

Boron Removal in Seawater Reverse Osmosis System

Thesis by
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ABSTRACT

Boron Removal in Seawater Reverse Osmosis Process

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Reverse osmosis successfully proves to remove more than 99% of solute in seawater, providing fresh water supply with satisfied quality. Due to some operational constraints, however, some trace contaminants removal, such as boron, cannot be achieved in one pass system. The stringent criterion for boron from World Health Organization (WHO) and Saudi Arabia local standard (0.5 mg/l) is hardly fulfilled by single pass sea water reverse osmosis (SWRO) plants. Some design processes have been proposed to deal with boron removal, but they are not economically efficient due to high energy and chemical consumption. The objective of this study was to study boron removal by different reverse osmosis membranes in two pH conditions, with and without antiscalant addition. Thus, it was expected to observe the possibility of operating single pass system and necessity to operate two pass system using low energy membrane. Five membrane samples were obtained from two different manufacturers. Three types of feed water pH were used, pH 8, pH 10, and pH 10 with antiscalant addition. Experiment was conducted in parallel to compare membrane performance from two manufacturers. Filtration was run with fully recycle mode for three days. Sample of permeate and feed were taken every 12 hours, and analyzed for their boron and TDS concentration. Membrane samples were also tested for their surface charge. The results showed

that boron rejection increases as the feed pH increases. This was caused by dissociation of boric acid to negatively charged borate ion and more negatively charged membrane surface at elevated pH which enhance boron rejection. This study found that single pass reverse osmosis system, with and without elevating the pH, may not be possible to be applied because of two reasons. First, permeate quality in term of boron, does not fulfill WHO and local Saudi Arabia regulations. Second, severe scaling occurs due to operation in alkaline condition, since Ca and Mg concentration are still high to cause precipitation. Using low energy membrane at pH 10 may be considered, since it gives comparable performance to ordinary brackish water membranes in term of boron and TDS rejections, but consume less energy.

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LIST OF SYMBOLS

ζ	:	Zeta potential (mV)
dU/dp	:	Slope of streaming potential versus pressure (mV/bar)
dI/dp	:	Slope of streaming current versus pressure (mA/bar)
η	:	Electrolyte viscosity (mPa.s)
ε	:	Vacuum permittivity
ε_0	:	Dielectric constant of electrolyte
L	:	Length of streaming channel (mm)
A	:	Cross-section of streaming channel (mm ²)
R	:	Resistance inside the measuring cell (kOhm)

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CHAPTER I: INTRODUCTION

I.1 Background

The water stress occurs around the world due to the trend of growing population coupled with industrialization and urbanization. This means that the water resources availability is less than the demand [1]. It is predicted that the world's population will reach about 9 billion by 2050 [2]. Global annual water demand in 2005 was 2,408 billion cubic meters. With the assumption of 2% annual growth and no improvement in technology or water efficiency, water demand will grow to 6,906 billion cubic meters by 2030. The world's water supply will remain constant in year 2005-2030 at 4,222 billion cubic meters if there is no technological innovation. This number will slightly increase to 4,886 billion cubic meters if the improvement in technology and infrastructure takes place up to year 2030. This condition still shows that water demand in the year 2030 will exceed around 30%, or 2,020 billion cubic meters, of water supply [3]. International Water Management Institute (IWMI) reported to BBC News that one third of the world population faces water scarcity. This falls into four categories, which is depicted on Figure I.1. Lack of investment that leads to poor infrastructure and unequal distribution of water causes an economic water scarcity. Physical scarcity occurs when the availability of water resources cannot meet the demand. Most of these are in arid region such as Middle East and North Africa (MENA). If the water used for agriculture is up to 70 times more than used as drinking water and other domestic purposes, a region is said going to be water scarce. If this continues, there will be emerging problems such as

river pollution, declining groundwater supply, and inequality of distribution. In geographical locations with little or no water scarcity, there are enormous water resources relative to the consumption, only less than 25% of water from rivers is withdrawn for human activities purposes [4].

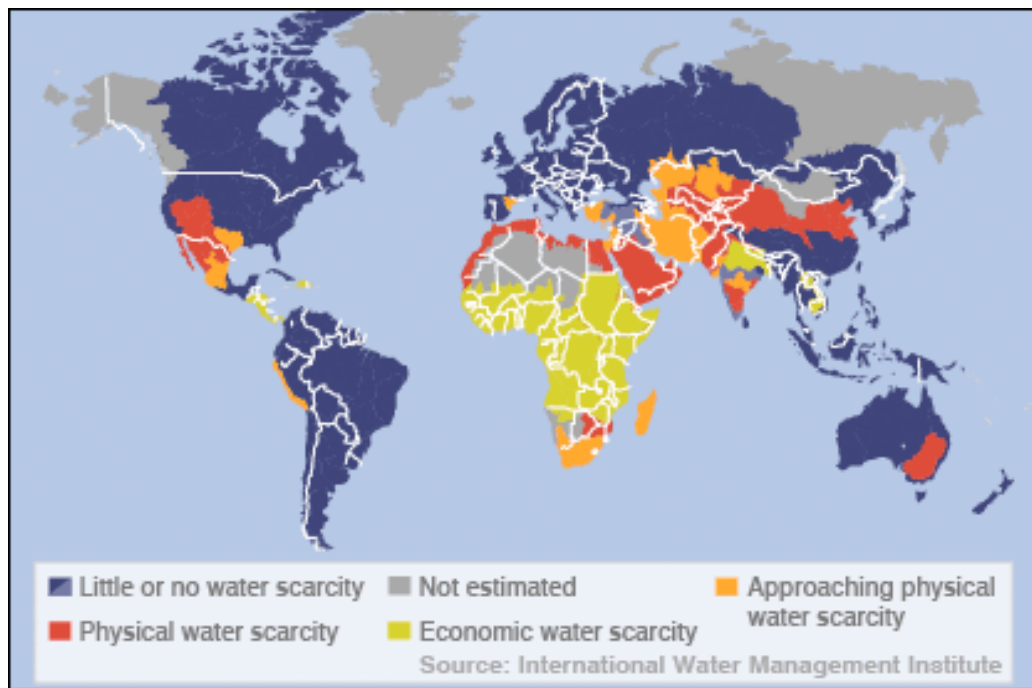


Figure I.1. Map details of global water stress

In addition, Organization for Economic Co-operation and Development (OECD) reported that unsustainable use, poor management of water resources, and climate change will worsen the water scarcity. It is estimated that people living in areas affected by severe water scarcity will increase by another 1 billion to over 3.9 billion in 2030 [5].

Water scarcity has given a challenge to find alternative water resources. Many efforts have been made to fill the gap between water supply and demand. Desalting seawater has become alternative fresh water resources, especially in arid region, such as MENA, where rainfall is one of the lowest in the world. This is supported by the fact that earth is covered by more than 97% saline water and nearly 2% is in the form of snow and ice, leaving less than 1% for agriculture, drinking water, and other human activities purposes [6]. As illustrates in Figure I.2, desalination from seawater takes up to 60% of total worldwide installed desalination capacity.

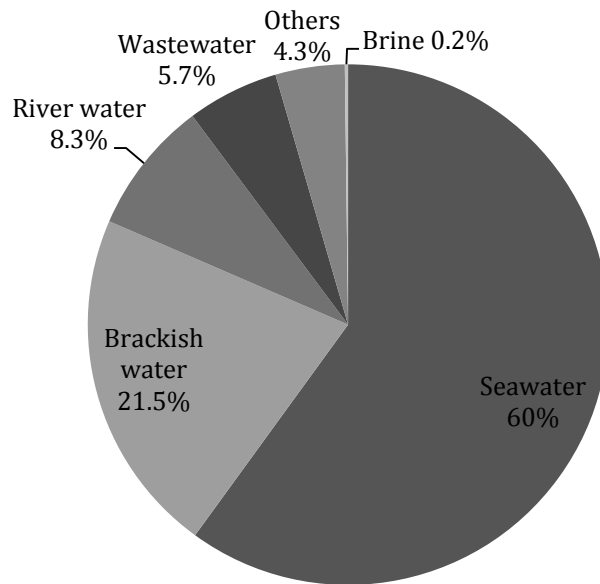


Figure I.2. Total worldwide installed desalination capacity by feed water quality [7]

Desalination technology is commonly classified in two categories: thermal driven and pressure driven by membrane separation processes. There is also electro dialysis technology, but it is used mostly for brackish water as it has low

recovery for high concentration feed. Among those technologies, multistage stage flash (MSF) desalination is the mature technology which has been used widely, especially in MENA region, due to abundant source of energy and water quality assurance. However, reverse osmosis (RO) is currently more dominant due to its less energy intensive and installation space compared to thermal processes. Until 2010, RO plant installation reached up to 60% of all desalination processes [8, 9]. Technologies used in installed desalination plants worldwide are depicted in Figure I.3.

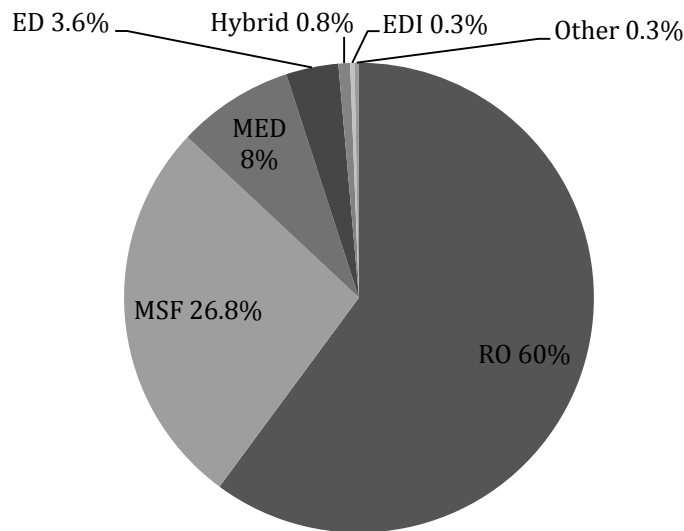


Figure I.3. Total worldwide installed capacity (65.2 million m³/d) by technology [7]

Many improvements in RO, such as process design optimization, better efficiency, energy recovery devices, and new membranes development, have helped to reduce the cost of desalted water [10]. It is predicted that in 2020, desalination industry will produce 120 mega ton per day of fresh water, of which 71.2% is produced by

membrane based desalination processes [11]. As illustrated in Figure I.4, Saudi Arabia has the second largest installed membrane desalination capacity in the world, around 5 million m³/day [7].

