two proteins tested was not affected by boron. The result was not in line with the other study conducted by Barranco *et al.* (2007). The latter study indicated that boron intake of 0.6 – 11.9 mg/L in ground water coincided with 37% in prostate cancer incidence. They also reported that boric acid (0 – 1000 μM) decreased Bcl-2 protein production. Bcl-2 is an integral inner mitochondrial membrane protein with relative molecular mass of 25000 and it is one of the key regulators which are essential for proper cell development, tissue homeostasis and protection against foreign pathogens.

Yoon ***et al*.** (2005) indicated that removal of trace elements by membrane could be affected by electrolytes, pH and conductivity of the solution. Experimental results were used to compare with predicted transport parameters, solute flux and diffusion coefficient, calculated from the irreversible thermodynamic model. It was noted that solute permeability decreased with increased pH and decreased conductivity. Although the predicted solute flux and experimental data were in good agreement for UF and NF membranes (R^2 value more than 0.8), model prediction for RO membrane had a poor R^2 value of less than 0.5. Therefore, there is a need to verify the conclusion that diffusion is dominant for RO membrane. It would also be useful to study the influence of a wider range of salt concentration and pH. In addition, it would be worthwhile to look into the potential alterations of solubility and diffusion of solute at different ionic strength which were not discussed in their study.

Geffen *et al*. (2006) evaluated the boron removal by RO membrane using polyol as the complex-forming compounds to enhance boron removal. Their study was based on the similar principle as that of boron-selective ion exchange resin to remove boron. They tried to make use of nuclear magnetic resonance (NMR) technique to support the experimental result of better boron removal where boron-polyol complex was formed. They reported the use of mannitol at molar ratios of 5 – 10 (approximately 500 – 1000 mg/L of mannitol to remove 5 mg/L of boron) to achieve better boron removal by SWRO. While complex formation could be an alternative for enhanced boron removal, the required diol dosage was too much to be practically feasible. Possibility to use mannitol for enhanced boron removal by RO membrane was also discussed in a study conducted by Raven (1980). However, complex formation could only be useful if suitable diols or metal salts, which would be effective at low dosage, could be found. In addition, Geffen *et al.* (2006) predicted that a higher ionic strength of the solution could also enhance the boron removal by RO membrane. In fact, Wilf (2007) also indicated that boron removal could be better at higher salinity. This phenomenon is attributed to the belief that pK_a of solute will be shifted to a lower value at a higher ionic strength of the solution and that in turn leads to the dissociation of solute at lower pH and transformation of solute into charged ions. Consequently, better boron removal by RO membrane could be achieved via charge repulsion when the solution contains more negatively charged borate ion. However, their predictions overlook the impacts of ionic strength on membrane surface charge and enhanced diffusion. Experimental investigation is necessary to verify the phenomenon proposed in their studies.

Shift of pK_a was also mentioned in the study of boron removal by adsorption method conducted by Choi and Chen (1979). A total of nine adsorbents ranging from activated carbons, activated aluminas to activated bauxites were tested for boron removal. It was noted that optimum pH shifted to more alkaline region when the solution salinity increased. The observed effect was different for various types of background solutions. It was also speculated that the observed decrease in boron removal at higher salinity might be due to competition with other chemical species or blocking effect on active sites. However, optimum pH no longer changed after reaching certain level of salinity. The phenomena of salinity effect in adsorption method could also unlock the understanding of boron removal by RO membranes. Boron removal efficiency generally increased with decreasing initial concentration for adsorption method. Besides, composition of solution matrix and surface properties of the solid may also affect the boron removal. They reported that shift in optimum pH was related to the type of surface hydroxyl compounds of metals. For example, maximum adsorption of boron would be at pH 8 – 9 for hydroxyl iron forms and pH 7 for aluminum forms. However, no further analysis of the hypothesis was reported.

They also reported the coincidence of maximum adsorption at around pK_a value of boric acid with the explanation that adsorption of undissociated molecules to proton dissociation at the surface of adsorbent. The dissociated protons subsequently react with surface hydroxyl group of neutral site to form water and readily displaced by anion. Since active sites of adsorbent possess different affinity, surface characteristics of adsorbent should be thoroughly investigated to maximize the efficiency of adsorption process.

Polat *et al*. (2004) examined some controlled conditions on removal of boron by coal and fly ash. They proposed that removal was taken place via co-precipitation of magnesium hydroxide and boron. Although seawater was treated with coal, boron removal was associated with magnesium (Mg) depletion and calcium (Ca) enrichment. On the other hand, Mg was enriched and Ca was depleted in the residual fly ash. Generally, pH, liquid/solid ratio and contact time are key factors to optimize the adsorption. However, effect of salinity on boron removal capacity by some materials has been suggested without further investigation. While abundant fly ash could be made use of for boron removal at adsorption/ precipitation step of desalination pretreatment, the authors noted potential of environmental hazard by leaching of radioactive and heavy metals. Mechanism of boron retention by fly ash was suggested as co-precipitation between Ca-rich fly ash and Mg-rich seawater. Although adsorption and precipitation methods could be used for boron removal in water treatment, substantial amount of chemicals requirement and sludge generation would make them practically not feasible especially for large installations such as desalination plant. Required reaction time of more than 6 hours to complete the process could be considered practically very long, too. Thus, it is necessary to consider the use of more efficient methods such as RO process with better precaution and understanding.

Redondo *et al*. (2003) analyzed field data of SWRO on boron rejection and reviewed four configurations with either BWRO or ion exchange resin to enhance boron removal at competitive cost. Use of ion exchange process to treat 25% of permeate stream added an extra 7 – 9 cents per m^3 of product water. If IDE process or Ashkelon process (four stages RO with steps of segregation) could be introduced, typical production cost would be US$ 0.38 – 0.50 for 1 m^3 of product water with a boron concentration of 0.6 – 1.0 mg/L and US$ 0.47 – 0.60 for product water with a boron concentration of 0.3 – 0.5 mg/L. Although prospect of better boron removal at higher pH was discussed, pilot plant seemed to operate only under conservative condition. Integrity of membrane was not reported for long-term operation of SWRO at pH 10. They also pointed out that boron removal is primarily controlled by membrane chemistry and less by size exclusion. However, there was no further discussion or investigation about impacts of salinity on the change of pK_a, membrane surface potential and finally improving or worsening the boron removal.

Zhao *et al*. (2005) evaluated the effects of membrane surface properties and water qualities on mass transfer coefficients of water and solute. Their study focused mainly on rejection of major components both organic and inorganic present in the solution by low pressure RO membranes. Results of pilot study with 4 different membranes indicated that membrane with increasing hydrophilic property and roughness enhanced mass transfer coefficient of water and solute, K_w and K_s. However, the study on the effect of natural organic matter (NOM) mass loading on the change of K_s indicated that lower NOM fouling could maintain a more constant inorganic solute mass transfer. The study was conducted at an average conductivity of 1534 μS/cm and average pH of 8.3. Zhao *et al.* (2005) suggested that interaction between membrane and different solute concentrations could significantly influence the salt rejection of membrane. When the removal of trace elements is the main concern, impact of major ions on trace element rejection by membrane should also be taken into account. Although their study indicated the impact of surface characteristics on K_s of major ions, more research work still needs to be done on impacts of NOM, salinity and membrane surface characteristics on the changes of trace element K_s.

Physical properties and thermodynamic parameters of solution could also affect mass transfer in RO membranes. Ghiu *et al.* (2003) proposed that smaller ions with larger hydrated radii would be rejected at a higher rate. It should be noted that borate ion at higher pH also possess larger hydrated radii and this could account for the observation that borate ion could be retained easier than boric acid by membrane. Enthalpy (ΔH) and entropy (ΔS) of hydration, via thermodynamic parameter Gibb free energy, could provide a more precise quantification of the degree of hydration and its effect on the final retention of ions by membrane. However, use of the equation deduced from the model of Kimura (1995) and Sourirajan (Sourirajan and Matsuura, 1985) with the assumption that same salt diffusivity in the solution and in membrane phase needs to be justified.

Regarding zeta potential, one of the studies put focus on the impact of different cations and humic acid on membrane surface potential and hence on membrane fouling (Elimelech and Childress, 1996). When $CaCl_2$ was added, the membrane acquired a higher positive zeta potential. In contrast, when humic acid was introduced, membrane became more negatively charged. They pointed out that further research in zeta potential characterization would be necessary to determine the relationship between membrane surface charge and its performance in terms of both membrane fouling and salt rejection. Khedr *et al.* (1985) investigated the streaming potential or zeta potential of CA membranes and reported that divalent cations introduced higher streaming potential than that of monovalent ones. In addition, they tried to relate the streaming potential result to the electro-osmotic coefficient rather than its impact on salt rejection. In fact, streaming potential trend could also be used to relate the tendency of salt rejection, such as boron removal, through charge repulsion or enhanced diffusion mechanism. Luxbacher *et al.* (2007) reported that streaming potential could provide information about interaction between membrane and ions to understand separation performance. Kaneko and Yamamoto (1976) also suggested the better use of EKA to study the impact of membrane surface potential on RO performance. They observed that zeta potential values of membranes seem to increase with increasing feed concentrations (10^{-5} to 10^{-1} N) of different solutions (NaCl, KCl, $MgCl_2$, $MgSO_4$, Na_2SO_4) for CA membranes investigated under their study. They reported that trend of streaming potential became less negative at higher salt concentration and showed positive values between 10^{-2} to 10^{-1} N. They briefly speculated that changes in surface potential might lead to interaction of ions and polymer chains of membrane rather than suggesting potential salt rejection mechanism. Koseoglu *et al.* (2008) made an attempt to compare boron removal from two extreme situations of distilled deionized water (DDW) and seawater (SW). They found that salinity in seawater negatively impacts boron removal by TFC RO from Dow and Toray at pH 8.2. However, the impact of salinity at pH 10.5 on boron removal was reported to be insignificant. Their observation showed similar trend as that reported by others (Oo and Song, 2009). In the study of Koseoglu *et al.* (2008), lower boron removal was attributed to the super saturation effect. In fact, super saturation at membrane surface not only causes concentration polarization but may also change membrane surface characteristics, adsorption of counter-ions, selective permeability, Donnan exclusion of membrane, etc. Neither the change of pK_a value nor the possible boron removal mechanism was discussed in the study of Koseoglu *et al*. (2008).

Hou *et al.* (2010) studied the boron removal by direct contact membrane distillation. Their results indicated that boron removal is less dependent on pH and salt concentration by membrane distillation process. When the system was operated at a temperature gradient of 30 °C between feed and permeate streams at pH 3 – 11, boron removal was reported to be stable at >99%. Boron removal efficiency was also found to be stable at a temperature gradient of up to 60 °C. This observation should be verified as higher temperature could theoretically encourage diffusion and hamper the rejection. They also reported that boron removal in membrane distillation process was not sensitive to salt types with a concentration of up to 5000 mg/L. This result is more comprehensive since water permeation occurs through membrane as evaporation process. Unless waste heat is available, membrane distillation process will require substantial amount of energy to raise the temperature of feed solution to maintain a temperature gradient between feed stream and stripping (product) stream. In addition to the need of heated solution, membrane flux and integrity are other challenging issues for this process to be practically feasible at large-scale installations.

Zalska *et al*. (2009) investigated the boron removal from wastewater by electrodialytic desalination. They found that an increase in pH and desalination degree would lead to enhanced boron transport. Optimal pH in the first stage of a two-stage electrodialytic process was found to be 3. Control of boron mobility might be similar to the study by Melnik *et al*. (1999) where the electrodialytic system could be optimized for low and high pH with different ion exchange resin pairs, homogeneous or heterogeneous types. Melnik *et al.* (1999) managed to remove boron from 4.5 mg/L to approximately 0.3 mg/L with a salinity of 0.2 g/L. At a higher boron concentration of 40 mg/L, removal efficiency dropped to 32%. Lower boron removal and handling capacity might be due to lower salinity or inefficient cell design. Boron concentration of 75 mg/L and TDS 1.8 g/L used in the study of Zalska *et al.* (2009) was found to be optimal for both boron removal and desalination at lowest fouling potential. It could be attributed to difficulty to operate the process stably at highest energy efficiency. Besides, application of ion exchange resin for boron removal of feed water with high organic loading could be challenging because it has been known that cleaning of resin fouled with organics is very difficult. Owing to the limitation that cell voltage dropped from 2.0 to 0.3 volt, which means poor current efficiency, they estimated the possible cost of \$0.30 per m^3 for boron removal treatment under optimum conditions. This process seems to be not suitable or economical for treating fluids with high TDS.

Liu *et al*. (2009) explored the boron adsorption by composite magnetic particles. They used the pure Fe_3O_4 and composite magnetic particles derived from Fe_3O_4 and bis-(trimethoxysilylpropyl)-amine (TSPA). Adsorption of boron was about 50% better with magnetic particles TSPA and adsorption was better at pH 2.2 – 6.0 than that at pH 11.7. They also found that adsorption of boron on fly ash decreased at higher ionic strength, similar to that reported in other studies on adsorption process. However, adsorption of boron by polymer supported iminodipropylene glycol was reported to be insensitive in the presence of Ca and Mg ions. Liu *et al.* (2009) proposed that adsorption process takes place on both boric acid and borate by either hydrogen bonding, electrostatic and hydrophobic attractions depending on solution pH. Adsorption could take place either at outer sphere or inner sphere, too. This finding seemed to be attributed to the formation of covalent bond with hydroxyl containing adsorbents. For all the particles investigated by them, boron adsorption was reported to be highest at neutral pH and lowest at alkaline pH, possibly due to electrostatic repulsion. Their illustration of adsorption on iron particle might be one of the reasons for enhanced boron removal observed in the study conducted by Qin *et al.* (2005). Difficulty for synthesis of particles, their stability and regeneration needs are typical concerns of applying adsorption process. If this method is to be used as an upstream process, any leaching of iron compound into RO stream could also cause detrimental impact to RO membranes.

Bryjak *et al*. (2008) explored the removal of boron from seawater by adsorption-membrane hybrid process. They used the crushed boron-selective ion exchange resin for adsorption together with microfiltration membrane. Their results showed that it would take 30 minutes contact time to reduce boron from 10 mg/L to 2 mg/L. When the initial boron concentration was 2 mg/L, it took 2 – 3 minutes to bring boron down to less than detection limit. However, the use of 1 g/L crushed resin in the suspension may cause a higher operating pressure for microfiltration membrane. In addition, resin in continuous suspension and turbulence may quickly become powder and shorten the life span. Organic fouling could be another detrimental impact on ion exchange resin for wastewater application.

Okay *et al***.** (1985) evaluated the adsorption and ion exchange methods for removing boron at 100 – 500 mg/L level from mine drainage in Turkey. They found that with an

Mg/B molar ratio of 20, 85% of boron could be effectively removed by magnesium oxide. Temperature affected significantly on contact time required for boron removal and 40 °C was found to be optimal with a contact time of 2 hours for more than 85% removal. It should be noted that boron removal by MgO adsorption could be lower at lower initial concentration. The observed trend is different from that reported by Choi and Chen (1979). It might be due to different testing conditions such as range of boron concentration, different dosage and type of adsorbent, etc. In addition, it was necessary to recover the MgO once every 3 cycles. Their method would potentially require 5 kg of MgO to treat 1 m^3 of wastewater. Nevertheless, they claimed that ion exchange method is still more costly due to its regeneration requirement. Although they suggested the recovery of boric acid from regenerating solution, there could still be practical limitations such as heating a large volume of solution and removing other impurities of mine drainage. In practice, ion exchange could hardly be used for wastewater treatment because of its sensitivity to a wide variety of organics and suspended solids normally found in the wastewater. With the information of boron concentration in the river to be 1 – 7 mg/L, alternative consideration should be given for partial treatment of river water by RO system as a reclamation method.

Simonnot *et al*. (2000) revisited the technique of boron removal by the ion exchange method in relation to ionic strength and pH of the solution. When boron was removed by resin, adsorption of other ions also took place at negligible amount when the feed water salinity was more than 5 milli-equivalent or being gasified with carbon dioxide at 0.74 bar. It was also noted that boron-selective resin IRA743 of Rohm and Haas used by Simonnot *et al.* (2000) could adsorb boron as well as other ions and thus it would be necessary to elute the exhausted resin with caustic for regeneration. Since ion exchange resins are sensitive to impurities present in the water, this method is normally suitable only for boron removal of relatively clean water to produce ultrapure water (UPW). Hydrodynamics is not favourable for small column due to poor distribution too. Other limitation is the need to handle substantial amount of regeneration chemicals for final disposal. Reuse of acid for regeneration was tested and reported to be possible. However, there was no indicative data in their study for the amount of acid which could be saved. Besides, the process was not authorized as drinking water process in France at the time when the study was conducted.