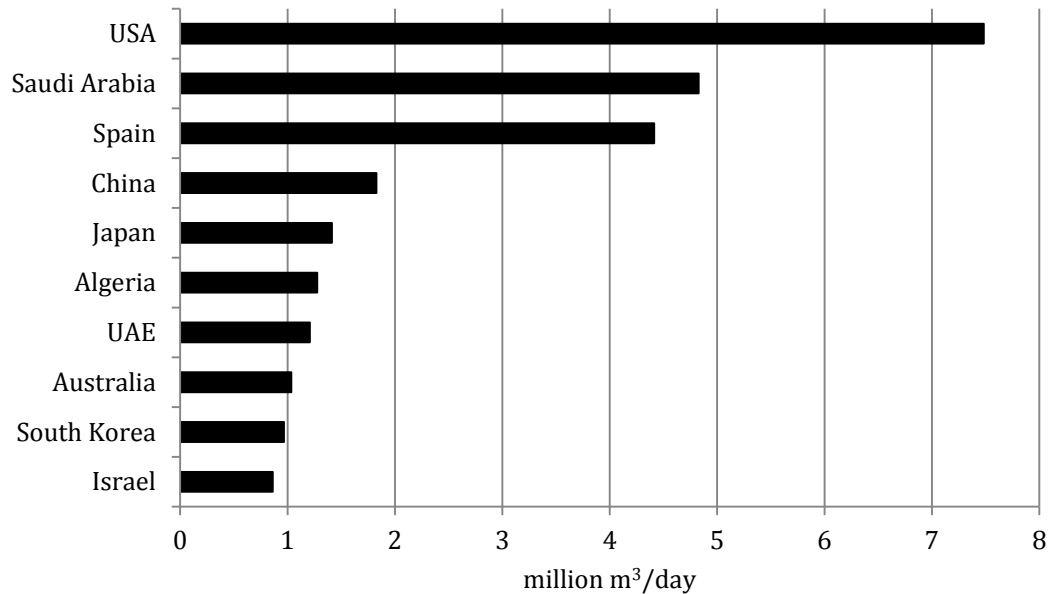


Figure I.4. Top ten countries by total installed membrane capacity from 1945 to 2010

RO has successfully proven to remove almost all the solutes in the seawater, provided fresh water supply for decades. However, trace contaminant such as boron is still present in product water. This is due to boron exist as un-dissociated boric acid (H_3BO_3), which has small molecular size, at natural seawater pH. Thus, some amount of boron diffuses through the membrane [8, 10, 12-15]. Boron was first included in drinking water requirement in 1984 by the World Health Organization (WHO). However, no action was taken considering that boron had not been found to be harmful. Since the experiment to animal in laboratory showed that boron was

harmful, WHO set a guideline value for boron in drinking water of 0.3 mg/l in 1993 [16].

The problem of high boron concentration in desalinated water plants was observed in Israel in 1997, where partial discolored leaves was found due to the toxicity of boron [14]. In 1998, WHO increased the provisional guideline for boron to 0.5 mg/l [9, 10, 12, 14, 15, 17-20] because of the difficulty of boron removal during the water treatment processes. However, this guideline varies in different regions. California Department of Public Health (CPDH) set a guideline of 1 mg/l, which is also applicable in Japan [12]. Oman set the guideline of 0.5 mg/l [21]. Boron guideline compiled by EU is 1 mg/l [20]. Some countries such as South Korea (1 mg/l), New Zealand (1.4 mg/l), Australia (4 mg/l), and Canada (5 mg/l) regulated higher values than WHO recommendation because of two reasons. First, there is lacks of data confirming adverse effects on human health. Second, the targeted value is hardly achieved and cost effective [8].

This stringent criterion for boron is hardly fulfilled by RO plant operating single pass, especially when the high recovery target is set. Even though the removal of TDS using high rejection membranes satisfies the drinking water requirement, but it is not the case for boron. Boron removal essentially depends on operating condition and water quality, especially pH [12]. In natural seawater pH (7.5-8.5), the rejection of boron is less than 80%, whereas rejection of other inorganic ions is up to 99.8% [15]. Thus, there are some options for operating RO including the use of two pass

with elevated pH in the second pass, specific boron adsorption resin, treating first pass RO permeate with electrodialysis, NF-RO hybrid process, and adsorption membrane filtration. However, these scenarios are not economically viable since more energy and chemical consumption, antiscalant and base, are required for the second pass and the resin is somehow difficult to be regenerated [12, 15, 22, 23].

I.2 Problem definition

Although WHO currently applies regulated boron to be 0.5 mg/l, there is a lack of reports about comprehensive toxicological assessment to support this guideline. The Drinking Water Quality Committee at WHO recommended new boron guideline value to be 2.4 mg/l for drinking water quality [8]. It will be incorporated in the Guidelines for Drinking Water Quality 4th edition which is going to be published in this year 2011 [22, 24]. Although this new guideline is based on the human health perspective, some RO plants may still set the boron in product water of 0.5 mg/l or lower to be fit with the agricultural requirement since some crops are sensitive to boron, especially in the MENA region where most of the fresh water is supplied from desalination plants. Another reason that supports this revision is based on the extensive study conducted in the UK and USA on dietary of boron. The results suggested that intake of boron from air and food is lower than predicted. This fact drives to 10% to 40% increased in the allocation to drinking water without interfering the Tolerable Daily Intake (TDI) [8].

Despite this fact, boron limit in Saudi Arabia still follows currently applied WHO regulation. The boron guideline in Saudi Arabia of 0.5 mg/l is regulated by the Ministry of Agriculture and Water (MAW) [25] and SASO (Saudi Arabian Standards Organization) [8].

In addition, minimization or elimination of chemicals (alkali and antiscalant) used, especially when using two pass system, may help RO plants to operate more efficiently and environmentally friendly. It also helps to ease post treatment process concentrate handling. Thus, it is necessary to study boron removal in RO processes, particularly in Saudi Arabia, in order to apply the most effective and efficient desalination system as well as to keep boron level as low as 0.5 mg/l.

I.3 Research objectives

The aim of this study is to evaluate boron removal by different RO membranes in two different pH conditions, with and without antiscalant addition. In addition, membranes zeta potential and scaling potential are investigated. As a consequence, it is expected to observe:

1. possibility to achieve required boron level by single pass system, with and without elevating the pH
2. necessity to use two pass system to achieve required boron level, with and without elevating the pH, by using low energy membrane

CHAPTER II: THEORETICAL BACKGROUND

II.1 Boron overview

II.1.1 Boron occurrence in environment

Boron naturally occurs in soil, rocks, and water. Boron concentration in the air is from ocean, geothermal steam, and evaporation of seawater. The latter gives the most contribution [26]. In seawater boron is found in the range of 4-5 mg/l, but it can be higher in the gulf region. Smaller portion is from human activities such as coal fired, geothermal power plants, chemical plants, and rocket fuels. Since borate has low volatility, boron would not be expected to be present in significant value in the atmosphere [26]. Boron may also be found in food, through which boron exposure to human mostly occurs. Its presence in food relates to boron content in soil where crops are cultivated. Thus, it highly depends on the location. High concentration in soil originated from marine sediments. Boron in prepared food can be in range of non detectable to 26 µg/g of product. It is suggested that the boron intake from food and water is about 5-6 mg/day, and about 7 mg/day if wine is also consumed [27]. Boron occurrence in environment also comes from human activities, such as using the detergent, fungicide, disinfectant, insecticide and fertilizer. Boron is also found in cosmetics, soap, shampoo, and other personal care products (baby oil, lipstick, cream, and lotion). However, the absorption of boron by skin contact is low because the uptake is not efficient. Boron is also found in animal tissue, however human exposure through meat consumption is negligible [28].

II.1.2 Importance and toxicity of boron

Boron is possibly classified as a possible micro nutrient for humans by The National Academy of Science Institute of Medicine. Boron gives important contribution to crops growth. Small amount of boron intake influences cellular function and effectiveness of other nutrients. There is an interaction between boron and vitamin D, as well as with calcium, to affect estrogen metabolism and cerebral activities. The mean dietary intake for male adults is around 1.5 mg/day [27]. The short term exposure results the mild diarrhea and irritation in the diaper area for infant. Boron has been used in medicine component for epilepsy, malaria, etc. Patients have been treated with this medication suffered from indigestion, anorexia, and dermatitis. But if the dose is reduced from 5 to 2.5 mg/kg-day the symptoms disappeared. A study in the high and low borate region concluded that there was no distinction of the live birth. Further study came up with the conclusion that there was no reproduction disorder caused by boron exposure. Another specific study was accomplished to compare the boron mine workers and another group of men. It was observed that the only substantial reproductive impact was the delay in pregnancies and decrease in mean birth mean among boron workers. Also, there was lack of report observed the carcinogenicity of boron and its compounds in human [27].

In animal, low intake of boron might affect cellular malfunction and activity of other nutrients [27]. Boric acid is highly toxic to insects and is widely applied as one component in insecticide. Crops need small amount of boron for their growth. This was the reason boron is one of the component in fertilizer as sodium borate and

boric acid. Excess boron exposure may cause leaves damage, reduce fruit yield, and induce early ripening. The optimal boron concentration for agriculture ranges from 0.3 mg/l to 0.5 mg/l [28]. Table II.1 presents the boron tolerance range limits for agricultural crops.

Table II.1. Boron tolerance range limit for agricultural crops [8]

Tolerance	B in soil water (mg/l)	Agricultural crops
Extremely sensitive	<0.5	Blackberry, lemon
Very sensitive	0.5 – 0.75	Avocado, grapefruit, orange, apricot, peach, cherry, plum, persimmon, Kadota fig, grape, walnut, pecan, onion
Sensitive	0.75 – 1	Garlic, sweet potato, wheat, sunflower, mung bean, sesame, lupine, strawberry, Jerusalem artichoke, kidney bean, snap bean, lima bean, peanut
Moderately sensitive	1 – 2	Broccoli, red pepper, pea, carrot, radish, potato, cucumber, lettuce
Moderately tolerant	2 - 4	Cabbage, turnip, Kentucky bluegrass, barley, cowpea, oats, corn, artichoke, tobacco, mustard, sweet clover, squash, muskmelon, cauliflower
Tolerant	4 – 6	Alfalfa, purple vetch, parsley, red beet, sugar beet, tomato
Very tolerant	6 – 10	Sorghum, cotton, celery
Extremely tolerant	10 – 10.5	Asparagus

II.1.3 Boron chemistry

Boron is non metallic element in Group III of the periodic table. It has atomic number 5 and atomic weight of 10.81. Boron concentration in the earth crust is estimated to be less than 10ppm. It is an electron-deficient element that has a strong affinity and a tendency to form highly stable covalent bonds with electronegative

atoms such as oxygen to form either planar trigonal BO_3 or the negatively charged tetrahedral BO_4^- . Thus, boron is often found in compounds with oxygen [27].

Depending on the boron concentration in aqueous environment, dissolved boron exists as several species. At low boron concentration (≤ 216 mg/l), dissolved boron is mainly observed as the mononuclear boron species, B(OH)_3 and B(OH)_4^- . At higher concentration with increased pH, polynuclear boron such as $\text{B}_2\text{O(OH)}_6^{2-}$ or those incorporating B_3O_3 rings such as $\text{B}_3\text{O}_3(\text{OH})_4^-$, $\text{B}_4\text{O}_5(\text{OH})_4^{2-}$, and $\text{B}_5\text{O}_6(\text{OH})_4^-$ are formed. The existences of polynuclear boron ions are insignificant at the concentrations lower than around 290 mg/l. Since boron concentration in seawater is about 4.8 mg/l, only mononuclear species B(OH)_3 and B(OH)_4^- exist in seawater [8]. Boron in water at the natural pH is mostly found as un-dissociated boric acid. It is a Lewis acid since it attracts hydroxide (OH^-) ion from water and releases hydrogen (H^+) ion. In the opposite direction of borate to boric acid, it releases an OH^- ion which re-binds with an H^+ ion to form water [18].



In the natural seawater pH 7 the species of H_3BO_3 is 99.3% and in pH 8 is 93.2% of the total boron. The rejection of boric acid is about 82-92% for most SWRO commercial membranes and around 30-80% for BWRO membranes [18].

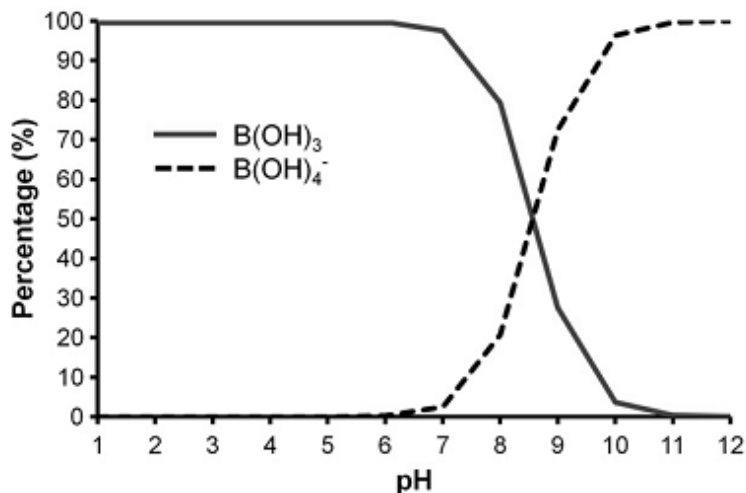


Figure II.1. Effect of pH on boric acid and borate distribution in seawater [8]

Moreover, at pH 10.5 boron rejection is more than 98%. In this pH, almost all boron is in the form of borate ions. Effect of pH on boric acid and borate distribution in seawater is illustrated in Figure II.1. The diffusion of boric acid through the membrane is suspected to be the reason of low rejection of boric acid [8, 10]. This is due to the average radius of boric acid (2.1 Å) is roughly double the size of water molecule that enables to form hydrogen bonds with the active groups of the membrane [10, 14, 16]. Illustration of water, boric acid, borate, sodium, and chloride molecules is depicted in Figure II. 2 [17]. Also, since boron is an electron deficient element, the crystal radius of boric acid is quite large, in the range of 0.244-0.261 nm [17]. On the other hand, boric acid is poorly hydrate, therefore it has small hydrated radius [23]. Borate ion permeation through membranes substantially depends on the diffusive transport since it is found that solvent coupling is insignificant for borate ion. Thus, borate ion is rejected in a similar way as other anionic species such as chloride and sulfate [17].

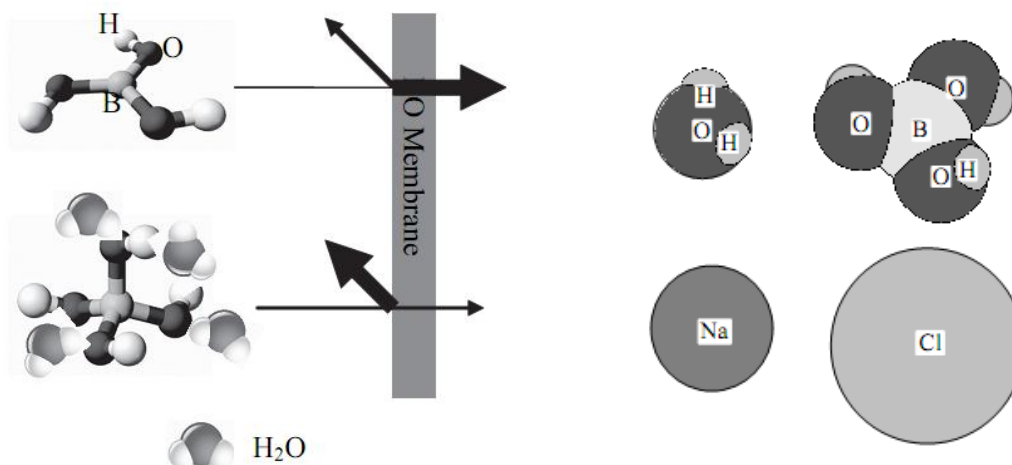


Figure II.2. Comparison of water, boric acid, borate, sodium ion, and chloride ion molecules [14, 28]

II.2 Factors influencing boron removal

II.2.1 Membrane chemistry and behavior

In the early stage, cellulose acetate asymmetric membrane was developed for RO process. Although cellulose acetate membranes are more tolerant to chlorine, it has some disadvantages such as susceptibility to biodegradation, narrow pH range (4-8), small temperature range (0-35°C), and hydrolysis of functional group by acids and alkalies. Thus, thin film composite polyamide membranes have been developed by several manufacturers: DOW/Filmtec, Nitto Denko/Hydranautics, and TORAY, to overcome those disadvantages. Two membranes structure for reverse osmosis process are available today, asymmetric and thin film composite. Asymmetric membranes are produced by casting polymer-containing dope into a homogenous film by single step phase inversion method. This results a dense surface skin on porous support layer. Both skin and support layer have same chemical composition. Thin film composite membrane is synthesized through two steps. First, thick porous

support layer is fabricated. Second, an ultrathin skin layer is coated on top of the support layer. The skin and support layer have different chemical composition [29].

Each layer in thin film composite membranes can be optimized independently. This becomes an important benefit of thin film composite. The support layer can be optimized for maximum strength and compression resistance. Ultrathin skin layer can be optimized for the species selectivity and desired flux. Other advantages include wide pH range, less sensitivity to biological attack, and good hydraulic stability. The skin layer can be produced from various materials, including linear and crosslinked polymers. Linear polymer is less desirable since it performs less hydrophilicity and chemical resistance. However, composite membranes are more sensitive to chlorine than cellulose acetate. Even with small amount of chlorine, its performance can decrease rapidly [29]. Figure II.3 shows an example of crosslinked fully aromatic polyamide ultra-thin composite membrane (UTC) is fabricated by TORAY Company. It has an excellent feature using 1, 3, 5-triamonobenzene (TAB) as polyamine component [30].

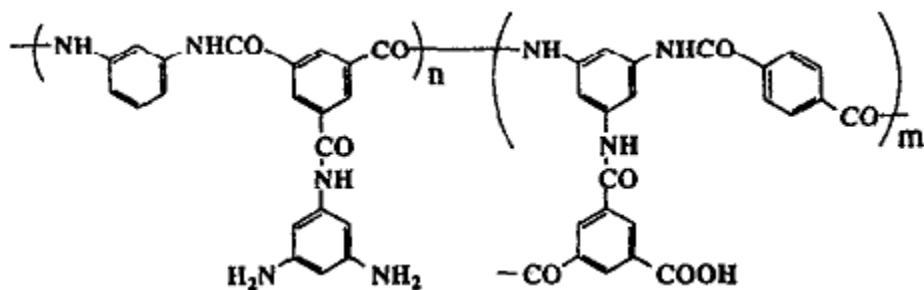


Figure II.3. Chemical structure of crosslinked fully aromatic polyamide UTC [30]

Polymeric membranes produce a surface charge when brought into contact with an aqueous solution. The surface charge is due to the dissociation of surface ionic group or adsorption of ion from solution close to the surface. It will attract counter ions and against the co-ions. The interface between a membrane surface and surrounding aqueous solution exhibits a charge distribution which is different from the bulk aqueous solution. In the model of the electrochemical double layer (EDL), this charge distribution is divided into a stationary and a diffuse layer. Ions are strongly attracted to the surface and immobile in the stationary, or often defined as stern layer. In the diffuse layer, ions are less affected by the surface charge and the charge density gradually decreases. Plane of shear exists between these layers. one from another. This electric double layer model is illustrated in Figure II.4. The zeta potential is assigned to the potential decay between the solid surface and the bulk liquid phase at this shear plane. The application of an external force parallel to the solid/liquid interface leads to a relative motion between the stationary and mobile layers and to a charge separation which gives experimental access to the zeta potential [31, 32].

The electrokinetic analyzer determines the zeta potential at the solid/liquid interface of macroscopic surfaces based on the quantification of streaming potential and streaming current. Streaming potential is the potential induced when an aqueous based electrolyte solution flows through the measuring cell containing the stationary membrane sample. Depending on the flow resistance of a permeable sample (capillary bundle) or of a gap created between flat solid surfaces, a pressure

difference is detected across the measuring cell. The electrolyte flow is generated by a dual syringe pump system and causes a charge separation in the flow direction along the measuring cell [31].

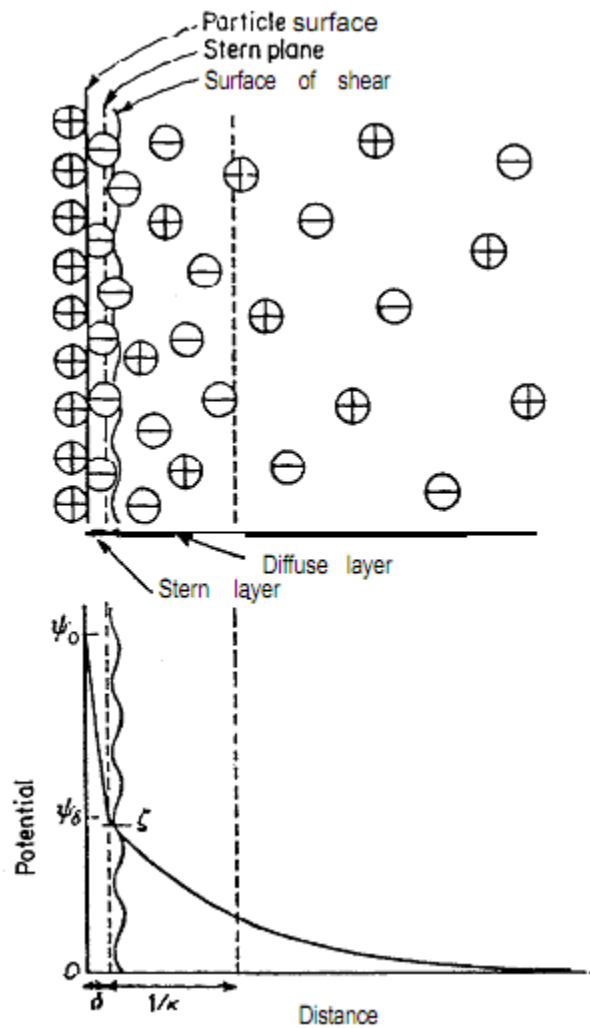


Figure II.4. Electric double layer model [29]

The resulting potential difference (streaming potential) or electrical current (streaming current) is detected by measuring electrodes that are connected at the

electrolyte inlet and outlet of the measuring cell. The measured values of Δp (pressure difference across the measuring cell) and ΔU (streaming potential) or ΔI (streaming current) serve to calculate the zeta potential. During a measurement the pressure is increased continuously in both flow directions and Δp and ΔU or ΔI are recorded [31].