Cost assessment for boron removal from the SWRO permeate by ion exchange process was conducted by Nadav (1999). He reported that extra costs needed for boron removal, due to regeneration, water loss and resin, were approximately US$ 0.07 and 0.05 per m^3 of product water for resin lives of 4 and 8 years, respectively. Other assumptions for cost estimation were 6.5% discount rate, 10 year depreciation period for initial investment, 20 year service period and 90% availability throughout the life of process. Boron in RO permeate was reduced from 1.8 mg/L to below detection limit in their report. Different regeneration methods were also evaluated and it was reported that acid regeneration followed by hydroxide could prolong the resin operation cycle. The study with a column size of 4 inch diameter and 2.3 meter height was conducted at Eilat desalination plant.

Nadav (1999) also introduced the effect of boron in water on agricultural products. It was also noted that deficiency in boron could result in poor budding, excessive branching and retarded growth. In contrast, a high boron level may cause boron poisoning; yellowish spots on the leaves, accelerated decay and plant expiration. Optimal range of boron concentration was reported to be 0.3 to 0.5 mg/L. Since study of Nadav (1999) was an application research, possibility of flow splitting was also discussed. To be practical, boron removal process should be cost effective, highly efficient and take advantage of high purity nature of SWRO permeate. Although effect of salinity on boron adsorption was expected on most of the studies, there have been no thorough studies on this particular area. It was also the same for the studies on boron removal by RO membranes.

Melnik *et al*. (1999) studied the boron behavior and removal by electrodialysis. Their study used different types of ion exchange membranes to determine the optimum electrodialysis conditions for removing boron from seawater and ground water. It was noted that 0.3 – 0.5 mg/L boron in dialyzate was obtained at a pH range of 2 – 8 using homogeneous ion exchange membrane when the feed boron is 4.5 mg/L. The study pointed out that a minimum NaCl concentration of 0.2 g/L must be maintained to efficiently operate electrodialysis. By adding anionite in desalination chamber, applied voltage was reduced and energy consumption was cut down by 30%. When the feed boron concentration was 40 mg/L in a sample of seawater at Kamchatka in Russia, boron in dialyzate was 27 mg/L, which corresponds to a removal efficiency of only 32%. No reason was given for the low rejection when feed boron concentration was high. It might be due to long contact time of fluid with ion exchange membrane causing more boron transport into the dialyzate. Since electrodialysis process is an energy intensive method, the study tried to find the optimum pH for different type of membrane pairs. The optimal values were reported to be pH 2 – 8 and >10 for homogeneous and heterogeneous types, respectively. However, there was no explanation or suggestion to further improve efficiency at different desalination capacities. When conventional electrodialysis would be terminated at a minimal salt concentration of 1 g/L, they managed to set-up the arrangement of ion exchange membranes to operate the system until salinity went down to 0.2 g/L.

The discussions of Melnik *et al*. (1999) about boron removal by the influence of solution pH, membrane types, degree of desalination and boron concentration in the feed water were related to boron transport via ion exchange membrane. However, it could not be confirmed whether boron removal by ion exchange membrane is via chelate formation of boric acid or borate. Hint was given to assess the mechanism by checking the NMR of ^{11}B on membrane. Boron transport mechanism across cation-exchange membranes could be of scientific interest. Similar to most of the studies on ion exchange resin or membrane, their study did not look into the impact of impurities especially organic foulants on membrane for long-term operation. It should be noted that search of factors that make boron retention more efficient is a very topical problem not only in practice but also in academic research. In addition, proper selection and use of instrument is important to overcome technical uncertainty.

Ludwig (2004) analyzed the hybrid systems in seawater desalination with different aspects of power plant design, RO plant configuration, resource conservation, environmental impacts, water quality and product capacity. Although this study provided indicative facts for policy planning, it was suggested to evaluate those factors by operating a pilot-scale plant for 6 – 12 months. A process based on liquid-to-liquid transport of ions (facilitated ion transfer) has been investigated by Pieruz *et al*. (2004). They tried to selectively transfer the borate ions present in RO product to an immiscible phase. However, no experimental data or possible application was provided. It might be due to the fact that facilitated transfer process is not practical for handling large volume such as those in desalination or municipal water treatment system.

While RO process has been popular for desalination and water reclamation, forward osmosis (FO) process emerged as a potential alternative that is also environmental friendly. Since FO method depends on chemical potential difference, energy consumption could also be lower. Many studies were conducted on improvement of membrane for better flux, optimal operating condition and to develop efficient osmotic agents which could easily be separated and reused. However, there is hardly any attention on trace element removal by FO process.

In general, boron can be removed by different methods and their removal efficiencies depend on a wide range of control factors. For reverse osmosis process, typical control factors are pH, flux, recovery, temperature, membrane type, membrane life, salt concentration, salt type and process design. For adsorption process, it depends on pH, concentration, ratio of adsorbent, salinity, surface properties, contact time, and temperature, etc. Control factors for ion exchange method are pH, flow rate, functional group or active site, regeneration method and temperature.

Finally, it should be highlighted that enhanced boron removal by RO membranes has mostly been achieved by raising pH of RO feed. Most of the studies conducted in the past also focused on this approach and suggested that boron removal mechanism was either charge repulsion or size exclusion. However, its removal mechanism was not clearly defined and thoroughly investigated. There is a lack of study on the boron removal influenced by interplay between pH and ionic strength of solution. Although there have been limited studies on the impact of salinity on removal of major ions by RO membrane, there is a lack of study on the impact of salinity on removal of trace elements. In addition, interaction between solution chemistry and membrane surface characteristics could have an impact on boron removal mechanism. While zeta potential of RO/NF membranes at different pH has been investigated in the past, little attention has been given to the impact of salinity on zeta potential of membrane. Thus, there is a need to thoroughly explore and investigate the impact of salinity on membrane surface potential and boron removal by different RO membranes. Although boron removal could be improved by complex formation at a very high dosage of diol, enhanced boron removal via complex formation should be explored further toward lower diol dosage to make the technique practically feasible.

2.2 Boron chemistry

Boron in nature is normally found as minerals in different combinations of both metals and non-metals. Boric acid and boron salts are widely used in many industries such as glass, leather, carpets, cosmetics and photographic chemicals. It can also be used as mild acid for disinfection. Owing to its ability to withstand high temperature, other forms of boron are widely used in welding, cutting fluid, high-energy fuels and microchips.

Boron in surface or ground water is normally present as boric acid and borate ions. Boron at low concentration in aqueous solution is known to exist mainly as boric acid. Molecular weight of H_3BO_3 or $B(OH)_3$ is 61.83. The unit cell is normally triclinic, containing four molecules of boric acid. Respective dimensions are a_1 = 7.039 Å, a_2 = 7.053 Å, a_3 = 6.578 Å, $\alpha_1 = 92.58°$, $\alpha_2 = 101.17°$ and $\alpha_3 = 119.83°$ (Adams, 1965) where a_1, a_2, a_3 are bond lengths and α_1, α_2 α_3 represent bond angles. The other source indicates the dimension of a single molecule at 4 Å (Toray, 2008). Boric acid is a weak Lewis acid and thus it will combine with available OH group to form $B(OH)_4^-$ at high pH region. Equilibrium of boric acid and borate ion can be expressed as follow:

$$B(OH)_3 + OH^- \rightarrow B(OH)_4^- \qquad pK_a: 9.25$$

Boron can form many varieties with hydroxyl group at high concentration. The typical form in water at low concentration and neutral pH is boric acid (Adams, 1965). When ionic strength of the solution is high, pK_a value of the trace compounds, such as boric acid, could be lower due to the changes in activity of borate ion by the increased ionic strength of solution. If the pK_a is the only factor to influence the boron removal efficiency by RO membrane, it will be correct to assume that boron removal could be better at higher salinity. Since other factors such as membrane surface characteristics and other components could also play a role in boron removal, it is necessary to explore the boron removal under high salinity and influence of different pH. It will also be interesting to verify the results using analytical instruments such as Electro Kinetic Analyzer (EKA).

Boric acid can also form complex with organic diols such as mannitol, sorbitol, ribitol, erythritol and glycerol according to Raven (1980). The focus of his study was mainly on boron transport in plants. In fact, transport of boron through semi-permeable biological membrane and chromatographic transport by complex formation is quite interesting for other applications. Although Raven (1980) proposed that transport of boron in biological membrane is via borate form, there were groups who believed that the opposite way should be more appropriate. On the other hand, optimum pH for complex formation especially for boron removal by RO membrane has not been adequately explored. If optimum pH is known, it may explain the mechanism of complex formation via boric acid or borate. Formation of complex might be verified by analytical instruments such as NMR or FTIR. However, measurement of boron complex at a very low concentration by those instruments could be very challenging.

2.3 Surface characteristics of RO membranes

Generally, RO membranes could be positively, neutral or negatively charged. Surface roughness and hydrophobic nature of membrane surface could also vary for different applications. The information of membrane surface characteristics at standard test conditions could normally be obtained from respective RO membrane manufacturers.

Thin film composite (TFC) polyamide reverse osmosis membrane is widely accepted as the optimal material by membrane industry (Belfer *et al*., 1998). In the study of Belfer *et al*. (1998), surface modification of commercial RO was attempted by grafting methacrylic acid and polyethylene-glycol-methacrylate through changing grafting time without any compromise of RO performance. Another group tried different monomers to prepare and characterize the thin film composite polyamide-urethane seawater RO membrane (Liu *et al*., 2008). They used metaphenylenediamine (MPD) and 5-chloroformyloxy isophthaloyl chloride (CFIC) under different reaction time, pH of MPD solution, CFIC concentration, additive isopropyl alcohol content, curing temperature and time. They suggested that the chemical structure of surface functional groups as follow:

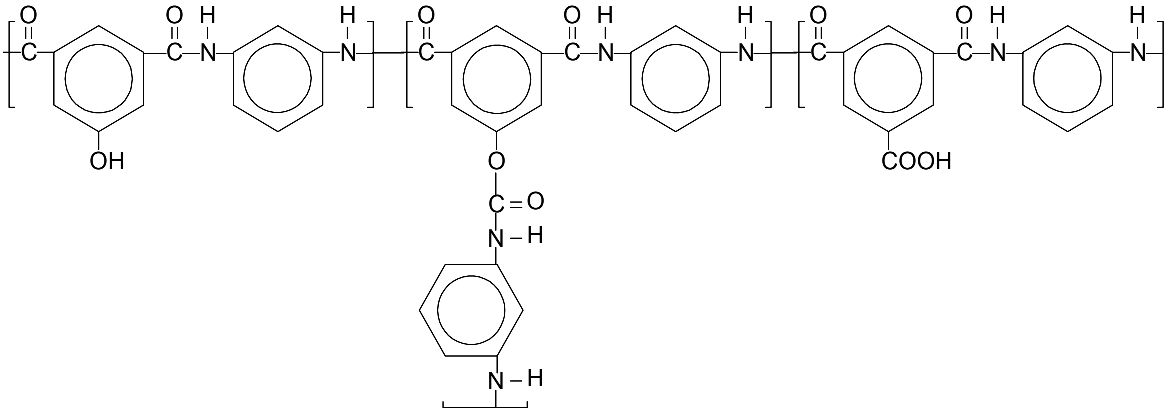

Figure 2.1 Structure of polyamide-urethane skin layer

As shown in Fig. 2.1, the polymer chain is expected to include cross-linked structure, non cross-linked structure containing carboxylic acid group and linear structure containing hydroxyl group. Carboxylic acid and hydroxyl group formations could be attributed to partial hydrolysis of acyl chloride and chloroformyloxy units of CFIC molecule during interfacial polymerization. According to analysis of atomic composition, they reported that higher oxygen to nitrogen (O/N) ratio (1.525 for BWRO and 1.748 for SWRO) was obtained for their membranes compared to the typical O/N ratio of 1.33 for totally cross-linked polyamide-urethane. Although the objective of their study was to prepare an RO membrane with better flux rate and salt rejection, permeability was found to be lower without any improvement of NaCl and boron rejection when their membrane was compared with commercial membranes. They explained that the lower flux might be attributed to lesser formation sites of cross-linked polyamide-urethane which led to a thicker skin layer of 0.65 μm compared to commercial RO membranes of 0.2 – 0.5 μm. Generally, thin film composite polyamide membranes contain ionizable groups of carboxyl and amide in their polymer chain. They will normally be exposed at the skin of membranes and facing the aqueous solution. Thus, surface charge of membrane generally could be positive or negative depending on the pH and dominant ions in the solution.

Another example of RO membrane surface structure was reported by Rana *et al.* (2011) and shown in Fig. 2.2. They explored a new method to fabricate TFC membranes of reduced fouling by adding LSMM (hydrophilic surface modifying macromolecule, polyurethane end-capped with polyethylene glycol). TFC membrane preparation technique was based on inter-facial polymerization (IFP) between the di-amine (*m*-phenylenediamine, MPD) in the aqueous phase (2 and 3.4 wt%) and tri-acid chloride (trimesoyl chloride, TMC) in the organic phase (in cyclohexane 0.2 wt%). In general, surface of TFC polyamide membrane normally contain functional groups such as amide (N-H) and carboxyl (C=O).

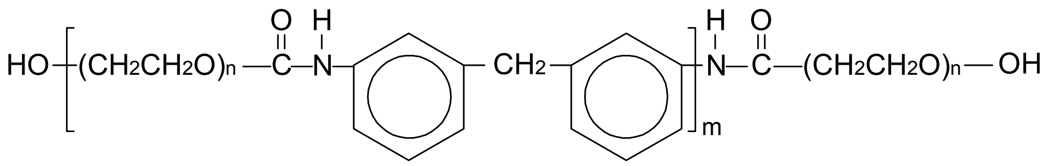

Figure 2.2 Structure of polyamide skin layer incorporated with LSMM

Norberg *et al.* (2007) examined a range of commercial NF and RO membranes under microscope for their surface characteristics in terms of surface potential, hydrophobic nature and surface roughness. They reported that (i) surface potential ranged from –4 mV to –20 mV, (ii) contact angle varied between 37° and 73°, and (iii) mean roughness was 6 – 130 nm. Generally, CA membranes possess a smooth surface with low negative surface charge. TFC NF membranes are normally more negative, –10 mV to –20 mV, whereas TFC RO membranes characteristics vary widely in surface potential and roughness. They suggested using membrane with neutral or low negative surface charge for minimum fouling to handle feed water which contains charged organics or colloids. For water that has high potential of organic and bio-fouling, membrane should be relatively neutral and hydrophilic. In order to minimize colloidal fouling, one should select membrane with a smooth surface. Results of their pilot study for four months generally demonstrated the above-mentioned effects of different membranes. However, the drop in feed pressure observed at the end of their pilot study was not clearly explained. Besides, it was not clearly stated whether the drop of feed pressure and increase of differential pressure were linear throughout their pilot study or more pronounced during the initial period of operation. As the measurements in that study were only conducted at a TDS level of about 1000 mg/L, exploration should be extended to other TDS level such as that of seawater.

Deshmukh and Childress (2001) investigated the influence of source water type and chemistry on zeta potential of RO membranes. They have tested tertiary treated wastewater effluent, river water, membrane storage chemicals, and pesticide. Presence of divalent cations in river was given as the reason for having positive zeta potential when using river water. When zeta potential was measured in the presence of wastewater, negative potential was obtained and they suggested that organic acids might be the cause of negative zeta potential for RO membranes tested. They suggested that streaming potential measurement could be used as a good preliminary diagnostic tool to identify a potential cause of membrane fouling. The study was conducted at the pH range of 3 – 9. If the measurement could be extended to different salt types and concentrations, results would be more useful for those applications with high salt concentration.

As RO process is a pressure driven system, Matsumoto *et al.* (2007) explored the surface potential across RO membranes under pressure gradient. It should be noted that method to measure membrane potential was conducted under filtration mode where zeta potential measurement was performed at cross-flow mode without any permeate flow. In fact, they were trying to see the charge density at the boundary layer of membranes. Their reason to maintain a feed and permeate concentration ratio of 5 was not clearly explained. It might be due to the intension of maintaining 80% rejection by membranes under their study. They applied a pressure gradient range of 0.0 – 0.3 MPa. When the concentration of solution was low at 0.001 M of NaCl, it was noted that a higher pressure gradient led to a more positive membrane potential. However, pressure gradient seems to have no impact on membrane potential with a high concentration of 0.5 M, either NaCl or $MgCl_2$. Nonetheless, similar membrane potential for one membrane might not imply that zeta potential or streaming potential could also be similar at high salinity for different membranes. Besides, zeta potential may play an important role in the explanation of different salt rejections and respective rejection mechanisms by different RO membranes. Measurement of zeta potential was conducted at the pH range of 3 – 10. Thus, there is a need to further study and understand the change of zeta potential at different salinities.