The relationship between the measurable streaming potential and the zeta potential is defined as Helmholtz – Smoluchowski equation [29, 31].

$$\zeta = \frac{dU}{dp} \times \frac{\eta}{\varepsilon \times \varepsilon_0} \times \frac{L}{A \times R} \quad (\text{II.3})$$

$$\zeta = \frac{dI}{dp} \times \frac{\eta}{\varepsilon \times \varepsilon_0} \times \frac{L}{A} \quad (\text{II.4})$$

There are some assumptions made for this equation: laminar flow, insignificant surface conductivity, the thickness of electric double layer is negligible compared to width of the flow channel, there is capillary or parallel plate geometry, no axial concentration gradient occurs in the flow channel, and the surface has homogenous properties. Some efforts have been done to make a better membrane for boron removal: reduce membrane affinity for boron and enhanced interaction of membrane with water, also compaction of the membrane molecular [9, 10].

II.2.2 Effect of pH, temperature, and salinity

Rejection of materials through membranes is based on size exclusion, charge repulsion or solution-diffusion model. At lower pH, boron exists as non dissociated boric acid molecule. The rejection is not maximum because the absence of ionic strength and the hydration. Also, the dissociated form is larger which will enhance the rejection by size exclusion [18]. In addition, increasing the pH causes more negative charge on the membrane surface. In this situation, boron rejection is enhanced with the existing charge repulsion between borate ion and the negative surface charge.

Boron rejection is not directly coupled with TDS rejection. It can be said that high TDS rejection tends to perform high boron rejection. However, it does not give an indication that two commercial membranes having same TDS rejection will demonstrate the same boron rejection and vice versa. Boron rejection is mainly driven by diffusion, which is influenced by the membrane chemistry and to a lesser extent by convective transport, whereas salts rejection is driven by both transports. Membrane products which are specified as high rejection products, in contrast, have more dominant convective transport in determining salts rejection. Boron rejection tends to increase with temperature. Salt rejection decreases as the pH increases. This is a proof that boron rejection does not correlate with the salt rejection [10]. Higher boron rejection is shown as the permeate flux increases. This is due to the faster transport of water through the membrane whereas solute transport is relatively constant. Ionic strength adversely affects the boron rejection. It is

suggested that the boron removal is done in the lower salinity, i.e. second pass of RO plant. However, the cause of this effect, either by membrane surface neutralization or faster diffusion of boron through membrane, still needs to be further investigated [19]. It was reported on a study using SW30HR-380, BW30-400, and BW30LE-440 that the rejection improves significantly with increasing pH. This is due to a shift to dissociated boron species (99-99.8% rejection). However small portion of non dissociated boron is still present, contributing to passage of total boron. At pH 11 and above, the rejections (99-99.5%) are all the same among the three membranes [18].

II. 3 Overview of boron removal technologies

Several system configurations to increase boron removal have been studied and applied in SWRO plants. Increasing pH seems to be the most applicable in large scale SWRO plant. However, high pH leads to severe inorganic scaling, especially carbonate scaling. This practice is not feasible to be applied to single pass SWRO system, but it can be an option when treating brackish water. Multiple pass is an alternative choice, but it leads to more cost and energy intensive. Other process configuration, listed in Table II.2, have been studied to enhance boron removal performance with feasible economic point of view, however they might also have advantages and disadvantages, as listed in Table II.3.

Table II.2. Process options to produce drinking water with satisfied boron concentration in permeate [8, 16]

Process option	Flow diagram
SWRO + elevated-pH BWRO + concentrate adsorption by boron selective resin	
Single SWRO	
SWRO + permeate adsorption by boron selective resin	
SWRO + elevated-pH BWRO	
SWRO + elevated pH BWRO/permeate adsorption by boron selective resin	
SWRO + BWRO - boron selective resin	
Cascade design	

Table II.3. Summary of process option analysis for boron removal [15]

Category	Methods	Advantages	Disadvantages
Physical-chemical treatment	Flocculation-precipitation	High efficiency (90%)	Complex process Sludge handling Reagent cost
Adsorption process	Ion exchange resin	High efficiency (90-99%) No degasification Low capital investment Simple operation High boron selectivity	Boron specific resin Resin cost and regeneration Waste management Fouling associated issues High operating cost
Membrane process	Electrodialysis	High efficiency (90-96%) Minimum chemical addition Well-recognized process Reduce energy requirement	High capital and operational cost Waste management Low conductivity of dialyzate Chloride influence Frequent electrode replacement
	1, 2 or 3 stage RO in alkaline condition	High efficiency (90-95%) at pH 10-11 Simple operation Easy to scale up	Boron specific membrane Chemical cost Membrane stability Membrane scaling High energy cost Frequent membrane monitoring
	2 or 3 pass RO with alkaline condition	High efficiency (90-95%) at pH 10-11 Simple operation Cost efficient for drinking water with 0.5 mg/l requirement Easy to scale up	Boron specific membrane High energy consumption Low overall recovery Membrane scaling Frequent membrane monitoring
	Cascade design	High efficiency ($\geq 90\%$) No membrane scaling Low water cost	Complex process Chemical dosage control Membrane cost
Hybrid design	RO + ion exchange	High efficiency ($\geq 90\%$) Low energy consumption Cost efficient for irrigation with 0.5 mg/l boron requirement	Complex process Boron specific resins Resin regeneration

II.4 Online SWRO plant profiles

II.4.1 Tuas (SingSpring) SWRO project

This plant was commissioned in September 2005 and became Singapore's first SWRO plant. It is designed to fulfill 10% of nation's demand. The feed water is open seawater intake having the TDS 35,000 mg/l. It has an oil content of 10 mg/l and SDI value up to 7 due to suspended solids, iron, and organic carbon. To remove oil and reduce SDI, feed water is coagulated using ferric chloride, followed by dissolved air filtration (DAF) and dual media gravity filters. Cartridge filter is placed before the RO module as guard filter to prevent any fouling that might occur. After this, the feed water is dosed with NaOH to increase the pH up to 8.2 to have some degree of boron removal in the first pass. The first pass consists of single stage with 45% recovery. To achieve boron level target, the plant utilizes second pass with increased pH to 10 which works in parallel with an ion exchange. The second pass has two stages, of which permeates are blended with the ion exchange outcome and finally blended with the first pass permeate. This plant utilizes DWEER isobaric energy recovery device [33]. Process flow diagram of Tuas SWRO plant is depicted in Figure II.5.

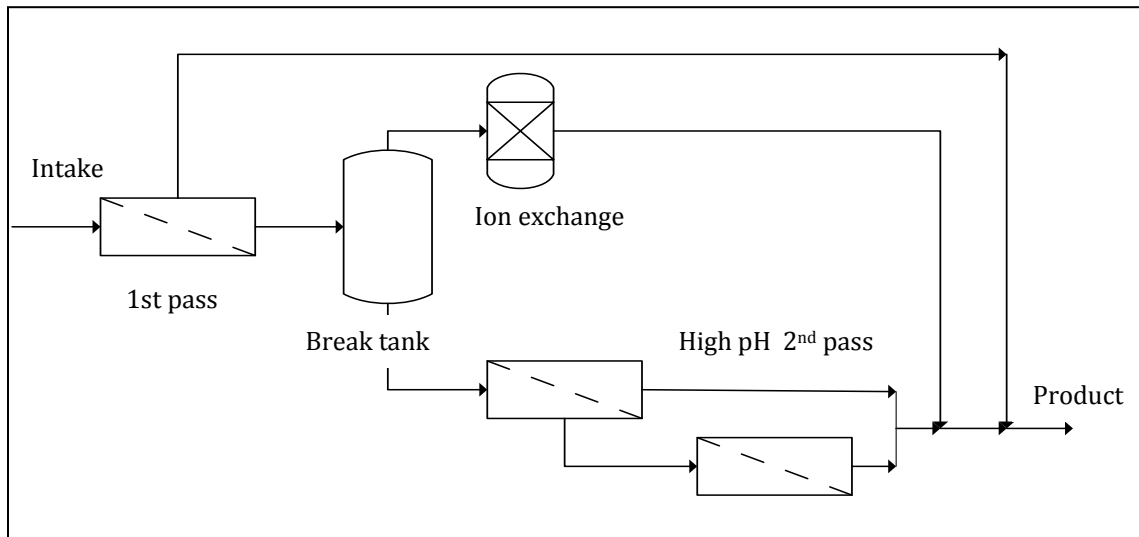


Figure II.5. Tuas process flow diagram [33]

II.4.2 Ashkelon SWRO project

The first phase of this plant was commissioned in July 2005 and second phase in December 2005. It applies 4-stages, partial 2-pass RO system. The first pass of the first and second stage operates at low pH in order to most of the salts and increase recovery without having membrane scaling. The second pass of the first and second stage operates in alkaline condition ($\text{pH} > 10$) to successfully reach high boron rejection. With configuration, boron concentration in the product is less than 0.4 mg/l.

Having the design capacity of 326,144 m³/day, it becomes the largest SWRO in operation in the world. The plant use an open sea, submerged intake, and pre treatment consist of ferric chloride coagulation prior to dual media gravity filtration.

It operates on overall product recovery of 40.7% and successfully reduces the TDS from 40,679 mg/l to 300 mg/l. DWEER isobaric is used as an energy recovery device. The concentrate is disposed back to the sea [33]. Process flow diagram of Ashkelon SWRO plant is depicted in Figure II.6.