Zeta potential of polyethersulfone nanofiltration membrane was also measured by Ernst *et al.* (2000) to establish a relation with the rejection rates in single salt solutions. When Na_2SO_4 solution concentration was higher than 8×10^{-5} M, rejection decreased from 80% at 8×10^{-5} M to about 20% at 5×10^{-3} M. On the other hand, zeta potential shifted to more negative value till 1×10^{-3} M of Na_2SO_4 and then showed positive value of 30 mV at 8×10^{-3} M. They also pointed out that reversal point of salt rejection and zeta potential might not occur at the same salt concentration. It could be due to differences between conducting rejection test and measuring zeta potential. During the rejection test, there was a permeate flow through membrane but zeta potential measurement involved only cross-flow without producing permeate flow. When the study was continued with KCl solution, zeta potential shifted from –3 mV to –20 mV and salt rejection decreased from 70% to <10% for respective salt concentration range of 10^{-5} M to 10^{-2} M. Although assumption was made that approach of more SO_4^- ions to membrane surface caused more negative zeta potential at low range of salt concentrations, there was no suggestion whether salt rejection took place via charge repulsion, diffusion or size exclusion mechanisms. If rejection could be indicated for individual ions, better removal of anions could be interpreted as charge repulsion mechanism by negative surface potential of membrane. Impact of salt concentrations on RO membranes surface potential and removal of trace elements still need further investigations.

When Hyung and Kim (2006) studied the boron removal by seawater RO membranes at different pH and temperature, they also measured the zeta potential at a pH range of 4-10. A model was developed from irreversible thermodynamic model coupled with film theory to predict boron removal in SWRO design. Experimental results showed that linear relation of boron removal and other ions would be valid only at neutral pH. When higher pH was used for better boron removal, the relationship established at neutral pH would no longer be valid. There was more evident when they established a mechanistic predictive model to predict the boron removal by RO membranes (Mane *et al.*, 2009).

The result obtained by Hyung and Kim (2006) suggests that there could be a correlation to estimate boron concentration from salinity which was previously established by Taniguchi *et al*. (2004). Although impacts of pH and temperature on boric acid speciation, and hence boron removal, were included in the modified model developed by Hyung and Kim (2006), impacts of salinity and membrane surface characteristics were neglected. They did propose boron removal at higher pH by charge repulsion mechanism. In addition to charge repulsion mechanism for boron removal, they implicated lower diffusion of borate ion as the additional factor for better boron removal. From the angle of transport parameter, reflection coefficient, they proposed that most of the RO membranes maintain a coefficient close to unity for borate ion which explains the near perfect boron removal at high pH for most RO membranes while removal varies largely at neutral pH where boron in solution mostly exists as boric acid. Borate ion permeation was associated with diffusive transport rather than solvent coupling or size exclusion mechanism. Percent contribution of borate at different pH was directly related to reduction of overall boron permeability. And, boron removal was projected to be higher at higher pH. This phenomenon will be valid only if diffusion is the key mechanism for boron removal and need to be investigated for different types of membranes. In terms of temperature, its dependence on solute permeability overtakes that of hydraulic permeability. They noted the importance of pH and temperature as well as ionic strength on boron removal by RO membranes. However, impact of ionic strength was not elaborated further and included in the proposed model presented in their study.

2.4 Transport of solutes and solvents through RO membranes

According to the solution-diffusion model developed by Lonsdale *et al.* (1965), flux of solvent (water) and solute (salt) can be expressed as:

$$J_w = P_w\,(\Delta P - \Delta\pi) \qquad (2.1)$$

$$J_s = P_s\,(c'_w - c'') \qquad (2.2)$$

where J_w is the water flux (m^3/m^2-s), J_s is the salt flux (kg/m^2-s), P_w is the water permeability (m^3/m^2-s-Pa), P_s is the salt permeability (m/s), ΔP is the pressure difference across the membrane (Pa), $\Delta\pi$ is the osmotic pressure difference between feed and permeate at membrane surface (Pa), c'_w is the feed salt concentration at membrane surface (kg/m^3), and c'' is the concentration of salt in permeate (kg/m^3).

Alternatively, solute transport through membrane could be characterized by equations of Kedem and Katchalsky (1958) considering both diffusion and convection of solute as follow:

$$J_s = \omega\,\Delta\Pi + (1 - \sigma)\,C_{avg}\,J_v \qquad (2.3)$$

$$J_v = L_p\,(\Delta P - \sigma\,\Delta\Pi) \qquad (2.4)$$

where J_s is the solute flux (mol/m^2-s) of diffusion and convection, ω is the solute permeability (mol/m^2-s-Pa), $\Delta\Pi$ is the osmotic pressure difference (Pa), σ is the molecular reflection coefficient (dimensionless), C_{avg} is the bulk fluid interfacial concentration between feed and permeate side (mol/m^3), J_v is the solvent flux (m^3/m^2-s), and L_p is solvent permeability (m^3/m^2-s-Pa). From the thermodynamic transport model equations given above, Yoon *et al.* (2005) used the following equation to calculate the solute permeability.

$$\omega = D_p / (l\ R\ T) = D_w\ H / (l\ R\ T) \qquad (2.5)$$

where D_p is the hindered diffusion coefficient of solute through membrane (cm^2/s), D_w is real diffusion coefficient of solute in water (cm^2/s), H is the partitioning coefficient (dimensionless), l is the membrane thickness (m), R is the gas constant (J-atm/K-mol), and T is the absolute temperature (K). D_p of the solute based on Fick's law can be expressed by the following equation according to Wee and White (1999).

$$C_{B(t)} - C_{A(t)} = \left(C_{B(t0)} - C_{A(t0)}\right)\exp\left[-A\frac{D_p}{l}\left(\frac{1}{V_B} + \frac{1}{V_A}\right)t\right] \qquad (2.6)$$

where C_B is the concentration in the fluid adjacent to the permeate surface of the membrane (mol/m^3), C_A is the concentration in the fluid adjacent to the feed surface of the membrane (mol/m^3), D_p is the hindered diffusion coefficient of solute through membrane (m^2/s), A is the effective membrane area (m^2), V_A is volume of the feed side of membrane (m^3), V_B is the volume of the permeate side of the membrane (m^3) and t is the time during the diffusion test period (s).

It should be noted that in the equation of solution-diffusion model, the interaction between J_v and J_s was not included. Although the equation from irreversible thermodynamics included the third coefficient, reflection coefficient (σ), it was ambiguous about possibility to take an average of feed and permeate salt concentrations (Kimura, 1995).

Zhao *et al.* (2005) described the mass transfer coefficient of water and solute in a simplified way which can be calculated directly from experimental data as follow:

$$K_w = Q_p / [\ A \times ((\Delta P - \Delta\Pi) \times 1.026^{(T-25)}\ ] \qquad (2.7)$$

$$K_s = Q_p\ C_p / [\ A \times (\ (C_f + C_c)/2 - C_p)\ ] \qquad (2.8)$$

where K_w is the mass transfer coefficient of water (m^3/m^2-s-Pa), Q_p is the permeate flow (m^3/s), K_s is the mass transfer coefficient of solute (mol/m^2-s), C_f , C_c and C_p represent concentrations of solute in feed, concentrate and permeate, respectively. In fact, K_w and K_s are similar to J_w and J_s in the solution-diffusion model. They studied extensively about the effects of membrane surface characteristics and solute charge on the K_s values of major salts. Based on the results obtained in their studies, inorganic mass transfer coefficients were correlated to hydrophobicity and surface roughness. They also gave logical explanation of membrane fouling potential from the angle of membrane surface characteristics. A brief review of different RO theories conducted by Williams (2003) is another useful source for better understanding of RO principles.

Since diffusion coefficient of solute through membrane and partition coefficient are not universal, adjustment could be necessary to use equations of irreversible thermodynamics for different situations. Experimental data would still be required to estimate the transfer coefficient of solute at different ionic strength of solutions for different membranes.

Chapter 3 Materials and Methods

3.1 Materials

Three brackish water RO membranes (ESPA1, LFC1 and CPA2) and two high boron rejection membranes (ESPAB and SWC4+) from Hydranautics (Oceanside, California) were used in this study. BWRO membranes were initially selected because boron removal is generally improved further at the second pass of RO process where salt concentrations are normally low with minimal scaling problem. High boron rejection membranes were added into the study later to understand the performance of different types of membranes under same condition. Membrane characteristics in terms of surface potential at different pH and salinities are described more detail in Section 4.1. According to the manufacturer's specification, nominal salt rejections of ESPA1, LFC1, CPA2, ESPAB and SWC4+ membranes, at standard testing conditions, are 99.3%, 99.5%, 99.5%, 99.2% and 99.8%, respectively. Boron rejections of ESPAB and SWC4+, as per manufacturer's standard test condition, are 96 % at pH 10 and 93 % at standard testing conditions, respectively. Membranes were flushed with DI water and soaked in it for 24 hours before each experiment.

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 respective testing concentration while 0.1 M hydrochloric acid and 0.1 M caustic soda were prepared for pH adjustment during the study.

3.2 Experimental set-up and procedures

A flat sheet RO testing unit with 5 L of feed tank capacity was used in this study. The schematic diagram of the set-up is shown in Fig. 3.1. A rectangular flat sheet membrane with an effective surface area of 155 cm^2 (L × W: 30.48 cm × 5.08 cm) was used for the experiments. Feed water was pumped from the feed tank by a feed pump (CAT pump model 233 from Minneapolis, MN, USA), with a variable speed drive, to the membrane unit. Operating pressure was adjusted by a Parker needle valve V-3. Wika pressure indicators, PI-1 and PI-2, were used to record the inlet and outlet pressures of the membrane testing unit.

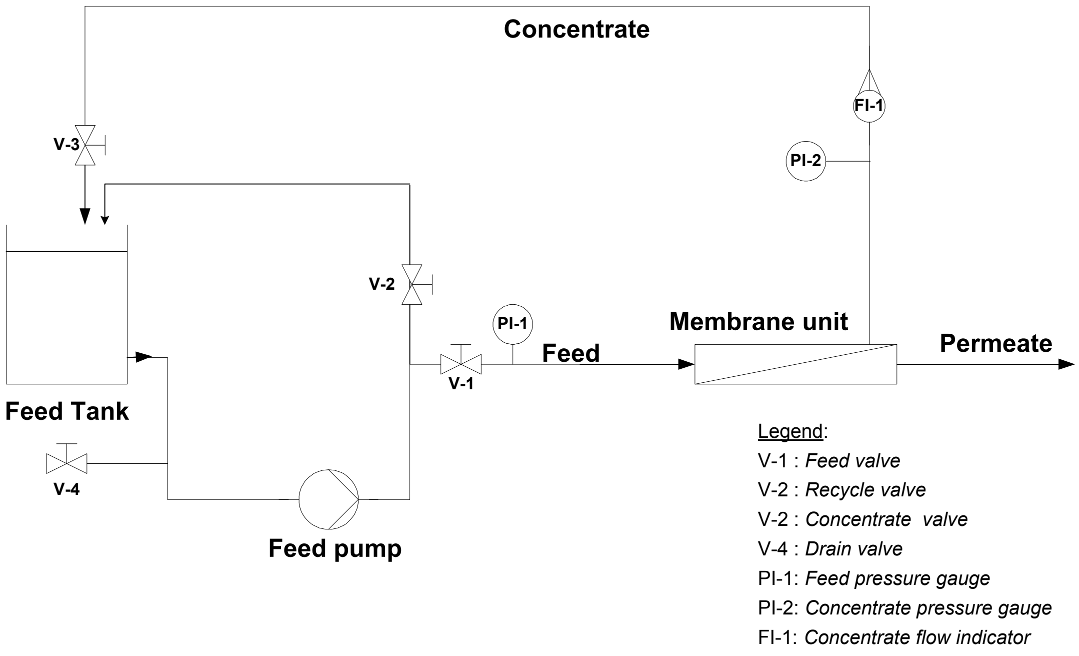

Figure 3.1 Schematic diagram of RO testing unit

Feed solution was prepared by adding boric acid into 5 L of DI water to obtain 5 mg/L of boron concentration. Appropriate amount of NaCl was then added and pH was adjusted by using 0.1 M NaOH. Samples were collected for analysis at about 1 hour after each operating condition was stable. In order to test at higher salt concentration, extra salt was dissolved into the same feed solution after collecting the samples for previous test. For testing at different salinities, the experiments were carried out at an average operating pressure range of 87 – 245 psi to compensate for the osmotic pressure of respective feed concentration. Namely, 87.5 psi for 500 mg/L NaCl in feed solution, 135 psi for 5000 mg/L, 187 psi for 10000 mg/L and 245 psi for 15000 mg/L. Temperature of feed solution was maintained at 23.5 – 25.5 °C during the experiments. The feed flow rate was maintained at 1 L/min and the cross-flow velocity of the feed stream was calculated to be approximately 0.3 m/s.

The RO system was operated at a full re-circulation mode (both permeate and concentrate were re-circulated to the feed tank) except for permeate sample collection. Permeate flux was maintained at constant with a variation of ±10% during the test to minimize the effect of flux on percent removal of boron. Membranes were thoroughly flushed with DI water for 15 minutes at the end of each test. No chemical cleaning was conducted during the experiment as no significant flux decline was observed.

Boron was analyzed by inductively-coupled plasma optical emission spectrometry (ICP-OES) model Optima 3000DV of Perkin Elmer from Waltham, MA, USA. Before each analysis, calibration was performed with standard solutions that contained 0.5, 1.0 and 5.0 mg/L of boron and a blank solution. It was repeated until R^2 value >0.999. For each sample, analysis of boron was conducted twice at replica mode with variation of results less than ±5% of measured value. Other parameters such as pH and temperature were measured by potable meters: Oakton pH10 and Oakton Temp5 (Eutech, Singapore). Permeate flow rate was checked by a digital balance (Precisa 4200C from Dietikon, Switzerland). Membrane performance in terms of percent removal of a particular component was defined by the following equation:

$$\text{Removal} = (1 - C_p / C_f) \times 100\% \qquad (3.1)$$

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

Anton Paar EKA, as shown in Fig. 3.2, was used to measure zeta potential of RO membranes. In EKA analyzer, PTFE spacer was placed between two membranes to assemble the measurement cell. Dimension of streaming channel was 74 mm x 10 mm x approximately 0.3 mm. Ag/AgCl electrodes were used for measuring streaming potential and electrodes were reversible**.** The streaming potential was measured at differential pressure increments from 20 mbar to 500 mbar. Average value of zeta potential was calculated based on repeated measurements obtained from both directions of flow in the cell. Before each measurement, pH calibration was done for 4, 7 and 9. Conductivity was calibrated with standard solution of 1413 μS/cm. Fairbrother-Mastin method which is similar to Helmholtz-Smoluchowski equation was used for calculating the apparent zeta potential as follow:

$$\zeta = (dU/dp) \times (\eta/\varepsilon\, \varepsilon_0) \times \kappa_B \qquad (3.2)$$

where the streaming potential dU, the differential pressure dp, and the electrolyte conductivity κ_B are measured parameters, whereas the viscosity η and the dielectric coefficient ε are tabulated values for water, and ε_0 is the vacuum permittivity. Relative static permittivity at room temperature and 1 kHz are 1 for vacuum and 78.4 for water at 25 °C. κ_B in Helmholtz equation is described as L/AR where L is length, A is cross sectional area and R is electrical resistance of channel. For the measurements of zeta potential at different pH, 500 mg/L of NaCl solution was used and pH was adjusted by using 0.1 M NaOH or 0.1 M HCl. For the measurements of zeta potential at different NaCl concentrations, pH of the solution was controlled within the range of ± 0.2 unit of the target value.

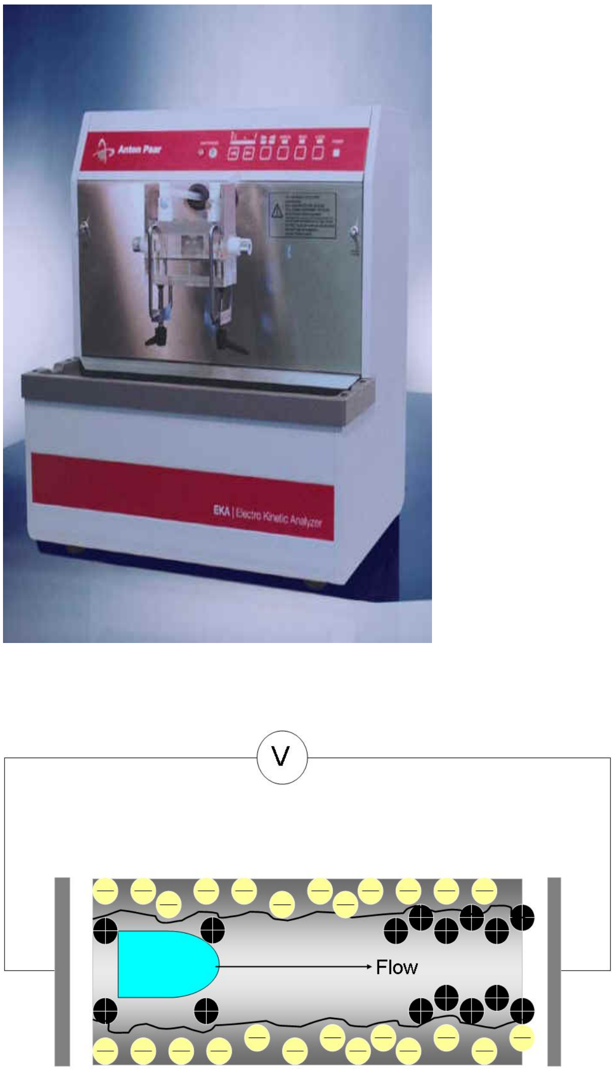

Figure 3.2 Picture and schematic diagram of EKA

Zeta potential is a measure of streaming potential, a potential induced when an electrolyte flows across a stationary but charged surface as shown in Fig. 3.2. It would quantify the electro kinetic effect of the surface property, flow characteristics and chemistry of the solution under the investigation. In other word, zeta potential is the potential at the plane of shear between the surface and solution where relative motion occurs between them. When there is relative motion, charged solid surface can produce one of four electro kinetic effects; electrophoresis, electroosmosis, sedimentation potential and streaming potential (Shaw, 1969). Measurement of streaming potential is preferred because measuring small electrical potentials is more convenient than the measurement of small flow rates. Streaming potential is generated when an electrolyte solution is forced by means of hydraulic pressure to flow through a porous plug of material, across a channel formed by two plates or down a capillary. The liquid in the channel carries a net charge. Its flow, caused by hydraulic pressure, gives rise to a streaming current and generates potential difference (Elimelech and Childress, 1996).