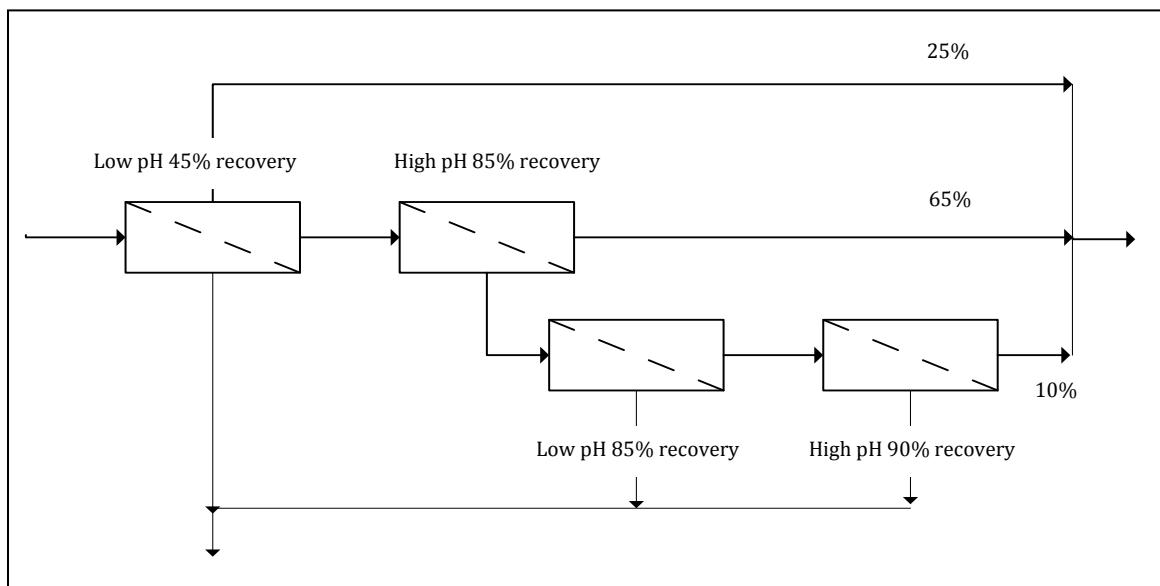


Figure II.6. Flow diagram of SWRO plant in Ashkelon [33]

CHAPTER III: MATERIALS AND METHODS

III.1 Materials

III.1.1 Membranes

Five flat sheet membranes samples were supplied by different membrane manufacturers. References of these membranes are SW1, SW2, BW1, BW2, and BW3. All samples were polyamide thin-film composite membrane. It is necessary to note that SW1 has the highest NaCl and boron rejection. It can be physically observed that SW2 is thinner than SW1 membrane and BW2 is thinner than BW1 and BW3 membranes. Specifications of these membranes from the manufacturer are summarized in Table III.1. SW2 and BW2 are membrane elements and commercialized as spiral wound module with different names. Their boron rejection was not specified by the manufacturer. Feed spacers and permeate carriers used in the experiment were also supplied from the membrane manufacturers and specified for each membrane. All membranes, feed spacers, and permeate carriers were only used once in each experiment.

Table III.1. Membranes specifications for one spiral wound module

Membrane Model	Min Salt Rejection (%)	Stabilized Boron Rejection (%)	Max Temp (°C)	Max Pressure (psi)	pH Range
SW1	99.7	93	45	1,200	2-11
SW2	99.6	-	40	600	3-9
BW1	99.4	83	45	600	2-11
BW2	99	-	45	600	3-9
BW3	99.3	68	45	600	2-11

III.1.2 Chemicals

Source of boron was naturally occurred in the feed seawater. All chemicals were reagent grade ACS, supplied by Fisher Scientific. SBS (Sodium bisulfite, NaHSO_3) of 1% was used as preservative solution for the membranes. NaOH concentrations of 1 M and 0.1 M were used to change the pH in the feed tank and for surface charge analysis, respectively. Samples were diluted in 2% HNO_3 for cations analysis using ICP-MS. No additional antiscalant was employed during the lab experiment. All chemicals were diluted in Milli-Q water.

III.2 Experimental set up

The experimental flow diagram is shown in Figure III.1 and the real view of experimental set up is illustrated in Figure III.2. Two lab scale crossflow filtration units (SEPA CF II, Steriltech) were installed in parallel to compare the performance of two membranes from different manufacturers. The unit accepts any flat sheet membranes 19 x 14 cm (7.5 x 5.5 in) for an effective membrane area of 155 cm² (24 in²). The holdup volume was 70 ml. The feed spacer and permeate carrier were cut into 14.6 x 19.5 cm (5.74 x 3.74 in) to fit in the cell. The double O-ring was placed in the cell body to provide a leak-proof seal. A 10 plus 5 mil of shim were used. The cell system required a hand pump in order to pressurize the cell holder, but is not used for liquid flow. Feed was pumped to the membrane using Baldor Reliance Super E[®] Motor (1.5 HP, 1760 rpm) equipped with pulsation dampener which is used to stabilize the oscillating flow from the pump. By this, the pump was able to deliver constant volume of water regardless of the circuit resistance or pressure.

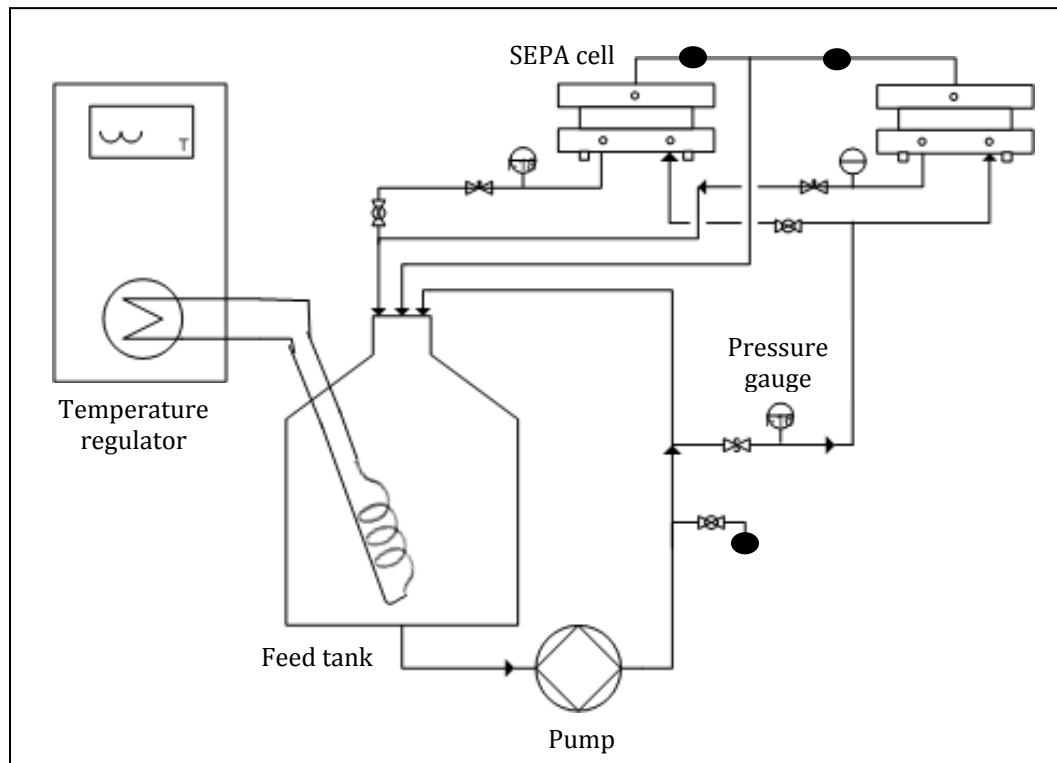


Figure III.1. Bench scale experimental set up

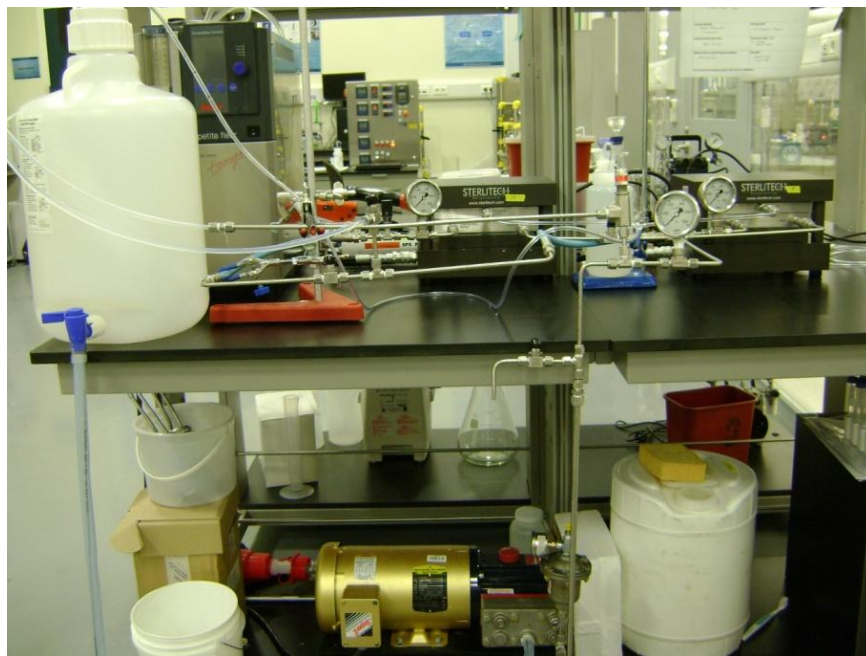


Figure III.2. Real view of bench scale experimental set up

NALGENE® polypropylene spigot was used to drain feed water from 20 liters (5 gal) feed tank. Feed and concentrate pressure were monitored using analogue pressure gauge supplied by WIKA Instrument Corporation. Applied pressure was adjusted through relief valve on the feed and needle valve on the concentrate side. Ball valves were used for system air purging and directing the flow. All valves and fittings were made of Stainless Steel and purchased from Swagelok®. Stainless steel tubing was used to hold high pressure, while plastic tubing was used for the permeate outlet. Thermoregulation of the feed water was done using Huber Petite Fleur w-NR. Silicon oil was circulated as thermal fluid in a closed loop inside the coil immersed in the feed tank to allow heat exchange.

III.3 Experimental procedure

III.3.1 Feed preparation

Feed was obtained from KAUST SWRO Plant and used directly as received. Water was collected from three different points (as indicated by black bold arrow on Figure III.3): feed of first pass (P1), permeate of first pass (P2), and feed of second pass (P3). Seawater membranes (SW) utilized water of feed for first pass as their feed. Brackish water membranes (BW) used permeates of first pass and feed of second pass as their feed. The feed pH was measured prior conducting the experiment and adjusted to the desired value by adding NaOH. Figure III.3 clearly shows that feed of first pass and feed of second pass contain antiscalant, while permeate of first pass does not. Also, the feed of second pass pH is 10, while two others are in pH 8.