Chapter 4 Results and Discussions

In general, boron removal experiment was initially conducted with iron salts or diols because those additives were reported to act as complex forming agents and could enhance boron removal by RO membranes (Geffen *et al.*, 2006; Qin *et al.*, 2005; Raven, 1980). However, dosage of additives was found too high to be practically feasible. The study was then revised with the focus on impact of pH, salinity and flux on boron removal by different membranes and explored the related removal mechanisms.

Since boron removal also depends on surface characteristics of RO membranes, the study has been extended to the investigation of zeta potential of membranes under different pH and salinities. In addition to BWRO membranes, high boron rejection membranes were also included in this study. The results obtained in this study provided useful information for desalination and other applications of RO membranes which require effective boron removal.

This chapter is arranged in a manner that results of zeta potential of RO membranes at different pH and salinities were presented and discussed in the early part of the chapter. Then, boron removal was investigated at different pH and salinities. It was later discussed under different scenarios where boron removal results were related to changes of zeta potential and other test conditions. Fundamental transport phenomenon of boron via diffusion and potential boron removal mechanisms such as size exclusion and charge repulsion were thoroughly reviewed. Together with interesting experimental results obtained in this study and logical relations established, possible boron removal mechanisms were proposed.

Toward the end of this chapter, experimental results with complex formation for enhanced boron removal were briefly presented for better understanding of other possibilities of enhanced boron removal by RO membranes although the required dosages for those alternatives seem to be practically not feasible.

4.1 Zeta potential of RO membranes

Zeta potential of RO membranes is one of the important surface characteristics that could be related to membrane fouling and performance in terms of salt rejection mechanisms. According to Matsumoto *et al*. (2007), zeta potential obtained from streaming potential measurement is an apparent value that could be used to predict membrane fouling and performance. In general, natural organic matter (NOM) and colloidal particles in water body are negatively charged. When they are brought in contact with barriers such as filters or membranes with similar surface charge, they could hardly attach to the surface and cause less problem of fouling.

On the other hand, NOM and colloid could easily foul the filter and membrane if respective charges of particles and zeta potentials are opposite. Zeta potential is not only an important indicator of membrane fouling, it plays critical role in membrane performance such as rejection of ions and molecules, especially when rejection process depends on charge repulsion mechanism. Thus, zeta potentials of different RO membranes were explored along with boron removal at different pH and salinities.

Generally, surface functional groups of polyamide RO membranes are in the form of carboxyl group and amide group which are ionizable under different pH, salt types and concentrations. When membranes are exposed to aqueous solutions, cations and anions in the solution will approach to the membrane surface at different rate. Anions are normally less hydrated and thus can move more closely to the membrane surface. The effect could be the influence of preferential adsorption of anions such as OH^- and Cl^- at neutral or alkaline pH causing negative zeta potential on most RO membranes (Childress and Elimelech, 1996). They suggested that adsorption of co-ions should take place for hydrophobic surface rather than hydrophilic membrane where dissociation of carboxyl groups could be the reason of causing negative membrane surface charge.

4.1.1 Zeta potential of RO membranes at different pH

Zeta potential of RO membranes was normally measured at different pH to understand its isoelectric point, its impact on fouling and sometimes in relation with mass transfer or salt rejection. While the zeta potential values at low salinity for LFC1 and CPA2 membranes were acquired from literature (Gerard *et al.*, 1998), those of ESPAB and SWC4+ were measured in this study (Oo and Ong, 2010) and their values are summarized in Table 4.1. According to Gerard *et al.* (1998), zeta potential of ESPA1 membrane was similar to that of CPA2 membrane**.**

It should be noted that LFC1 membrane showed minimal positive or negative potential at different pH and thus it is normally referred to as the low fouling membrane for water reclamation applications. This is because charged colloids and ions could not easily approach membrane surface to form links and aggregates. Fouling becomes more severe when there are more colloids or NOM and membrane surface charge is stronger. It should also be noted that low fouling LFC1 membrane typically becomes less effective after several chemical cleaning cycles. It could be due to the release of embedded poly-vinyl alcohol (PVA) which is used to modify the polyamide separation surface layer of LFC1 membrane. New generation LFC membrane might perform better if PVA impregnation process is improved. When zeta potential of CPA2 membrane was –15 mV, that of LFC1 showed only 1 mV at pH 5. When the pH was 10, zeta potential of CPA2 was –20 mV and that of LFC1 was only –2 mV as shown in Table 4.1**.** For better illustration, zeta potentials of RO membranes at different pH are also presented in Fig. 4.1.

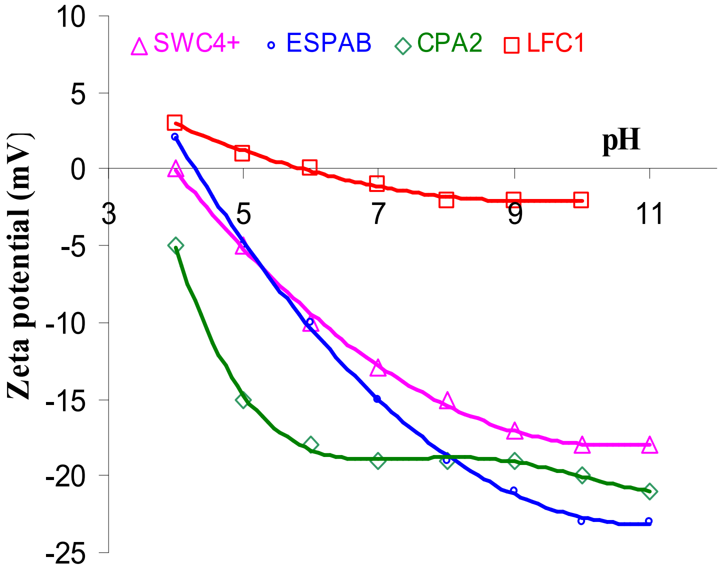

Figure 4.1 Zeta potential of RO membranes at different pH

Table 4.1 Zeta potential of RO membranes at different pH

pH	Zeta potential (mV)			
	CPA2	LFC1	ESPAB	SWC4+
4	–5	3	2	0
5	–15	1	–5	–5
6	–18	0	–10	–10
7	–20	–1	–15	–13
8	–19	–2	–19	–15
9	–19	–2	–21	–17
10	–20	–2	–23	–18
11	–21	not available	–23	–18

Surface potential of RO membranes was also reported to be more negative at higher pH by Childress and Elimelech (1996) and others (Belfer *et al*., 1998; Bellona *et al*., 2005; Gerard *et al*., 1998; Kaneko *et al*., 1996; Koseoglu *et al*., 2008; Schafer *et al*., 2004; Zhao *et al*., 2005). Iso-electric points of membranes used in their study could be located at the pH range of 3 – 5 which is similar to the results obtained in this study as shown in Fig. 4.1. They also stated that a polymeric membrane acquires surface charge when it is brought in contact with ionizable solution. This acquired surface charge influences the distribution of ions at the membrane-solution interface; co-ions are repelled from the membrane surface and counter-ions are attracted to it. The fundamental of the electrical double layer is the plane of shear which separates the fixed part of the electrical double layer from the mobile part. The electrical potential at the shear plane is called zeta (or electro-kinetic) potential.

Occurrence of negative zeta potential at higher pH for all membranes suggested that there could be significant electrostatic repulsion between the negatively charged membrane surface and the negatively charged ions such as borate investigated in this study and by other researchers (Pastor *et al*., 2001; Prats *et al*., 2000). When membrane is brought in contact with high concentration of cations, especially divalent ions, negative surface charge of membrane becomes less negative or even positive due to the influence of cations.

Boron at low concentration and pH less than 7 exists in the form of charge-neutral boric acid and it transforms into negatively charged borate ion only at alkaline pH with a pK_a value of 9.25 (Choi and Chen, 1979; Adams, 1965). Borate also has a larger molecular dimension than boric acid. Boric acid dimension was reported to be 4 Å by Toray (2008). Thus, better boron removal by RO membranes at higher pH could be attributed to either size exclusion or charge repulsion mechanisms. However, charge repulsion mechanism should not be a dominant factor when surface potential changed to positive value while boron removal was still high and this phenomenon will be discussed later in conjunction with boron removal by ESPAB and SWC4+ membranes operating at higher salinity (Section 4.2.2).

4.1.2 Zeta potential of RO membranes at different salinities

Zeta potential of RO membranes has earlier been reported to shift towards negative value at higher pH (Elimelech and Childress, 1996; Gerard *et al*., 1998; Oo and Ong, 2010). However, there is a lack of information concerning this tendency of zeta potential at different salinities especially at increasing salt concentration. In view of this, respective zeta potentials of ESPA1, LFC1, CPA2, ESPAB and SWC4+ membranes were also measured at different salinities and initially at pH 9 (Oo and Ong, 2010). The other reason to measure zeta potentials at different NaCl concentrations was to validate the speculation made in an earlier report (Oo and Song, 2009) that lower boron removal by brackish water RO membranes at higher salinity was partly due to a shift of zeta potential to positive values and hence less charge repulsion or perhaps enhanced diffusion took place. The results of zeta potential at different salinities are shown in Figs. 4.2 and 4.3.

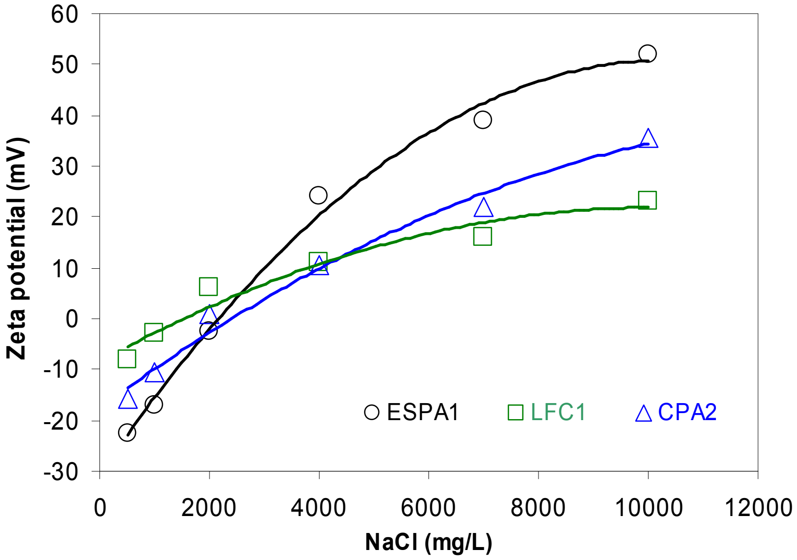

Figure 4.2 Effect of salinity on zeta potential of BWRO membranes at pH 9

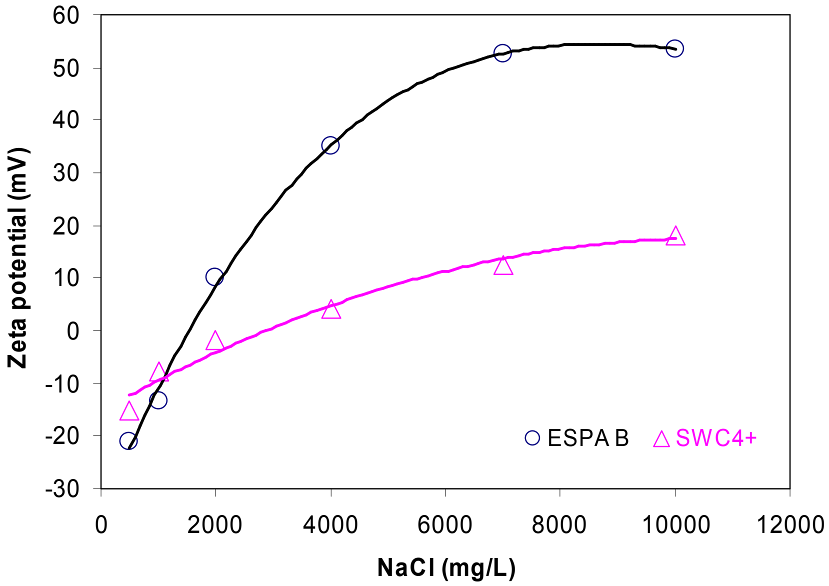

Figure 4.3 Effect of salinity on zeta potential of ESPAB and SWC4+ at pH 9

It was observed that the zeta potential of ESPA1 membrane was –22 mV at 500 mg/L of NaCl. It then slowly changed to a less negative value at higher salinity and reached a positive value of 52 mV at 10000 mg/L. While ESPAB membrane showed a similar zeta potential trend as that of ESPA1, it should be noted from Figs. 4.2 and 4.3 that the zeta potential slopes for CPA2, LFC1 and SWC4+ increased at slower rates towards the higher salinity region. At a NaCl concentration of 10000 mg/L, their zeta potentials were 36, 23 and 18 mV, respectively. Zeta potentials of all RO membranes used in this study were more or less negatively charged at pH 9 and 500 mg/L of NaCl. However, at higher NaCl concentrations, zeta potentials generally shifted towards the positive region. This phenomenon could be attributed to a stern layer that was densely shielded by positive ions as shown in Fig. 4.4 which was adapted from the literature (Elimelech and Childress, 1996).

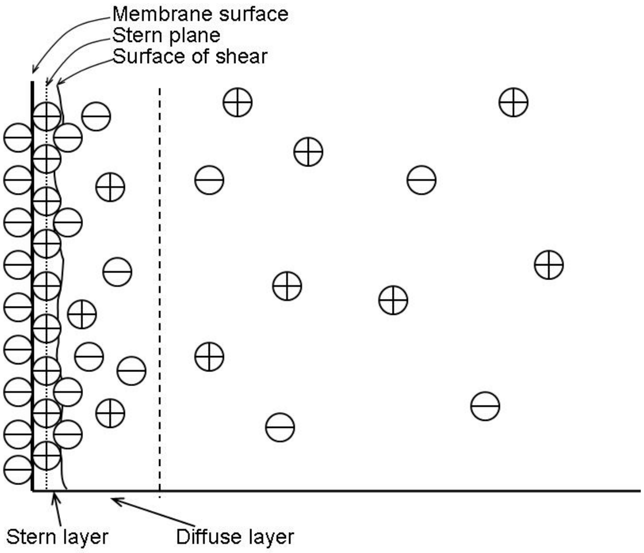

Figure 4.4 Model of electric double layer at membrane surface (Elimelech and Childress, 1996)

As the intrinsic surface potential of most RO membranes is negative, abundance positive ions could lead to the formation of a stern plane near membrane surface. Thus, it would reduce electrostatic repulsion portion of membrane separation and enhance the diffusion of solute at the same time. Yezek *et al*. (2005) reported that at neutral pH, steady state diffusion flux of ions or molecules through a membrane is believed to rely on ionic strength of the solution. At decreasing ionic strength, the flux of ions transport is increasingly limited by solution diffusion. With the situation of abundance positive ions near membrane surface, negatively charged colloids could easily approach there at higher salinity and cause severe fouling too. Isoelectric points of all RO membranes used in this study fell between 1000 – 3000 mg/L of NaCl when pH was 9. Thus, fouling of membrane by charged particles should be minimal at this region of medium salinity. Table 4.2 summarizes the zeta potentials of all RO membranes at different salinities and pH 9.

Table 4.2 Effect of salinity on zeta potential of RO membranes at pH 9

NaCl (mg/L)	Zeta potential (mV)				
	ESPA1	LFC1	CPA2	ESPAB	SWC4+
500	–22	–8	–16	–21	–15
1000	–17	–3	–10	–13	–8
2000	–2	6	1	10	–2
4000	24	11	10	35	4
7000	39	16	22	53	13
10000	52	23	36	54	18

According to Table 4.2, empirical equations for zeta potential of different membranes at different salinities and pH 9 could be expressed as follow:

ESPA1: $y = -8\,x^{2}\,10^{-07} + 0.0158\,x - 30.517$ (4.1)

LFC1: $y = -3\,x^{2}\,10^{-07} + 0.006\,x - 8.4565$ (4.2)

CPA2: $y = -3\,x^{2}\,10^{-07} + 0.008\,x - 17.649$ (4.3)

ESPAB: $y = -1\,x^{2}\,10^{-07} + 0.0216\,x - 31.214$ (4.4)

SWC4+: $y = -3\,x^{2}\,10^{-07} + 0.0062\,x - 15.343$ (4.5) where y is zeta potential (mV) and x is NaCl concentration (mg/L).