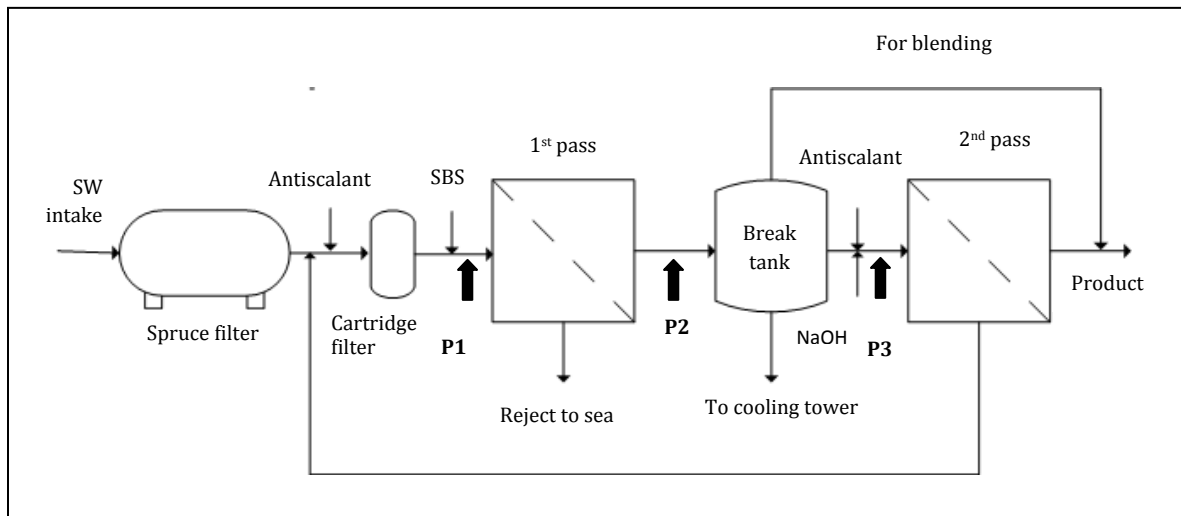


Figure III.3. Schematic diagram of KAUST SWRO Plant for feed sampling points

III.3.2 Membrane preparation

All membranes were received as flat sheets: dry sheets for SW1, BW2, and BW3 membranes, and sealed in preservative solution for SW2 and BW2 membranes. SW2 and BW2 membranes were then stored at 4°C, while SW1, BW1, and BW3 membranes were kept in room temperature inside a close container. They were cut into 19.1x14 cm, washed with flowing DI water, soaked in Milli-Q water, and stored in room temperature for at least 24 hours before being used. This was aimed to remove existing contaminants or preservatives on membranes. Membrane conditioning was conducted prior to the experiment. It was put properly inside the SEPA cell and pressurized gradually, 20 psi every two minutes, to the intended experiment pressure. Then it was left under that pressure for 10-12 hours. After the experiment, membrane was soaked in SBS solution and stored at 4°C for analysis.

This was to prevent any bacterial growth on the membrane surface. Before being analyzed, it was washed with Milli-Q water and dried in room temperature. Each membrane was only used once in each experiment.

III.3.3 Filtration experiment

The experiment was conducted in two pH conditions, natural seawater pH (around 8) and elevated pH 10. The membrane was sandwiched in between feed spacer and permeate carrier in the cell. Membrane's active layer was faced down. The O-ring was carefully placed properly in the grooves. Pressure given by the hand pump had to be higher than the operating pressure to avoid any leakage or membrane damage during the filtration experiment. After the cell was set, the spigot was opened. Relief and needle valves were fully opened. The experiment was conducted in fully closed loop mode. This meant that permeate and retentate were circulated in the feed tank. The pump was switched on and the ball valve was opened to remove air trapped in the entire system. After the air was completely purged, the ball valve was closed and the experiment was continued. Temperature range used in the experiment represented the actual operating temperature in the RO plant during summer (28-30°C). Pressure of 220 psi was applied to brackish water membranes and 160 psi for brackish water low energy membrane. The pressure was based on manufacturer recommendation. However, due to the limitation of experimental set up the pressure for seawater membranes could not be reached. Thus, pressure of 400 psi was chosen to operate seawater membranes. The operating conditions are summarized in Table III.2.

Table III.2. Operating conditions summary

Membrane	Temperature (°C)	Pressure (psi)	pH	Antiscalant
SW1, SW2	28 -30	400	8	Yes
			10	Yes
BW1, BW2	28 -30	220	8	No
			10	No
			10	Yes
BW3	28 -30	160	8	No
			10	No
			10	Yes

To be noted that SW1 was run in parallel with SW2 and BW1 was run in parallel with BW2. Since there are two operating conditions using pH 10 for BW membranes experiment, it is important to note that pH 10 is for operating condition without adding antiscalant and pH 10+ is for operating condition using antiscalant. This simplification will be used throughout this paper. To be noted, the antiscalant is injected from the KAUST SWRO Plant.

III.3.4 Sampling

Each experiment ran for three days. Samples of feed and permeate were taken every 12 hours. Permeate was taken from each cell outlet only for sampling purpose. After collecting some amount of samples, permeate flow was directed back to the feed tank. Feed samples were collected by opening the ball valve. The samples volume was about 50 ml. Sampling points are indicated by black bold dot on the Figure III.1. To avoid any leaching of borosilicate from the glassware, all sample bottles and feed tank were made of plastic (polyethylene) [17].

III.4 Analytical Methods

III.4.1 Membrane surface characterization

Membrane streaming potential or streaming current was measured by SurPASS (Anton Paar, GmbH, Graz, Austria) electrokinetic analyzer across a range of pH values. The dimension of the adjustable gap cell used was 10 mm x 20 mm and set to have cell height of approximately 100 μm . Three types of electrolyte solution: 0.001mg/l, 0.01 mg/l, and 0.1 mg/l NaCl were used as electrolyte. pH was adjusted by automatic titration mode by 0.1 M NaOH and 0.1 M HCl. pH range was set from 5 to 11 with the interval of 0.5. The titration liquid was dropped by 0.2 ml to achieve the desired pH range. The zeta potential was calculated using the Helmholtz-Smoluchowski equation, using streaming potential approach [31].

Scanning Electron Microscopy (SEM) analysis of membrane's surface area was done by Quanta 3D FEGSEM. Two magnifications of 6,000x and 24,000x were used for virgin membranes. The 8,000x magnification was used for used membranes to give a clearer picture if there were any deposits on the membranes surface. The Energy Dispersive X-ray (EDX) analysis was done in some spots on the virgin membranes surface to observed elements stick on the membrane surface. The measured values were averaged. A 5500 AFM (N9410S from Agilent) was used to characterize the membranes roughness. Using the scale of 10 μm , the values for each membrane were compared.

III.4.2 Boron analysis

Concentration of Boron was measured using Inductively Coupled Plasma – Mass Spectroscopy (ICP-MS) (Agilent 7500, ChemStation (G1834B)), equipped with an auto sampler. Three times replication were done for each sample to give an average value. Rhodium (Rh) was set as an internal standard. Tuning was on the He mode with He flow rate of 4 ml/min.

III.4.3 pH, TDS, and temperature measurement

Temperature in the feed tank and TDS in feed and permeate samples were checked when taking sample using Oakton CON 510 Series to make sure the feed temperature was in the desired value. pH was measured using Cyberscan pH 6000 (Eutech Instruments). The probe was washed and soaked in Milli-Q water for few minutes to make sure that there was no contamination from previous use.

CHAPTER IV: RESULTS AND DISCUSSION

IV. 1 Membranes surface characterization

IV. 1.1 Zeta potential of virgin membranes

Zeta potential measurement is necessary to study the contribution of membrane surface charge to ions rejection by charge repulsion mechanism. Five membrane samples were tested to get the profile of zeta potential at various pH and electrolyte solution conditions. As depicted in Figure IV.1, all membranes show more negative values as the pH increases. The value ranges from -5 to -45 mV as the pH increases from 5 to 11. In general, SW2 and BW2 exhibit more negative zeta potential than SW1 and BW1. However, the zeta potential value for BW3 membrane is comparable to SW2 and BW2 membranes. In addition, SW and BW membranes from the same manufacturer are in the similar zeta potential value range, although BW membrane's value is slightly lower than SW. These results are consistent with the previous reports [17, 19, 32, 34, 35] which note that most of polyamide membranes are negatively charged and the membrane surface charge density increases as the solution pH increases. Among membrane samples, SW2 has the lowest zeta potential value. Although at 0.01 M NaCl, BW2 has the lowest value.

As all the membranes used in this study are composite polyamide, the increase in zeta potential is might be due to the protonation of amine compound at low pH [32]. Moreover, treatment and added chemicals, such as surfactants, during membrane manufacturing process may also contribute to give the negative surface charge.

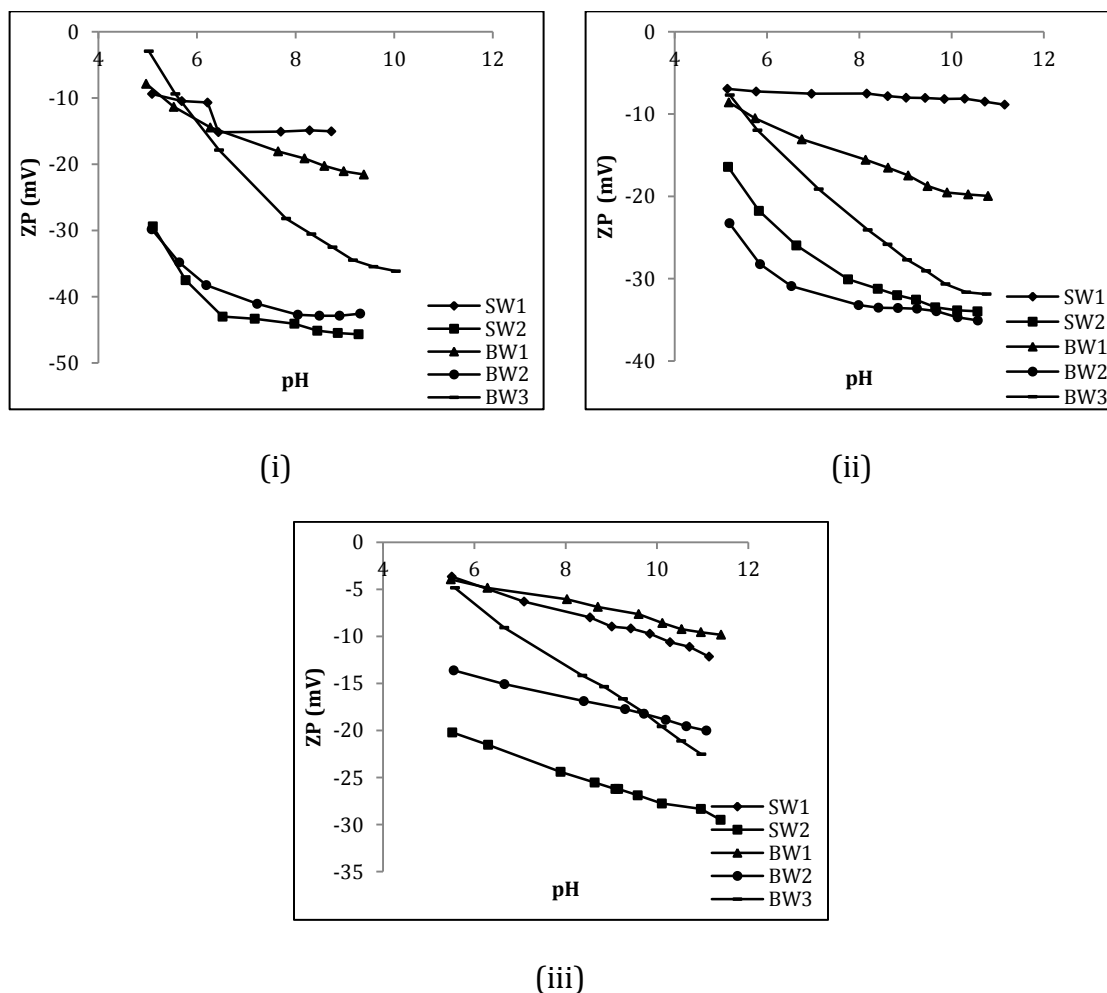


Figure IV.1. Zeta potential for new membranes at different electrolyte solutions:
 (i) 0.001 M NaCl (ii) 0.01 M NaCl (iii) 0.1 M NaCl