Generally, zeta potential trend of all RO membranes followed a second order polynomial equation with different intersection values. Lower values of intersection for LFC1 and SWC4+ membranes indicated the minimal negative surface potentials at zero salinity. At a salinity higher than 10000 mg/L of NaCl, surface zeta potential seemed to increase at a slower rate because the negative product of second order term would offset the positive increment of first order term.

For NF membranes, transport of ions to the membrane surface and through the pores take place according to the strength of electrostatic field formed under different types and strengths of solutions. The model for solute transport would normally consider the contribution of electrostatic repulsive force on ion transport by the effective volumetric charge density of membrane surface. One of the studies on the changes of surface potential at different salinities for NF membrane (Ernst *et al.* 2000) suggested that negative zeta potential decreased slowly due to excess adsorption of opposite ions up to a Na_2SO_4 concentration of 4×10^{-4} M and then increased towards positive zeta potential when the concentration was higher than 3×10^{-3} M.

Ernst *et al.* (2000) assumed that the reversal of sign could be attributed to over-compensation by counter-charged adsorption in the stern layer. And, it is obvious that adsorption of counter-charged ions Na^+ took place in their study. Since NF membranes are normally applied for handling divalent ions, impact of monovalent molecule, KCl, used in their study may not be significant. For KCl solution, change of zeta potentials at increasing concentration could no longer be related to characteristics of rejection rate of NF membrane. Generally, surface characteristics of membrane in terms of zeta potential would be critical when salt rejection mainly depends on different diffusion rates of respective ions.

Change of surface potential to more positively charged value has also been reported in the study of effect of source water types on zeta potential by Deshmukh and Childress (2001). They have indicated that the divalent cations, Ca^{2+} (approximately 0.4 mM) and Mg^{2+} (approximately 0.45 mM), found in river water lead to the formation of complex with membrane surface functional group and became less negatively charged. For a combination of 2 mg/L humic acid and 1 mg/L of atrazine, negatively charged functional groups of humic acid dominated the membrane surface charge causing more negative zeta potential. When the membrane was exposed to the storage chemical such as sodium meta-bisulfite ($Na_2S_2O_5$), meta-bisulfite could adsorb onto membrane surface and caused more negative zeta potential.

The other report on the study of the membrane surface potential in RO process (Kaneko and Yamamoto, 1976) also indicated that zeta potential values of CA membranes under their investigation tend to increase with feed concentrations higher than 10^{-1} N for different solutions (e.g., NaCl, KCl, $MgCl_2$, $MgSO_4$, Na_2SO_4). In the study of Matsumoto *et al.* (2007), positive zeta potential was reported at concentration <0.001 M of NaCl and $MgCl_2$ at a high pressure gradient of 0.3 MPa. Zeta potential was negative at the lower pressure gradient. At higher salt concentration, impact of pressure gradient on zeta potential faded away. They were puzzled with the concentration dependencies of zeta potential especially at high pressure gradient.

Investigation of zeta potential was also extended to measurement at different salinities and pH 7. Fig. 4.5 shows the zeta potential of BWRO membranes at pH 7 and different salinities while Fig. 4.6 illustrates the zeta potential of RO membranes with high boron rejection. Results of CPA2 and SWC4+ membranes were reported earlier (Oo and Ong, 2012). Trends of zeta potential changing from negative values at lower salinity to positive ones at higher salinity were very much similar to the corresponding trends observed with same membranes at pH 9. The changes in zeta potential were more pronounced for ESPA1, CPA2 and ESPAB membranes compared to LFC1 and SWC4+ membranes.

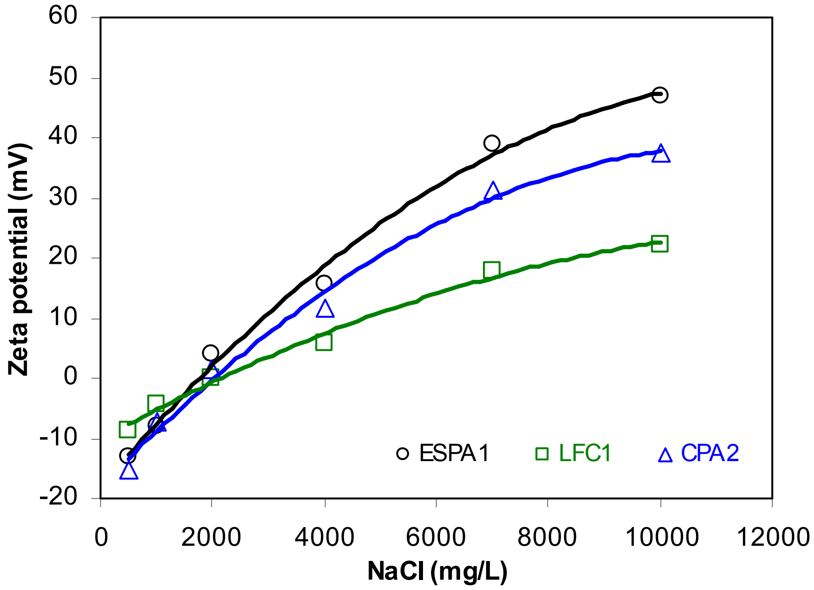

Figure 4.5 Effect of salinity on zeta potential of BWRO membranes at pH 7

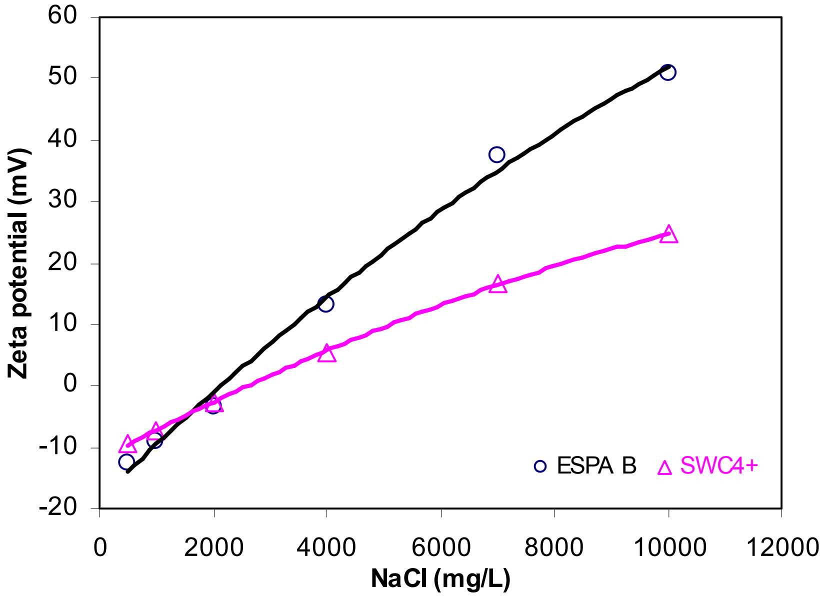

Figure 4.6 Effect of salinity on zeta potential of ESPAB and SWC4+ at pH 7

As shown in Fig. 4.5, zeta potential of ESPA1 membrane shifted from –15 mV at 500 mg/L of NaCl to +45 mV at 10000 mg/L of NaCl. In contrast, the corresponding values of LFC1 membrane shifted from –7 mV only to +20 mV, respectively. Zeta potential of ESPAB was similar to that of ESPA1 while zeta potential of SWC4+ indicated a similar trend as that of LFC1. Respective zeta potential values of all RO membranes are summarized in Table 4.3. As all membranes used in this study have intrinsic property of negative zeta potential at pH 7 and 9, it is logical that positively charged ions approach and accumulate near membrane surface which led to the formation of positive zeta potential layer especially at higher salt concentrations. This phenomenon is better illustrated in Fig. 4.4, model of electric double layer.

Table 4.3 Effect of salinity on zeta potential of RO membranes at pH 7

NaCl (mg/L)	Zeta potential (mV)				
	ESPA1	LFC1	CPA2	ESPAB	SWC4+
500	–13	–8	–15	–13	–9
1000	–8	–4	–7	–9	–7
2000	4	0	1	–3	–3
4000	16	6	12	13	6
7000	39	18	31	39	17
10000	47	22	37	51	25

When the values in Table 4.3 were analyzed, empirical equations for zeta potential of different membranes at different salinities and pH 7 were obtained as follow:

ESPA1: $y = -4\,x^{2}\,10^{-07} + 0.0110\,x - 18.285$ (4.6)

LFC1: $y = -2\,x^{2}\,10^{-07} + 0.0052\,x - 10.292$ (4.7)

CPA: $y = -4\,x^{2}\,10^{-07} + 0.0099\,x - 18.326$ (4.8)

ESPAB: $y = -2\,x^{2}\,10^{-07} + 0.0090\,x - 18.449$ (4.9)

SWC4+: $y = -1\,x^{2}\,10^{-07} + 0.0050\,x - 12.057$ (4.10)

where y is zeta potential (mV) and x is NaCl concentration (mg/L).

Generally, zeta potential trend of all RO membranes followed a second order polynomial equation with intersection values ranged from 10.292 to 18.449. Lower value indicated less negative surface potential at low salinity. When the salinity was higher than 10000 mg/L of NaCl, surface zeta potential seemed to increase at a slower rate because the negative product of second order term offset the positive increment of the first order term. As zeta potential changed at different salinities, it could be an indicator that ion diffusion via specific chemical interaction (Fatin-Rouge *et al.* 2003) or electrostatic effect (Nilsson *et al.* 1985; Johansson *et al.* 1993) could vary accordingly at different salinities.

Effect of divalent ions on zeta potential of different RO and NF membranes observed by Childress and Elimelech (1996) showed that divalent ions could have more influence on zeta potential of membrane. When 0.001 M $CaCl_2$ was used for thin film composite NF membrane, divalent cation Ca^{2+} seemed to approach membrane causing more positive surface charge. In the case of Na_2SO_4, divalent anion, SO_4^- could be the cause of making membrane surface more negatively charged. When both divalent cation Mg^{2+} and divalent anion SO_4^- were present in the solution, zeta potential of membrane above iso-electric point did not change substantially, possibly due the balancing effect between positive and negative charges.

In general, Childress and Elimelech (1996) suggested that complex formation of Ca^{2+} with membrane surface functional groups could be more favourable because RO membranes would be negatively charged above the iso-electric point. However, close approach of co-ion Cl^- could counteract the effect of dominant divalent ions on the membrane surface potential. Although 2 mg/L of humic acid may cause membrane surface more negatively charged, the impact of the humic acid adsorption to membrane surface could be enhanced further in the presence of divalent cation Ca^{2+}. Cationic surfactant (dodecyl trimethyl ammonium bromide) and anionic surfactant (sodium dodecyl sulfate) were also reported to be the cause of altered membrane surface potential at the concentration of 0.1 mM.

When surface potential of membrane changes from negative to positive value, ions with opposite charge could approach easier to membrane surface to form concentration polarization layer. Depending on affinity of opposite ions, those with stronger affinity to a charged surface could pass through membrane more rapidly by enhanced diffusion. At neutral pH and high salinity, positive membrane surface could be shielded by abundance of chloride ion Cl^{-} and better affinity with boric acid $B(OH)_3$ may cause enhanced diffusion. When pH of the solution is in alkaline region with low salinity, intrinsic membrane surface property would be negatively charged and borate ion could be easily repelled from membrane. At higher pH and higher salinity, positive membrane surface could be shielded more by hydroxyl ion OH^{-} and chloride ion Cl^{-} causing both pushing (by co-ions) and pulling (by membrane) of borate ions, $B(OH)_4^{-}$. It should also be noted that isoelectric points for all membranes fell within the similar salinity range of 1000 – 3000 mg/L of NaCl as that at pH 9.

4.2 Boron removal by RO membranes

Although RO membranes have been widely used as a barrier to remove dissolved ions, mechanisms responsible for their removals have thus far not been well understood. Two models, pore-flow model (Sourirajan and Matsuura, 1985) and solution-diffusion model (Lonsdale *et al.*, 1965) have long been referred and debated by many researchers. Modifications to both models have been attempted by others to seek a common ground for predicting the performance of RO membranes. Thus, a comprehensive study on RO performance under different situations (i.e., removal of charged or uncharged ions, removal at different pH and salinities, and removal by different types of RO membranes) will facilitate our understanding on boron removal mechanisms by RO membranes. In this study, boron removal by RO membranes was mainly investigated at different pH, fluxes and salinities using different types of RO membranes. Results obtained were analysed and discussed in terms of fundamental principles to identify possible boron removal mechanisms under different situations.

4.2.1 Boron removal at different pH and fluxes

Boron removal by RO membranes has mostly been studied at different pH in the past because enhanced boron removal was reported at higher pH **(**Taniguchi *et al*., 2001; Pastor *et al.,* 2001; Prats *et al*., 2000; Glueckstern *et al*., 2003; Magara *et al*., 1998**).** An example of boron removal by BWRO membranes at different pH values was conducted at the initial part of this study and results are presented in Fig. 4.7 (Oo and Song, 2009). This part of the experiment was conducted with DI water spiked with boric acid (5 mg/L boron) and 0.1 M caustic soda was added for pH adjustment.

According to pK_a value of boric acid, percent dissociation of boric acid to negatively charged borate would be minimal at around neutral pH as shown in Fig. 4.10. This phenomenon will be discussed in greater details in Section 4.2.2.

At a pH higher than pK_a value of boric acid, boron will primarily be in the form of negatively charged and larger sized borate ion. Thus, boron could be more readily removed by RO membranes attributed to stronger charge repulsion or enhanced size exclusion mechanism. This phenomenon could account for the poor boron removal observed at pH 7.5. Namely, the corresponding removal efficiencies were 25% for ESPA1, 48% for LFC1 and 52% for CPA2 membranes. Boron removal efficiency improved almost linearly with pH, up to 9.5. The boron removal results along with their respective standard deviation (SD) values are summarized in Table 4.4. In this study, it was confirmed that boron removal efficiencies obtained by ESPA1, LFC1 and CPA2 membranes increased with pH and that the removal efficiencies improved almost linearly over the pH range of 7.5 to 9.5 (Oo and Song, 2009).

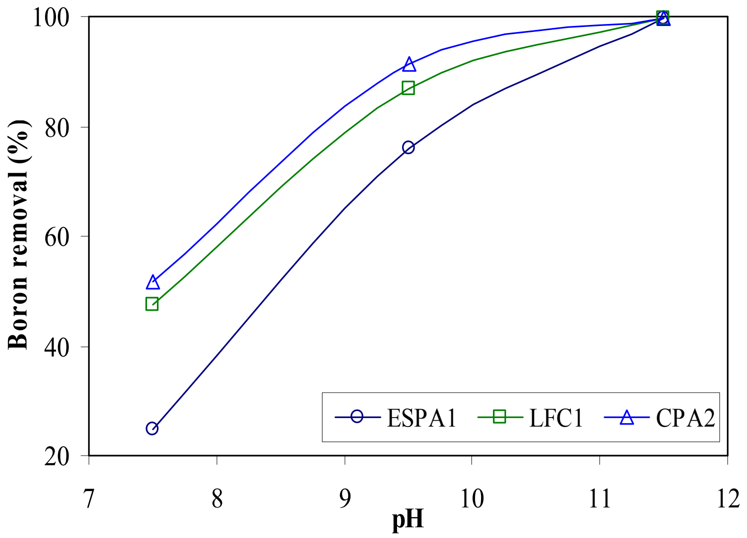

Figure 4.7 Effect of pH on boron removal by BWRO membranes

Table 4.4 Boron removal at different pH by BWRO membranes

Membrane	% boron removal at different pH		
	pH 7.5	pH 9.5	pH 11.5
ESPA1	25 (2.0)	76 (2.0)	>99 (na)
LFC1	48 (1.1)	87 (2.3)	>99 (na)
CPA2	52 (1.4)	91 (1.6)	>99 (na)

Note: values in bracket show SD, na *means not applicable*

When the pH reached 11.5, more than 99% of boron was removed because boric acid in the solution fully dissociated into borate form at this pH value. On the other hand, surface potential of the LFC1 and CPA2 membranes are negatively charged at pH higher than 7 and 6, respectively, as shown in Table 4.1. Trend of boron removal by RO membrane at different pH resembles the percent contribution borate at different pH. That is, boric acid in the solution gradually dissociates into borate ion at faster rate between pH 8.5 to 10.5 but gradually slow down towards pH 11.5. Therefore, the result of enhanced boron removal at higher pH could be explained by significant electrostatic repulsion which took place between the negatively charged membrane surface and the negatively charged borate ion, $B(OH)_4^-$, at higher pH. The results of boron removal observed in this study are well in line with the observation reported in other studies (Taniguchi *et al.*, 2001 and 2004; Pastor *et al.,* 2001; Prats *et al.*, 2000; Glueckstern *et al.*, 2003; Magara *et al.*, 1998).

Figure 4.8 (Oo and Ong, 2011) shows an illustrated comparison of results obtained from this study and those obtained in other studies. Boron removal generally reached >99 % at pH 10.5 – 11.5 in all three studies. Although impact of salt concentration was later investigated in this study, relation of salt concentration and boron removal has been overlooked in the other studies. While Taniguchi *et al.* (2004) tried to formulate a model to estimate boron concentration from salinity of product water, Hyuang and Kim (2006) argued that the relationship could be different at pH other than neutral and salinity at different levels. In general, salt rejection was in linear relation with boron rejection at a constant pH but different operating pressures. When pH was adjusted, rejection of other ions could no longer be used as an indicative mean for boron removal estimation, probably due to difficulty to establish the relationship between the changes of different pK_a values and diffusion coefficients of boron and other ions.

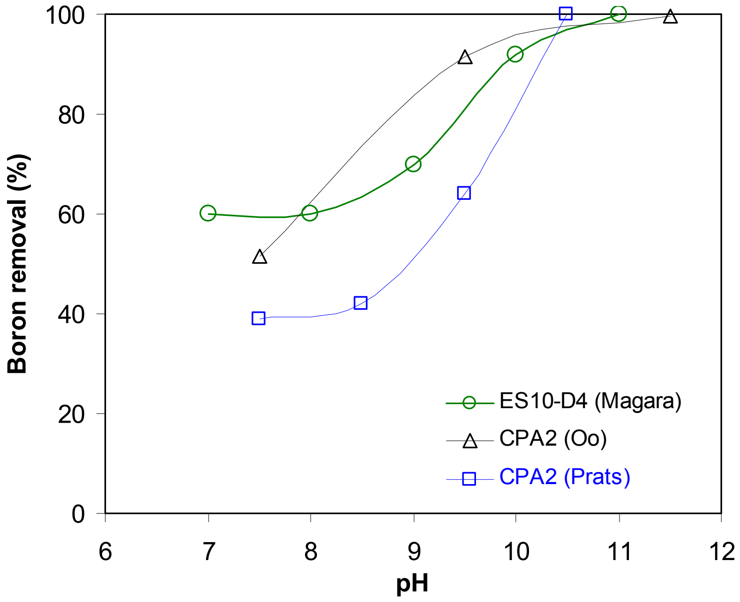

Figure 4.8 Effect of pH on boron removal by CPA2 membrane in different studies

While boron removal at neutral pH most likely follows the size exclusion mechanism, rejection of borate ion at raised pH might be improved by the effect of reduced diffusion and a result of increased charge repulsion. At very high ionic strength, Hyuang and Kim (2006) proposed that permeability constant of boron could be predicted by using permeability constants of boric acid and borate together with their respective percent contribution at different pH. And, permeability constant of total boron P_{sB} can be described as follow:

$$P_{sB} = \alpha_0 \times P_{s(H3BO3)} + \alpha_1 \times P_{s(H2BO3^-)} \tag{4.11}$$

where $P_{s(H3BO3)}$ and $P_{s(H2BO3^-)}$ are permeability constants of boric acid and borate ion, α_0 and α_1 represent fraction of boric acid and borate ion, respectively. It is also interesting that there is negligible impact of pH on mass transfer coefficients of boron but permeability constant decreases at increasing pH. For example, mass transfer coefficients of boron for SWC4+ membrane at pH 6.2 and 9.5 are 2.38×10^{-3} and 2.74×10^{-3} cm/s, respectively, while the corresponding values for permeability are 3.84×10^{-5} and 7.24×10^{-6} cm/s (Hyuang and Kim, 2006).

Although there is not much thorough analysis of boron removal either by size exclusion or charge repulsion, it is reasonable to assume that boron removal at neutral pH should be mainly due to size exclusion and that at higher pH could be contributed by both size exclusion and charge repulsion mechanisms. Contribution of membrane surface characteristics under different salinities will be analyzed and discussed in the section of impact of salinity on boron removal mechanism.

Owing to the ease of raising the pH, desalination plants typically adopt this approach partially or fully to remove boron in the second pass RO process. However, long-term operation of RO system at highly alkaline condition may require careful and thorough evaluation as membrane integrity or life span could be compromised.

Fig. 4.9 shows the effect of permeate flux on boron removal when the test was conducted at pH 10 and 15000 mg/L of NaCl. For ESPA1 membrane, boron removal became negative at lower flux as shown in Fig. 4.9. Boron removal by ESPA1 membrane was 41% at a flux of 39 L m^{-2} h^{-1} (lmh) and it became –3% and –26% at 19 lmh and 10 lmh, respectively. Negative rejection of sodium at high calcium concentration was normally observed and reported during the study of NF (Schafer *et al*., 2004). The phenomenon is called Donnan effect where ionic strength of divalent ions boosts the diffusion rate of monovalent ion. Enhanced diffusion of sodium ion into permeate side might also be due to the necessity to maintain electro-neutrality of solution. Trends of boron removal by LFC1 and CPA2 membranes were similar to that of ESPA1. They were 71%, 48% and 23% for CPA2 membrane at 25, 13 and 5 lmh, respectively. For LFC1 membrane, boron removals were 61%, 16% and –5% at 22, 9 and 4 lmh, respectively. Changing rate of removal efficiency was about 2.3% per lmh for ESPA1 membrane. Respective reductions of removal efficiency were approximately 3.7% and 2.4% for LFC1 and CPA2 membranes. Better boron removal at higher flux could be explained by a faster transport of water through membrane whereas solute transport is relatively constant at same pH, ionic strength and temperature.

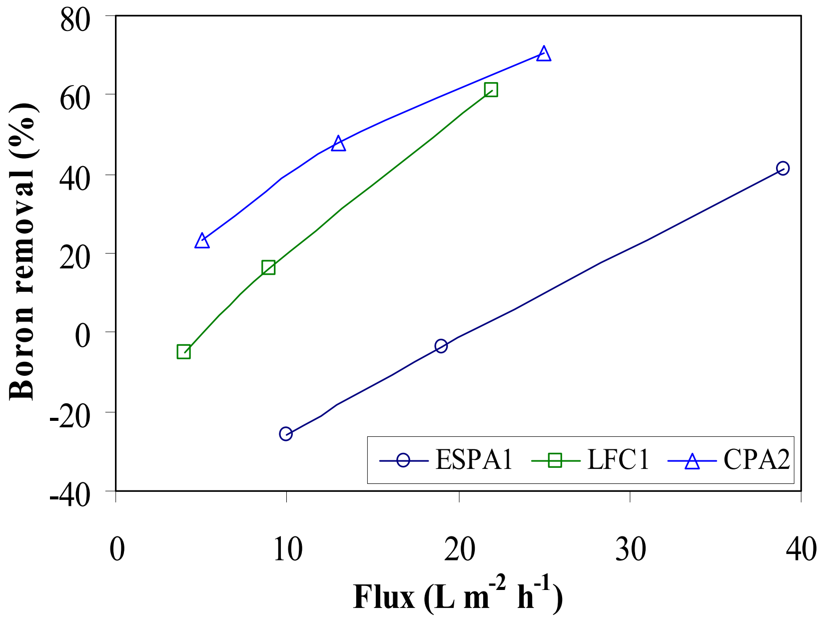

Figure 4.9 Effect of flux on boron removal at pH 10 and 15000 mg/L NaCl

Table 4.5 Boron removal by BWRO membranes at different fluxes

ESPA1	Flux (lmh)	39	19	10
	Removal (%)	41 (3.0)	–3 (0.3)	–26 (4.0)
CPA2	Flux (lmh)	25	13	5
	Removal (%)	71 (1.4)	48 (3.6)	23 (1.0)
LFC1	Flux (lmh)	22	9	4
	Removal (%)	61 (2.2)	16 (1.8)	–5 (4.0)

Note: values in bracket show SD, feed boron 5 mg/L.

4.2.2 Boron removal at different salinities and pH 9

A review of literature suggested that more borate ion will be formed at lower pH when the ionic strength of the solution is higher (Choi and Chen, 1979; Geffen *et al.*, 2006; Wilf, 2007). That is, pK_a of boric acid decreases from 9.25 at 0% salinity to 8.5 at 30% salinity by weight. A good illustrated example adapted from literature (Choi and Chen, 1979) is shown in Fig. 4.10. Change of pK_a, due to the changes in activity of borate ion by the increased ionic strength of solution, to a lower value indicates that the enhanced dissociation of boric acid into borate ion takes place at higher salinity.

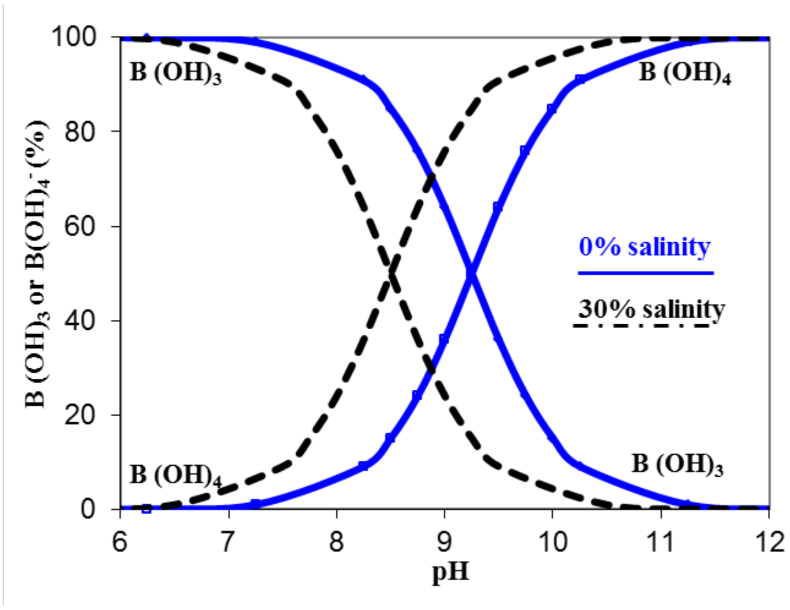

Figure 4.10 Distribution of $B(OH)_3$ and $B(OH)_4^-$ at different pH (Choi and Chen, 1979)

As shown in Fig. 4.10**,** at pH 9.0, negatively charged borate accounts for about 36% and 76% of the total boron in the solution at 0% and 30% salinities, respectively. At pH 10, borate will be at about 85% and 97% at 0% and 30% salinity, respectively. It should also be noted that the difference in borate compositions at different salinities is much lesser at pH value further away from either side of the region of 9. In particular, the difference in borate ion compositions is almost negligible at pH 7 between 0% and 30% salinities. The corresponding difference seems to be less than 3% between 0% and 30% salinities.

Projection of Fig. 4.10 theoretically suggested that there would be more borate at higher salinity than that at the lower salinity and the same pH. Therefore, it is expected that boron removal will be better at higher salinity (Geffen *et al.*, 2006; Wilf, 2007). However, experimental results obtained in this study (Oo and Song, 2009; Oo and Ong, 2010 and 2012) suggested an opposite and unexpected trend of boron removal depending on type of membrane and salinity region. One of the reasons of this observation might be due to the alteration of membrane surface potential at higher salinity. Thus, borate ion was not rejected well at high salinity by some of the membranes. Effect of ionic strength was initially tested at pH 9 because percent compositions of borate in the solution at different salinities differ significantly from each other.

Although exact pK_a value of boric acid at 1.6% salinity is not available, study of Choi and Chen (1979) suggested that pK_a value declined at log scale rather than linear scale towards higher salinity. Study of Wilf (2007) also suggested that pK_a value of seawater could be less than 9. According to Hyuang and Kim (2006), pK_a at different salinities and temperatures could be estimated as follow:

$$pK_a = 2291.9/T + 0.01756 \times T - 3.385 - 0.32051 \times S^{1/3} \qquad (4.12)$$

where T is the absolute temperature (K) and S is the concentration of chloride ion (mg/L).

With these references, percentages of borate at pH 9 were calculated to be 36% at 0% salinity (pK_a: 9.25) and 56% at 1.5% salinity (pK_a: 8.9). Therefore, difference of borate ion contents at 0 and 1.5% salinities could be approximately 20% which might still have impact on differences of boron removal.

The results of boron removal at different salinities for BWRO membranes are shown in Fig. 4.11 (Oo and Song, 2009). When CPA2 membrane was tested at pH 9 and different salinities, boron removal was 61% at 500 mg/L NaCl and it reduced to 59%, 53% and 45% at 5000, 10000 and 15000 mg/L, respectively. The trend of lower boron removal at higher salinity was similar for the other two BWRO membranes as shown in Fig 4.11. Boron removal by ESPA1 membrane was the lowest at all salinities among the three BWRO membranes tested. Boron removal efficiency was initially about 37% at 500 mg/L NaCl. It declined to 33%, 24% and 17% at 5000, 10000 and 15000 mg/L NaCl, respectively. Table 4.6 shows the boron removal of all RO membranes with their respective SD values.

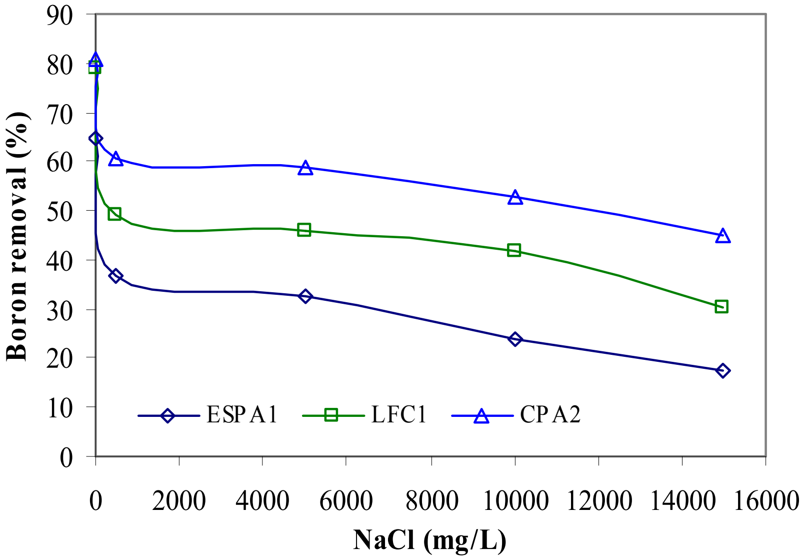

Figure 4.11 Effect of salinity on boron removals by BWRO membranes at pH 9

As the impact of borate composition could lead to different boron removal by different type of RO membranes, boron removals by ESPAB and SWC4+ membranes were investigated too. Under similar operating conditions, these two membranes generally provided better boron removal than those of BWRO membranes. While boron removal by BWRO membranes decreased towards higher salinity, boron removal by ESPAB and SWC4+, as shown in Fig. 4.12 (Oo and Ong, 2010), differed from those of BWRO membranes. When ESPAB membrane was tested at pH 9 and different salinities, boron removal was 89% at 500 mg/L of NaCl and it reduced to 67% at 2000 mg/L. It was then increased to 75% and 79% at 10000 and 15000 mg/L, respectively. Boron removal trend at higher salinity was similar for SWC4+ membrane as shown in Fig. 4.12. It was initially 95% at 500 mg/L NaCl and it reduced to 86% at 2000 mg/L. However, boron removal was then improved to 91% and 89% at 10000 and 15000 mg/L, respectively.

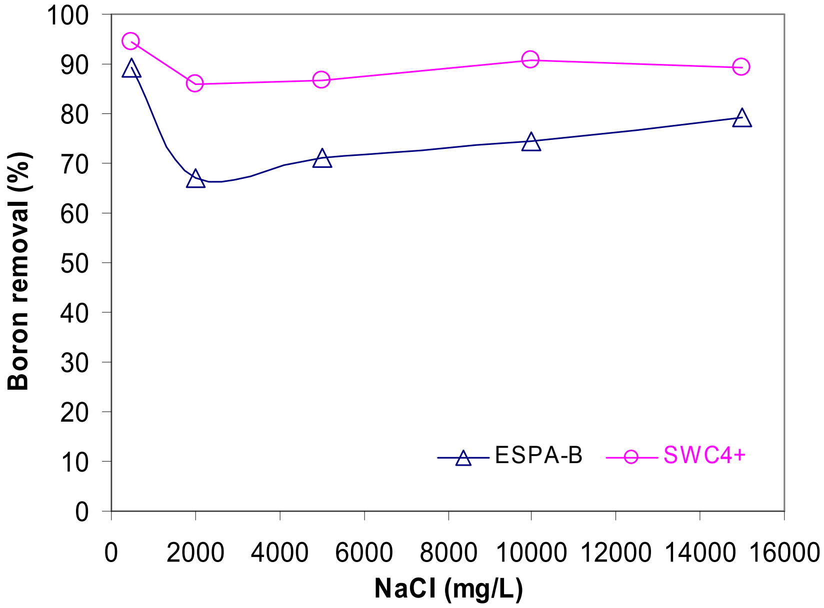

Figure 4.12 Effect of salinity on boron removals by ESPAB and SWC4+ at pH 9

Lower boron removal at higher salinity was also noted in one of the boron removal studies conducted by Koseoglu *et al.* (2008). However, they have reported for only two extreme conditions, DI water and seawater at pH 8.2. One of the membranes showed boron removal of >98% under testing with DI water and removal became 89 – 90% when tested with seawater. They briefly suggested that the phenomenon was governed by super-saturation effect near membrane surface rather than looking into the change of membrane surface characteristics.