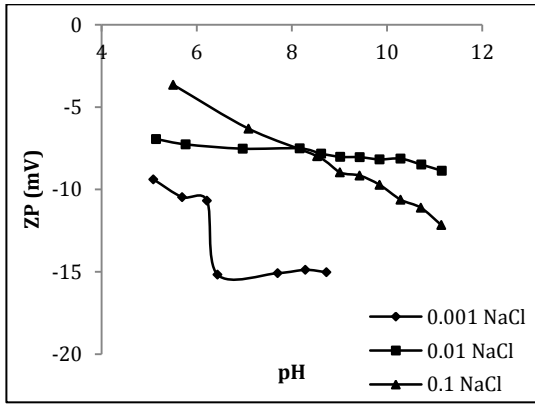
The composite membranes are fabricated by interfacial polymerization on the microporous support of monomeric aromatic polyamine, such as phenylene diamine in aqueous solution, with amine-reactive reactant comprises a polyfunctional acyl halide such as trimesoyl chloride. The addition of monomeric amine salt into the aqueous solution on the microporous support can substantially strengthened the membranes performance. In addition to this, an anionic surfactant, such as dodecyl benzyl sulfonate or sodium laurel sulfate, is incorporated to the aqueous solution to

adjust the pH. It is assumed that small amount of amine salt, un-reacted monomeric polyamine, or surfactants remained on the membrane surface, even after the drying process. Even though these impurities are not one component of aromatic polyamide membranes, they can contribute to membrane surface charge. Hydrolysis of a third acyl chloride group of trimesol chloride to carboxyl might happen during the interfacial polymerization, resulting in negatively charged carboxyl functional group. At low pH, the amine salts and monomeric polyamines are positively charged [35].

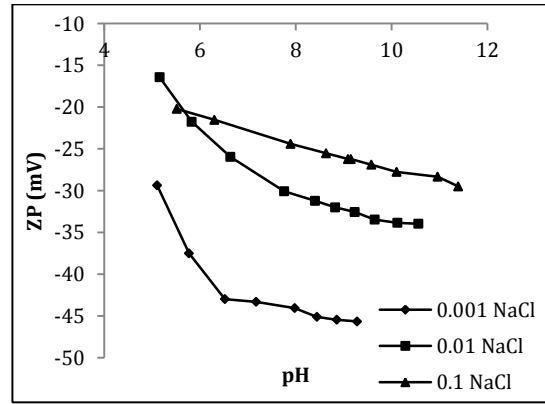


The anionic surfactants are mostly negatively charged at low pH (above 2), whereas carboxyl groups are uncharged. As consequence, overall zeta potential of composite polyamide membranes is positive at pH smaller than 3.5. As the pH increases, acidic functional group of carboxyl and remaining surfactants deprotonate, thus resulting the negative charge to the membrane [35].

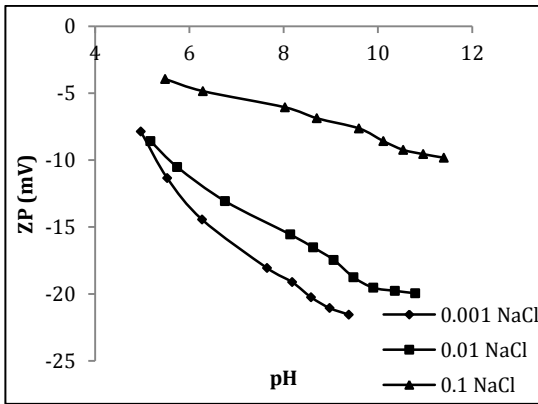
As it can be seen in Figure IV.2, membranes zeta potential was also measured at different electrolyte concentrations. It was observed that zeta potential shift to less negative value at higher NaCl concentration. Only SW1 membrane showed that at pH larger than 8, the zeta potential with 0.01 M NaCl is bigger than that of 0.1 M. This might be caused of the phenomena in stern layer which is densely shielded by positive ions as the NaCl concentration increases [23, 34].



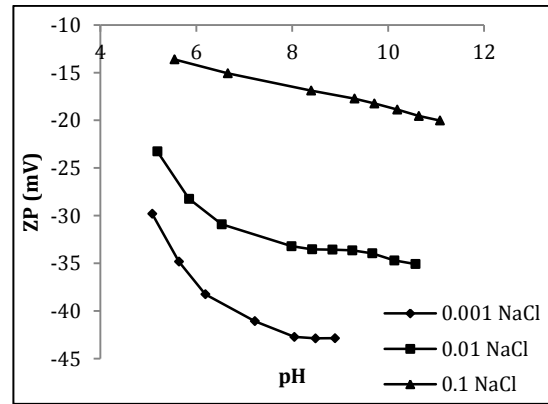
(i)



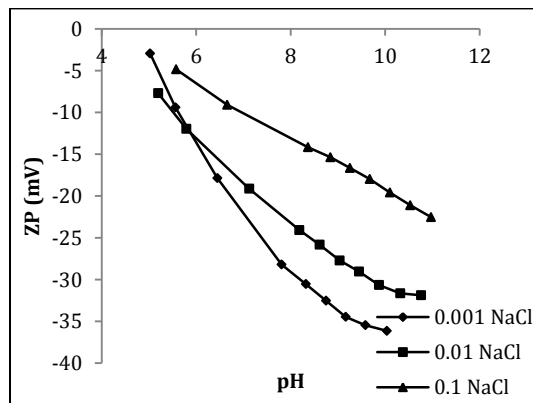
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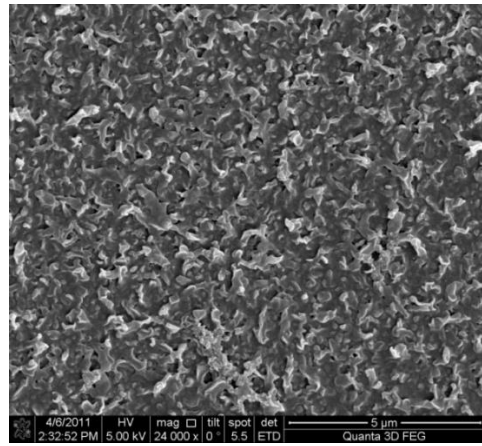
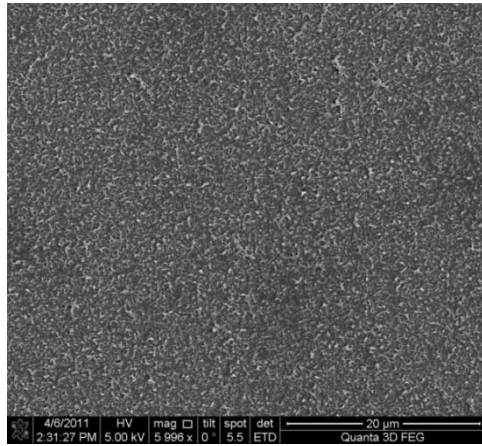


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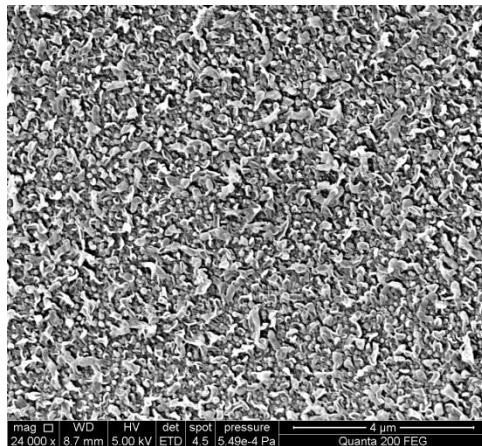
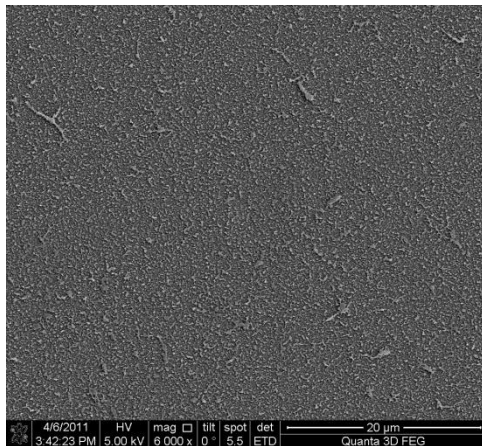
Figure IV.2. Zeta potential of new membranes at various pH and electrolyte solution
 (i) SW1 (ii) SW2 (iii) BW1 (iv) BW2 (v) BW3

IV.1.2 SEM analysis for virgin and used membranes

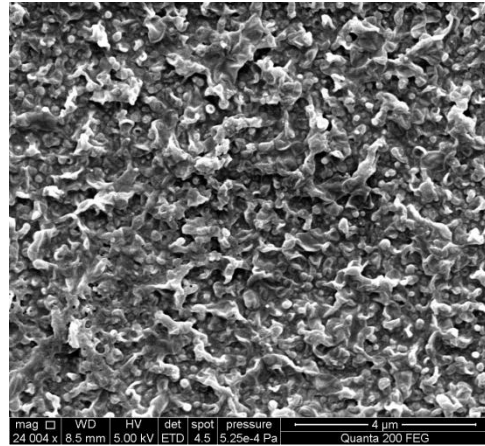
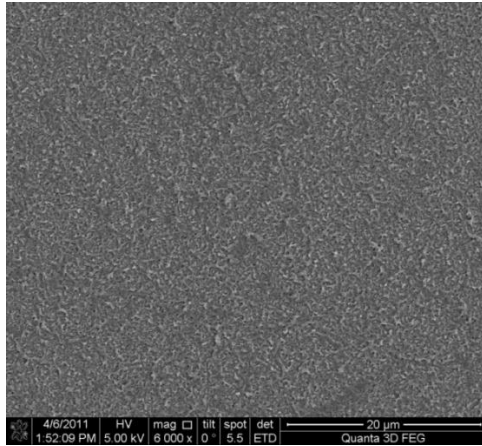
Membranes surface imaging of virgin and used membrane was done to observe any deposited materials on the membrane surface. Figure IV.3 shows SEM images for virgin membranes using magnification of 6,000x and 24,000x. Two magnifications were use to ensure that virgin membranes were clean.