Table 4.6 Effect of salinity on boron removal at pH 9

Membrane	% boron removal at different NaCl concentrations			
	500 mg/L	5000 mg/L	10000 mg/L	15000 mg/L
ESPA1	37 (0.6)	33 (1.1)	24 (1.3)	17 (2.4)
LFC1	49 (2.8)	46 (3.1)	42 (2.2)	30 (1.9)
CPA2	61 (0.6)	59 (2.1)	53 (3.4)	45 (0.3)
ESPAB	89 (2.6)	71 (2.0)	75 (1.1)	79 (0.1)
SWC4+	95 (3.0)	87 (1.4)	91 (0.5)	89 (2.0)

Note: values in bracket show SD, feed boron 5 mg/L.

The results of lower boron removal especially by BWRO membranes at higher salinity suggested that other effects such as charge neutralization or hindrance of membrane surface potential at high salinity (Schafer *et al.*, 2004) could be present. Charge neutralization could lead to easier approach of negative borate ion towards positively charged membrane surface. Thus, boron removal by charge repulsion mechanism could have been affected adversely. When the membrane surface is less negatively or more positively charged at higher salinity, boron removal by electrostatic repulsion between membrane surface and borate ion becomes less dominant. On the other hand, one of the past studies (Yoon *et al.*, 2005) indicated that membrane charge density was altered and might have brought about faster diffusion of ions through the membrane at higher ionic strength. It is therefore necessary to further investigate and verify the cause of lower boron removal observed at higher salinity. That is, whether it is caused by the alteration of membrane surface charge density (i.e., more negative or positive, at higher bulk concentration of salts) or by the changing rate of transport of boron at higher salt concentration.

Boron removal by BWRO membranes decreased with increasing salinity at pH 9. At pH 9, amide (N-H) and carboxyl (C=O) groups of membrane surface, as shown in Figs. 2.1 and 2.2, could exert a slightly negative charged ion, and thus surface potentials of most RO membranes showed negative values when they were measured at low ionic strength solutions. However, zeta potential value changed to positive values at higher salinities. With the shift of zeta potential towards positive value at higher salinity, one may expect that boron removal by these membranes would be altered by reduced charge repulsion. That is, when surface potential becomes positive at higher salinity, boron removal by those RO membranes would become less efficient. With such a situation, boron removal at high salinity could be expected mainly by size exclusion mechanism. Nonetheless, at higher salinity for BWRO membranes, there could be a certain extent of enhanced diffusion of boric acid which was better removed at lower salinity and even borate ion which should be removed more efficiently by RO membranes. In other words, the positive impact of salinity to lower the pK_a value, a condition for more borate formation at a same pH, was dominated by the negative effect of salinity to alter membrane surface to positive zeta potential which could be the cause of reduced boron removal by BWRO membranes observed at higher salinity.

On the other hand, results of boron removal observed by ESPAB and SWC4+ membranes suggested that boron removal by those membranes occurred mainly via size exclusion, especially at higher salinity. When surface potential at NaCl 500 mg/L was negative, boron removal by both membranes was most efficient. That is, at low salinity, boron removal benefited from both charge repulsion and size exclusion mechanisms. Once surface potential became neutral or positive at NaCl concentration 2000 mg/L or higher, boron removal acquired less contribution from charge repulsion of borate ion because zeta potential of membrane entered the region of positive values. Boron removal was minimal at around 2000 mg/L of NaCl. When salinity was higher than that level, positive impact of salinity to lower the pK_a value prevailed. Owing to lower pK_a, there was more borate formation and boron removal improved. This impact was more obvious in the performance of ESPAB. As intrinsic boron removal by SWC4+ was relatively high, the effect of lower pK_a due to high salinity was not as obvious as that of ESPAB. In view of the above, one could expect that size exclusion mechanism dominated at higher salinity. Thus, boron removal by these membranes at low salinity could partly be contributed by charge repulsion mechanism. Further studies should also be conducted to investigate and quantify boron removal by each mechanism on different RO membranes.

Similar pattern of having a concave shape rejection profile has also been reported by Bellona and Drewes (2005) in their study on surface charge and rejection of ibuprofen by NF membranes. Although pK_a of ibuprofen was about 4.9, the highest rejection of ibuprofen was obtained at pH 3 and the percent removal reduced towards pH around 5. But, rejection was increased again at pH beyond 7. One of the hypotheses proposed by them was that the initial removal mechanism was improved via adsorption of trace organic onto the membrane surface at pH 3. With membrane surface potential decreased further to more negative value at higher pH, enhanced removal of ibuprofen was attributed to the stronger electrostatic repulsion mechanism. It should be noted that initial rejection via adsorption can lead to partition and diffusion through membrane into the permeate during long-term operation. Other trace organics (2-naphthalensulfonic acid, 1,4-dihydroxybenzoic acid, acetic acid and glutaric acid) with pK_a values around 3 – 5 showed improved rejection at higher pH via enhanced charge repulsion.

Since enhanced removal of compounds could be achieved via stronger electrostatic repulsion mechanism, attention should be given to the situation where zeta potential of membrane shifts toward opposite charge of respective ions of interest. Change of zeta potential could not only be due to monovalent ions but also be due to divalent ions. If sieving effect is the key removal mechanism, investigation on the change of zeta potential may not be useful. Lee *et al.* (2001) also reported that lower urea rejection by RO membranes could be due to stronger interaction between urea and membrane which can achieve higher rejection on small ions such as sodium and chloride.

4.2.3 Boron removal at different salinities and pH 10

When the experiment was further conducted at pH 10, CPA2 membrane achieved a boron removal of 81% at 500 mg/L NaCl. It decreased to 77% and 71% when NaCl reached 2000 and 15000 mg/L, respectively, as shown in Fig. 4.13. For LFC1 membrane, boron removal decreased from 78% at 500 mg/L NaCl to 61% at 15000 mg/L NaCl. Removal efficiencies were 53% and 41% for ESPA1 membrane at 500 mg/L and 15000 mg/L NaCl, respectively. Effect of salinity on boron removal seemed to be less significant at pH 10 than that at pH 9. However, the observed trend of lower boron removal at higher salinity was similar to those observed at pH 9. Percent boron removal at different salinities and pH 10 for BWRO membranes with respective SD values are summarized in Table 4.7.

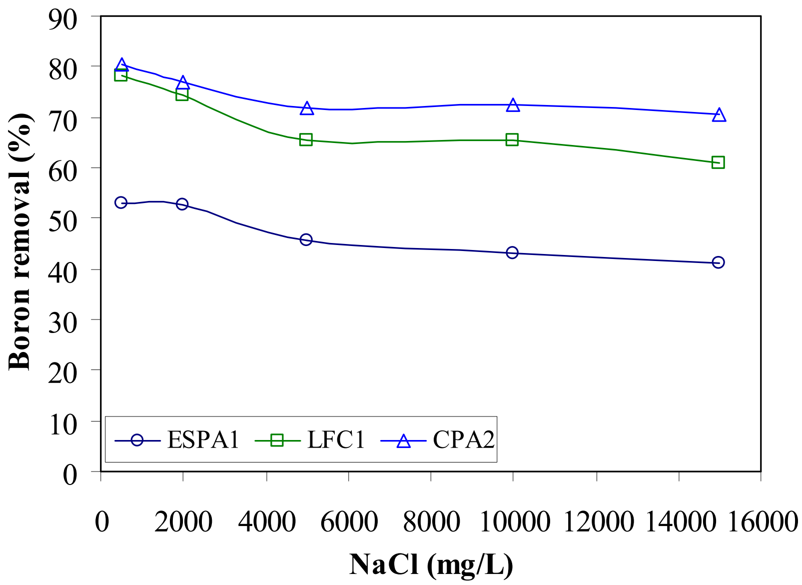

Figure 4.13 Effect of salinity on boron removal by BWRO membranes at pH 10

Similar result of less impact from salinity on boron removal at high pH was reported by Koseoglu *et al.* (2008). At pH 10.5, the difference in boron removal at different salinities faded away and they noted that positive impact of raising pH for more borate ion formation on boron rejection overtook the negative impact of higher dissolved solid level in seawater to alter the membrane surface potential. With the use of SWRO membranes in their study, boron removal was >98% for the tests with both

DI water and seawater. In a separate report, Koseoglu *et al.* (2008) indicated that boron removal is independent of feed boron concentration up to 6.6 mg/L. This observation is similar to the finding reported by Magara *et al*. (1998) who conducted study up to 35 mg/L of boron.

Table 4.7 Effect of salinity on boron removal at pH 10

Membrane	% boron removal at different NaCl concentrations			
	500 mg/L	5000 mg/L	10000 mg/L	15000 mg/L
ESPA1	53 (3.0)	46 (0.6)	43 (2.3)	41 (3.0)
LFC1	78 (2.7)	66 (0.3)	65 (0.8)	61 (2.2)
CPA2	81 (1.3)	72 (4.0)	73 (2.8)	71 (1.4)

Note: values in bracket show SD, feed boron 5 mg/L.

4.2.4 Boron removal at different salinities and pH 7

Since boron removal at different salinities and pH 9 showed different trends for BWRO membranes and high boron rejection RO membranes, this study further investigated boron removal by different RO membranes at different salinities and pH 7. This sub-study would facilitate one to assess the impact of salinity when there is little or no contribution from borate ion formation. Fig. 4.14 shows the effect of salinity on boron removal by BWRO membranes at pH 7 and Fig. 4.15 illustrates the results of high boron rejection membranes. Results of CPA2 and SWC4+ membranes were reported earlier (Oo and Ong, 2012).

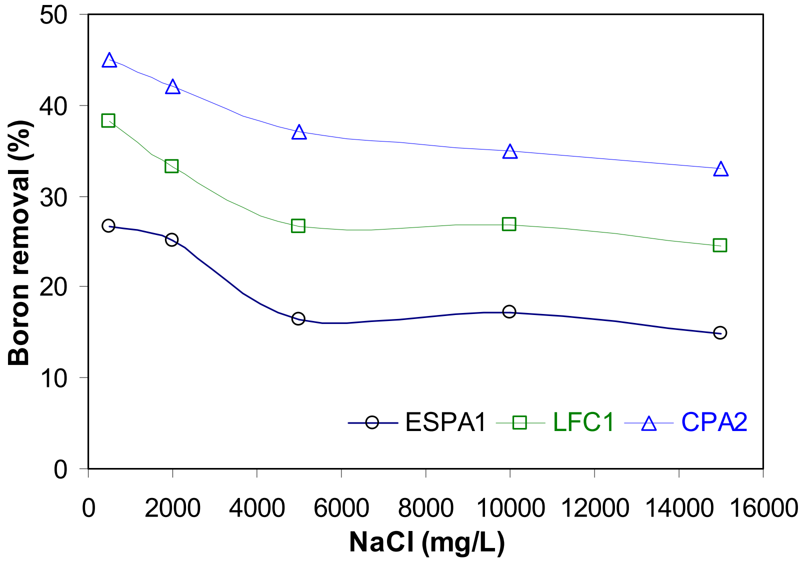

Figure 4.14 Effect of salinity on boron removal by BWRO membranes at pH 7

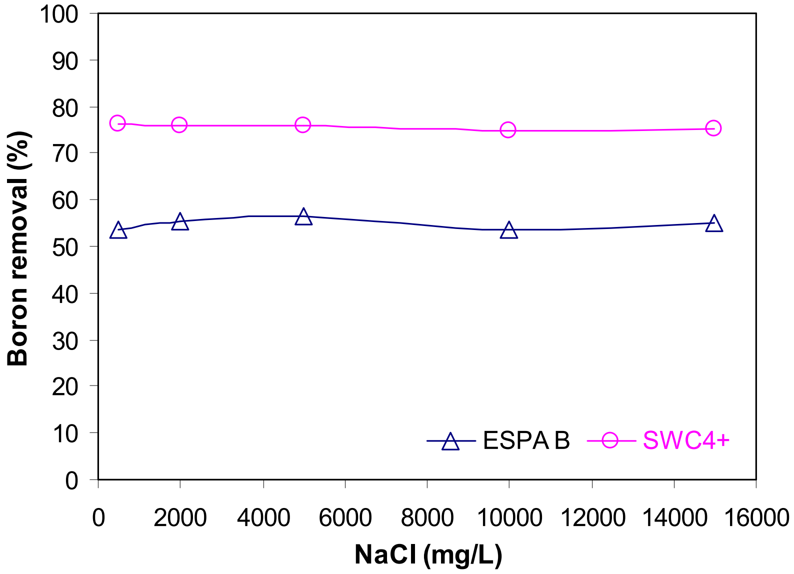

Figure 4.15 Effect of salinity on boron removal by ESPAB and SWC4+ at pH 7

Boron removal of CPA2 membrane was 45% at 500 mg/L of NaCl and it decreased to 37% and 33% at 5000 and 15000 mg/L of NaCl, respectively. LFC1 and ESPA1 membranes showed the similar trends toward higher salinity at pH 7. ESPA1 membrane provided the lowest boron removal among the three BWRO membranes studied under similar testing conditions. With a negligible amount of borate ion formed at pH 7, boron removal by BWRO membranes should mainly be attributed to size exclusion rather than charge repulsion mechanism at pH 7. When zeta potential was negative at low salinity, boron removal was highest for BWRO membranes. When salinity was higher, boron removal decreased. The results suggested that reduction of boron removal observed at higher salinity could be attributed to enhanced diffusion.

In the study on influence of biofouling on boron removal (Huertas *et al.*, 2008), decrease in boron rejection by fouled membrane was explained by hindered back-diffusion of boron through the biofilm which elevates the boron concentration adjacent to membrane surface. Wang *et al.* (2001) also reported that diffusivity of humic acid increases with decreasing pH and increasing calcium concentration, which can also be explained that humic acid molecules were compacted at low pH and high ionic strength.

On the other hand, boron removals by ESPAB and SWC4+ remained constant at different salinities as shown in Fig. 4.15 when solution pH was maintained at 7. The result was different from that observed at pH 9 where there was a decrease in boron removal towards 2000 mg/L of NaCl before the boron removal recovered again at higher salinity. At pH 7, boron removal of ESPAB was about 55% over the salinity range of 500 – 15000 mg/L of NaCl while that of SWC4+ was about 75%. With the similar shift of zeta potential to positive values at higher salinities and pH 7, stable boron removal at all salinities suggested that boron was removed mainly through size exclusion mechanism by these two membranes. Table 4.8 shows the summarized results of boron removal with their respective SD values. It should be noted that change of surface potential did not have any positive or negative roles in boron removal at pH 7. In addition, difference of borate ion formation at pH 7 for low and high salinities was negligibly small, less than 3% even between 0% and 30% salinities. That is, positive impact of borate formation, though negligibly small, for better boron removal might be balanced by the enhanced diffusion occurred at higher salinity.

Table 4.8 Effect of salinity on boron removal at pH 7

Membrane	% boron removal at different NaCl concentrations				
	500 mg/L	2000 mg/L	5000 mg/L	10000 mg/L	15000 mg/L
ESPA1	27 (0.4)	25 (1.5)	16 (0.2)	17 (0.5)	15 (1.6)
LFC1	38 (2.0)	33 (0.5)	27 (0.9)	27 (0.4)	24 (3.0)
CPA2	45 (1.3)	42 (0.1)	37 (1.7)	35 (0.2)	33 (1.9)
ESPAB	54 (0.1)	55 (1.8)	56 (1.5)	54 (2.5)	55 (0.6)
SWC4+	76 (1.0)	76 (0.5)	76 (0.3)	75 (0.6)	75 (0.3)

Note: values in bracket show SD, feed boron 5 mg/L.

Ernst *et al.* (2000) also indicated the difficulty to relate the change of zeta potential to salt rejection by PES NF membrane. It was attributed to the fact that zeta potential was measured without any filtration of water where salt rejection tests would not be completed without producing permeate. It means pore-structure influence was not considered for zeta potential measurement whereas the influence occurred during salt rejection test. They also reported that Na^+ seemed to alter zeta potential to positive value at 0.001 M of Na_2SO_4 but K^+ showed no impact to reverse zeta potential value while using 0.002 M KCl solution.

4.2.5 Effect of other components on boron removal

Initially, enhanced boron removal was attempted by iron complex formation because promising result was reported in the study of plating rinse water reuse (Qin *et al.* 2005). However, it was found later that simply adding iron salts alone could not improve boron removal even with a high concentration ratio of B:Fe at 1:10. The results are shown in Table 4.9. ESPA1 membrane was also used for the investigation in this study. Promising result of boron removal observed in the study conducted by Qin *et al*. (2005) might be due to other components which were normally kept as trade secret of the industry. Thus, further investigation was abandoned in this study.

Table 4.9 Boron removal at different Fe to B ratios

Fe : B	Fe in feed (mg/L)	Feed boron (mg/L)	Permeate boron (mg/L)	Rejection (%)
1	1	1.11	0.762	31
5	5	1.17	0.763	35
10	10	1.23	0.751	39
10	50	5.51	4.18	24

In addition, with the knowledge of possibility to form boron complex with mannitol, experiments were conducted to determine the required molar ratio of mannitol to obtain enhanced boron removal. Boron removal by RO membrane could also be improved through formation of boron-diol complex using other types of diol such as glycol. Mannitol was initially used as the complex forming agent to verify this concept. When the mannitol concentration was less than 4000 mg/L prepared in DI water spiked with 5 mg/L of boron, boron removal was not improved and remained at about 30 – 40% for ESPA1 membrane. When pH of the solution was adjusted to 7, boron removal was improved to about 70%. The results are summarized in Table 4.10 as a reference.

The required amount of 4000 mg/L mannitol noted in this study for enhanced boron removal was higher than the amount reported in the study of Geffen *et al.* (2006) where approximately 1000 mg/L of mannitol was used to remove 5 mg/L of boron. Possibility to use mannitol for enhanced boron removal by RO membrane was also discussed in a study conducted by Raven (1980). As each mannitol molecule possesses 6 hydroxyl groups, each molecule should theoretically be able to capture three boric acid molecules to form a complex. Glycol was also tried up to a concentration of 100 mg/L when boron concentration was set at 5 mg/L. Boron removal was not improved too. Experiment was then discontinued because it is not practical to dose such a large amount of mannitol or other diols for achieving enhanced boron removal.

Table 4.10 Boron removal at different mannitol concentrations

Feed pH	Mannitol in feed (mg/L)	Feed boron (mg/L)	Permeate boron (mg/L)	Rejection (%)
6.2	50	5.32	3.49	34
6.1	100	5.39	3.48	35
6.0	200	5.39	3.40	37
6.0	4000	5.46	3.42	37
7.0	4000	5.45	1.15	79

As concentration of mannitol was beyond practical limit for real world application, other test conditions to determine the optimal mannitol dosage were suspended. However, complex formation technique could possibly be applied if large molecular diols can be found and reused by trapping at UF type pretreatment. If the complex formation between boron and mannitol could be made effective, each mg/L of boron removal should only require approximately 6 mg/L of mannitol to form complex for enhanced boron removal by RO membranes.

4.2.6 Impact of pH on boron removal at low and high salinities

When experimental results were analyzed from the different angle, it was found that impact of pH on boron removal was more pronounced at pH <9 when salinity was low. As shown in Table 4.11, boron removal by CPA2 membrane improved 16% (from 45% to 61%) when pH was raised from 7 to 9 at 500 mg/L of NaCl. However, the improvement was only 12% (from 33% to 45%) at 15000 mg/L of NaCl. Improvement of boron removal by other two BWRO membranes were also more pronounced at pH <9 when salinity was low. Improvement of boron removal by ESPA1 and LFC1 membranes were 10% and 11%, respectively, when pH was less than 9 and NaCl concentration was 500 mg/L. The corresponding values were less at 2% and 6% when pH was less than 9 and NaCl concentration was 15000 mg/L.

On the other hand, the impact of pH on boron removal was more pronounced at pH>9 when salinity was high. As shown in Table 4.11, boron removal by CPA2 membrane improved by 20% (from 61% to 81%) when pH was raised from 9 to 10 at 500 mg/L of NaCl. The improvement was higher at 26% (from 45% to 71%) at 15000 mg/L of NaCl. Improvement of boron removal by the other two BWRO membranes were also more pronounced at pH >9 when salinity was high. Improvement of boron removal by ESPA1 and LFC1 membranes were 16% and 29%, respectively, when pH was more than 9 and NaCl concentration was 500 mg/L. The corresponding values were higher at 24% and 31% when pH was more than 9 and NaCl concentration was 15000 mg/L.

These results imply that boron removal at low salinity could be more effective at pH only up to 9. For pH higher than 9, boron removal could be improved faster at high salinity. However, it could be difficult to raise the pH at high salinity because scaling potential is higher and may cause operating problems and shorter membrane life span. Quick review on boron removal by CPA2 and ESPAB membranes at different pH and salinity with respective zeta potential is tabulated in Appendix 2.

Table 4.11 Boron removal at different pH and salinities

NaCl (mg/L)	pH	% boron removal of different membranes				
		CPA2	ESPA1	LFC1	ESPAB	SWC4+
500	7	45	27	38	54	76
	9	61	37	49	89	95
	10	81	53	78	--	--
15000	7	33	15	24	55	75
	9	45	17	30	79	89
	10	71	41	61	--	--

Chapter 5 Summary, Conclusions and Recommendations

5.1 Summary

Boron removal has been a challenging issue for membrane desalination industry. At this juncture, enhanced boron removal at membrane desalination plant has mostly been achieved by raising the pH of second pass RO feed. This study was conducted with the aim to achieve a better understanding on the impact of pH and salinity on boron removal by different RO membranes: ESPA1, CPA2, LFC1, ESPAB and SWC4+ from Hydranautics. A pH range of 7 to 11 and salinity range of 500 to 15000 mg/L of NaCl were used in this study. Although the impact of pH on boron removal has been investigated extensively elsewhere, this study was conducted to fill the research gap on the impact of salinity and interplay of pH and salinity on boron removal by different RO membranes. The investigation also looked into the impact of salinity on the surface potential of membrane. From the results of boron removal experiments and zeta potential measurements, possible boron removal mechanisms (charge repulsion, size exclusion or enhanced diffusion) were proposed under different salinities using various membranes. Interesting boron removal results obtained at different pH and salinities were also used to discuss the importance of interplay between pH and ionic strength on boron removal by RO membranes. While zeta potential of all RO membranes generally shifted towards a same direction at different salinities, trends of boron removal by BWRO membranes were found to be different from those of ESPAB and SWC4+ membranes. Enhanced boron removal by RO membranes via complex formation with iron, mannitol and glycol were also briefly investigated.

5.2 Conclusions

Boron removal was confirmed to improve at higher pH. Removal efficiencies by CPA2 membrane were 52%, 91% and >99% at pH 7.5, 9.5 and 11.5, respectively. The result obtained in this study was similar to those reported in the literature. Since pK_a value of boric acid is 9.25, there will be additional borate ion formation at different magnitude when the solution pH is in alkaline region. Borate ion is negatively charged and possesses a larger molecular dimension than boric acid. Thus, enhanced boron removal at higher pH is believed to be attributed to the formation of more borate ion.

Zeta potentials of RO membranes observed in this study generally showed more negative values at higher pH. Zeta potentials of CPA2 membrane were found to be –5, –20 and –21 mV at pH 4, 7 and 11, respectively. However, zeta potential values shifted to be positive at higher salinity. At pH 9, zeta potential of CPA2 membrane shifted from –16 mV to +36 mV at 500 mg/L and 10000 mg/L of NaCl, respectively. The trend was similar at pH 7. ESPA1 and ESPAB membranes showed the similar zeta potential trends as that of CPA2. For LFC1 and SWC4+ membranes, change of zeta potential at different salinities was less significant than that of CPA2 membrane. At pH 9, zeta potential of LFC1 membrane shifted from –8 mV to +23 mV at 500 mg/L and 10000 mg/L of NaCl, respectively.

Regardless of pH 7 or 9, isoelectric points of all membranes fell between 1000 and 3000 mg/L of NaCl. Impact of ionic strength on zeta potential was similar for all RO membranes investigated in this study. However, the impact of ionic strength or salinity on boron removal by BWRO membranes was different from that associated with ESPAB and SWC4+ membranes.

Experimental results obtained in this study showed that the increase in ionic strength might adversely affect the boron removal efficiency of BWRO membranes at a same pH. Boron removal by BWRO membranes decreased with increasing salinity at pH 9. Boron removals achieved with CPA2, LFC1 and ESPA1 membranes at pH 9 were 61%, 49% and 37% at 500 mg/L of NaCl, respectively. However, boron removals declined to 45%, 30% and 17% at 15000 mg/L of NaCl. Boron removal by CPA2 membrane at pH 9 indicated that reduced removal at high salinity could be attributed to the impact of hindered charge repulsion when zeta potential of membrane became positive. Nonetheless, there could also be certain extent of enhanced diffusion of boric acid and even borate especially at higher salinity.

In contrast, boron removals by ESPAB and SWC4+ decreased initially towards 2000 mg/L of NaCl at pH 9. Then, removal efficiency was slowly increased towards higher salinity. The concave shape trend of boron removal was more significant for ESPAB. Boron removal by ESPAB was 89% at 500 mg/L of NaCl and pH 9. The removal reduced to 65% at 2000 mg/L of NaCl and then increased to 79% at 15000 mg/L of NaCl. Removal efficiencies by SWC4+ were 95%, 86% and 89% at 500 mg/L, 2000 mg/L and 15000 mg/L of NaCl, respectively. Higher boron removal by these membranes at lower salinity could partly be attributed to charge repulsion mechanism. When the salinity is higher, pK_a value is lower and more borate ion will be formed. Since zeta potential becomes positive at higher salinity, one may expect a reduction of boron removal via charge repulsion mechanism. However, boron removal by these two membranes improved again at NaCl >2000 mg/L where more borate ions will be formed due to lower pK_a value. This phenomenon implied that size exclusion mechanism could be a dominating factor on enhanced boron removal at higher salinity. In view of this, these membranes should be exploited in practice for boron removal at higher salinity.

Impact of salinity on boron removal by BWRO membranes at pH 7 indicated similar trend as those observed at pH 9. The corresponding boron removal efficiencies achieved by CPA2, LFC1 and ESPA1 membranes at pH 7 were 45%, 38% and 27% at 500 mg/L of NaCl. Respective removal efficiencies reduced to 33%, 24% and 15% at 15000 mg/L of NaCl. This observation suggested that, at pH 7, the boron removal mechanism could be attributed to size exclusion in the absence of negatively charged borate ion contribution. Reduced boron removal at higher salinity might be due to enhanced diffusion by higher ionic strength of the solution. On the other hand, boron removal by ESPAB and SWC4+ remained almost constant at varying salinities and pH 7. ESPAB membrane showed boron removal of approximately 54 – 56% while boron removal by SWC4+ was 75 – 76% across all salinities investigated. Since there was no impact of positive zeta potential and borate ion formation on boron removal at pH 7, it could be concluded that size exclusion mechanism prevailed for boron removal by ESPAB and SWC4+ membranes. At pH 7, the impact of a lower pK_a value at higher salinity did not contribute to any difference in percent borate formation, too.

The above results suggested that boron could be better removed at lower salinity for all RO membranes, which supports the current practice to remove boron mainly in the second pass RO where feed salinity is low. The result of boron removal trend observed at different salinities, especially by BWRO membranes, was opposite to those expectations reported in the literature. As pK_a value was reported to be lower at higher salinity, better boron removal by RO membrane was proposed at higher salinity according to some literature. With the findings of this study, the interplay between pH and ionic strength was believed to be more critical to understand boron removal by different RO membranes.

It should also be noted that the impact of pH on boron removal was more pronounced at pH less than 9 when salinity was low. On the other hand, the impact of pH on boron removal was more pronounced at pH higher than 9 when salinity was high.

When boron removal was examined at different fluxes, removal by CPA2 membrane decreased from 71% at 25 lmh to 23% at 5 lmh. Thus, permeate flux should also be maintained practically as high as possible to maximize boron removal. This should not be a problem in the second pass RO where the permeate flux is designed to be high because there is less scaling potential from the permeate of first pass RO.

5.3 Recommendations

Further studies should be conducted to investigate and quantify this rather important aspect of boron removal at various pH and salinity by different types of RO membranes and respective removal mechanisms. A model should be developed from the study of wider range of pH, salinity and actual seawater.

Investigation should also be made to find a practically feasible complex-forming agent for enhanced boron removal by RO membranes.

Owing to availability of more advanced microscopic imaging techniques, impacts of other membrane surface characteristics such as roughness, contact angle, material and molecular structure on boron removal would also be interesting areas for further study.

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Appendix 1 Comparisons of different boron removal methods and their respective removal efficiencies

Item	Process	Water	Boron (mg/L)	Capacity	Removal (%)	Cost (cent/m^3)	Pro and con	Ref.
1	SWRO	SW	5 - 6	pilot	82 - 85	--	Flexible but need to raise pH	Glueckstern *et al.*
2	BWRO	SWRO product	1.2 - 2.0	pilot	62 - 80	4.6	Flexible but need to raise pH	Glueckstern *et al.*
3	BWRO + IX	SWRO product	1.2 - 2.0	pilot	80 - 90	4.2	Higher efficiency but need chemicals	Glueckstern *et al.*
4	SWRO+BWRO (Toray)	SW	5	140m^3/d	91 - 93	--	Flexible but need to raise pH	Taniguchi *et al.*
5	SWRO+BWRO+IX	SW	5	140m^3/d	91 - 93	--	Higher efficiency but need chemicals	Taniguchi *et al.*
6	SWRO (Dow)	SW	4 - 6	290m^3/h	90	--	Flexible but need to raise pH	Redondo *et al.*
7	SWRO+BWRO	SW	5 - 6	290m^3/h	95	--	Flexible but need to raise pH	Redondo *et al.*
8	BWRO or IX	SWRO product	1.0 - 2.0	--	--	7 - 9	Higher efficiency but need chemicals	Redondo *et al.*
9	BWRO	SWRO product	1.4 - 2.0	7.2 m^3/d	99	7.2	Flexible but need to raise pH	Pastor *et al.*
10	BWRO (NTR)	SWRO product	1.0	80-90 m^3/d	70	--	Flexible but need to raise pH	Magara *et al.*
11	RO	Metal plating	0.1 - 0.2	1.5 m^3/h	95	--	Cannot reproduce the result	Qin *et al.*
12	NF+NF	SW	4.6	pilot	74	--	Need complex-forming chemical	Tseng *et al.*

Item	Process	Water	Boron (mg/L)	Capacity	Removal (%)	Cost (cent/m^3)	Pro and con	Ref.
13	Adsorption (A/C)	Simulated SW	5	bench	90	--	Need contact time and adsorbent	Choi *et al.*
14	Adsorption (MgO)	Simav river	100 - 500	bench	70-90	142	Need contact time and adsorbent	Okay *et al.*
15	Ion Exchange(IRA743)	Simav river	100 - 500	bench	90	costly	Efficient but need regeneration chemicals	Okay *et al.*
16	Ion Exchange(IRA743)	SWRO product	1.8	140-280 L/h	99	7	Efficient but need regeneration chemicals	Okay *et al.*
17	EDI	SW	4.0 - 4.5	bench	90	--	Efficient but need current	Melnik *et al.*
18	electrocoagulation	WW	100-1000	bench	80-95	--	Efficient but need current	Yilmaz *et al.*
19	coagulation	WW	15	bench	30 - 80	--	Moderate and need high dosage	Hassan *et al.*
20	co-precipitation (ash)	SW	5.3	bench	97	--	Efficient but bulk sludge generated	Polat *et al.*
21	facilitated transport	--	--	--	--	--	No data published yet	Pieruz *et al.*
22	Complex with diol	Simulated SW	5	bench	90	--	Efficient but need high dose of diol	Geffen *et al.*
23	Adsorption, MF	SW	5	bench	>99	--	Efficient but not tested for long term	Bryjak *et al.*
24	Magnetic particles	Simulated SW	5	bench	>90	--	Efficient at pH <6 and expensive	Liu *et al.*
25	Membrane distillation	Simulated SW	5	bench	>99	--	Efficient but expensive	Hou *et al.*

SW: seawater, WW: wastewater

Appendix 2 Quick review of boron removal by CPA2 and ESPAB membranes at different pH and salinities

Membrane	pH	Salinity	Zeta	B-removal	Reason	Note
CPA2	7	Low	–	Higher (45%)	No charge repulsion Size exclusion	No borate
		High	+	Lower (33%)	No charge repulsion Enhanced diffusion	Little borate, <1%
	9	Low	–	Higher (61%)	Charge repulsion and Size exclusion too	Less borate, 36%
		High	+	Lower (45%)	Less charge repulsion and Enhanced diffusion	More borate, 56%
ESPAB	7	Low	–	Flat (54%)	No charge repulsion Size exclusion	No borate
		High	+	Flat (55%)	Size exclusion No impact of positive zeta potential and salinity	Little borate, <1%
	9	Low	–	Highest (89%)	Size exclusion and Charge repulsion	Less borate, 36%
		High	+	Higher (79%)	Size exclusion Less charge repulsion	More borate, 56%

List of publications from this study

Papers published in journals

(1) Oo M. H. and Song L. (2009) Effect of pH and ionic strength on boron removal by RO membranes, *Desalination* 246, 605–612.

(2) Oo M. H. and Ong S. L. (2010) Implication of zeta potential at different salinities on boron removal by RO membranes, *Journal of Membrane Science* 352, 1–6.

(3) Oo M. H. and Ong S. L. (2012) Removal of boron by RO membranes: impact of pH and salinity, *Desalination and Water Treatment*, 39, 83-87.

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