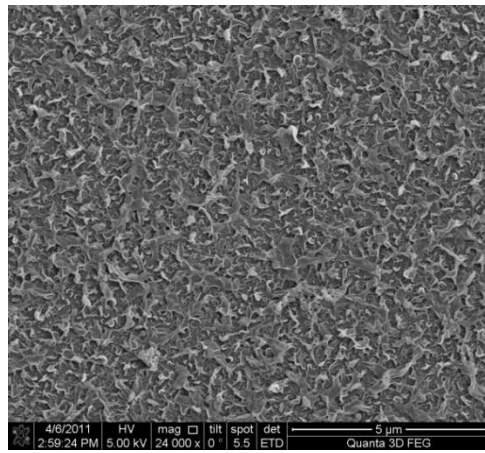
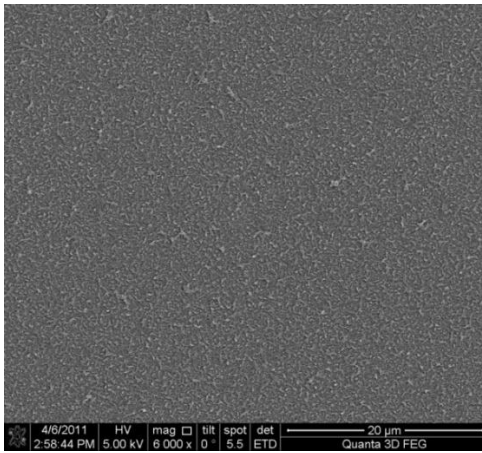
(i)



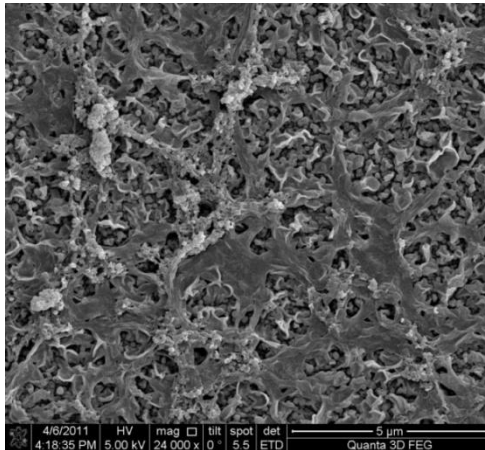
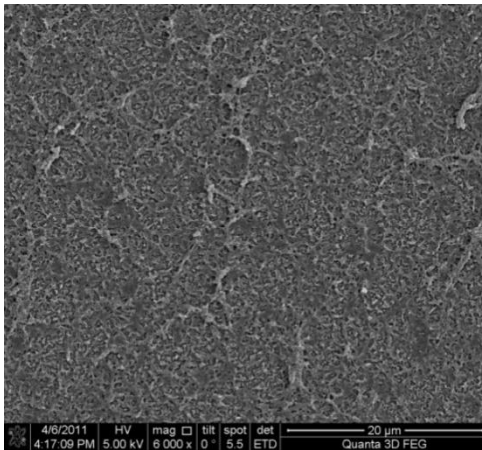
(ii)



(iii)



(iv)

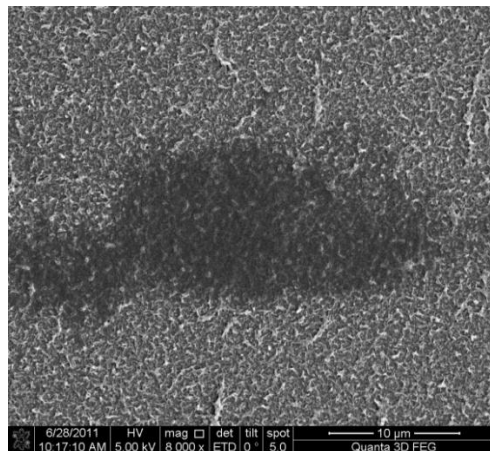


(v)

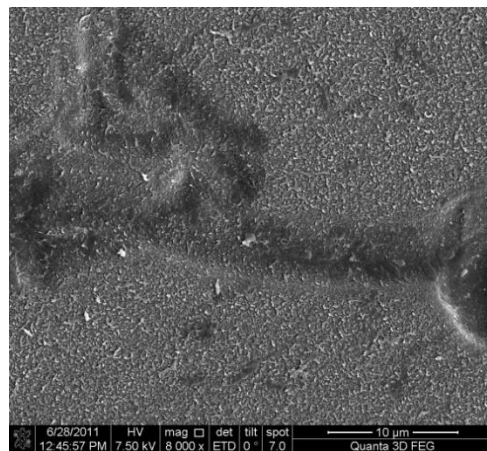
Figure IV.3. SEM images for virgin membranes with 6000x (left) and 24000x (right) magnifications

(i) SW1 (ii) SW2 (iii) BW1 (iv) BW2 (v) BW3

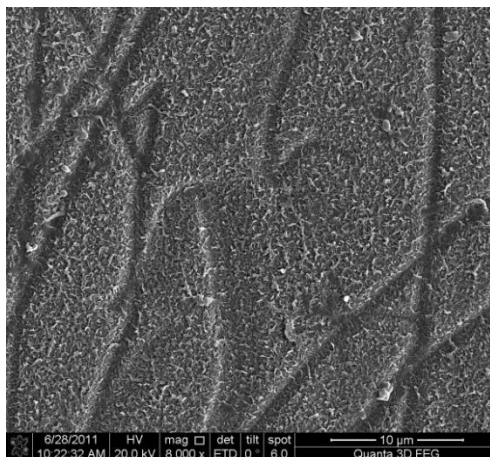
Lower magnifications of 6,000x, 8,000x, or 12,000x were applied for the used membranes. It is expected that any deposits can be clearly seen, in terms of shape, count, and position on the membrane surface, with lower magnification. Figure IV.4 shows SEM images for the used SW membranes which were operated in parallel at one pH value.



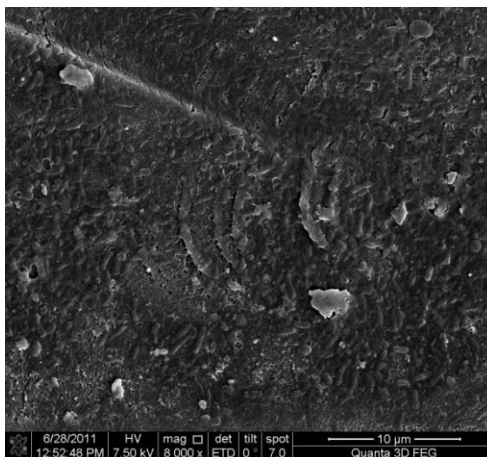
(i)



(ii)



(iii)

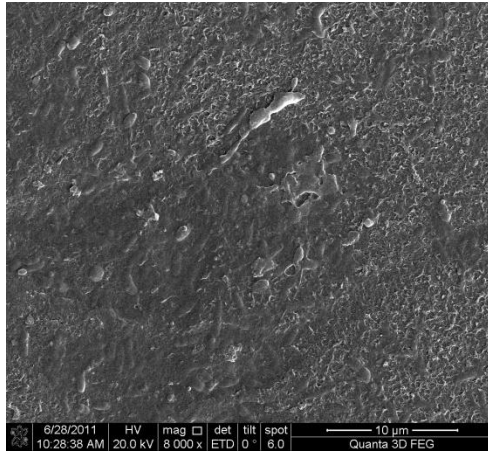


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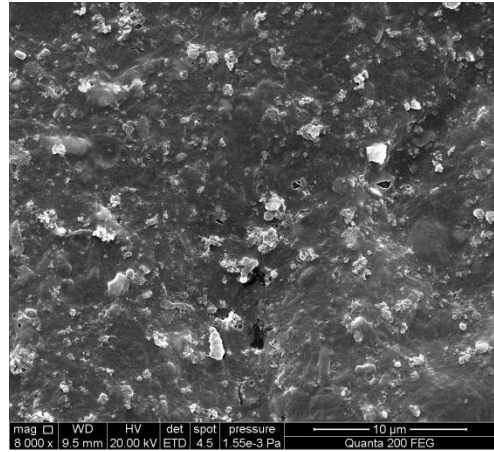
Figure IV.4. SEM images for used SW membranes
(i) SW1 pH 8 (ii) SW2 pH 8 (iii) SW1 pH 10 (iv) SW2 pH 10

Membranes operated at pH 8 shows relatively clean surfaces, no substantial deposits occur. However, folded-like shaped was found on SW2 membrane surface. This might come from the sample preparation failure. Despite the fact that precipitation will be worsen at high pH [36], SW1 membrane surface operated at pH 10 is considered to be clean, only folded-like shape appear on the surface. Again, this might come from the manufacturing process. In contrast, more deposits are found on the SW2 membrane surface operated at pH 10. This may be due to more interaction between deposit materials with the membrane surface.

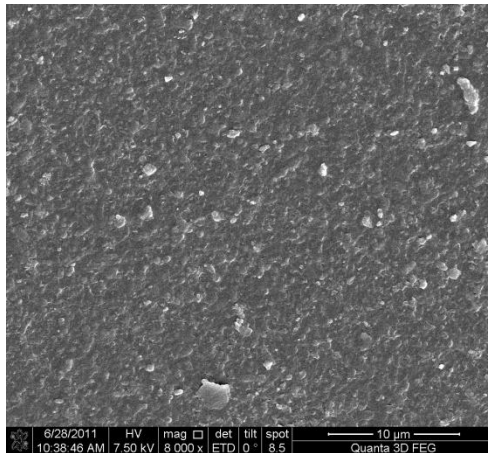
As shown in Figure IV.5, some rod-like deposits were found on the used BW membrane surfaces. This is suspected as an organism, such as bacteria, which is not expected to appear in the feed water, as it came from permeate of the first pass SWRO closed system. Its existence in this experiment might be come from contact with the container and air during feed water transportation from the plant to the lab. As in SW results, more severe deposits were observed on the BW membrane surfaces operated at pH 10 with and without antiscalant addition. It was found that sludge-like layer covered the entire membrane surface. There are two possible explanations for this fact. First, the crystal deposits might occur, but they were distorted by the presence of antiscalant, thus no firm shape crystals were formed. Second, the crystal deposits were still in the growth phase when the experiment was stopped and membranes samples were dried for analysis [37]. In general, BW2 membranes had more deposits on their surface, even at pH 8. Again, this may be due to more interaction between deposited materials with the membrane surface.



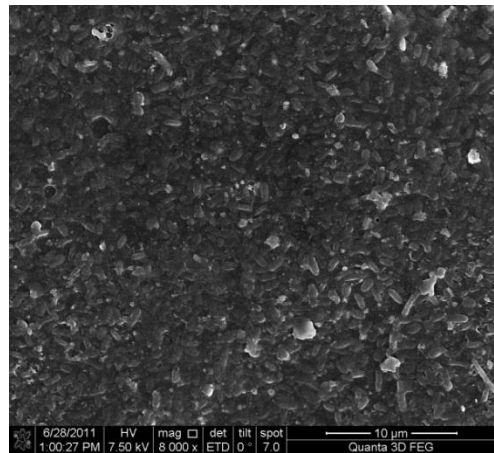
(i)



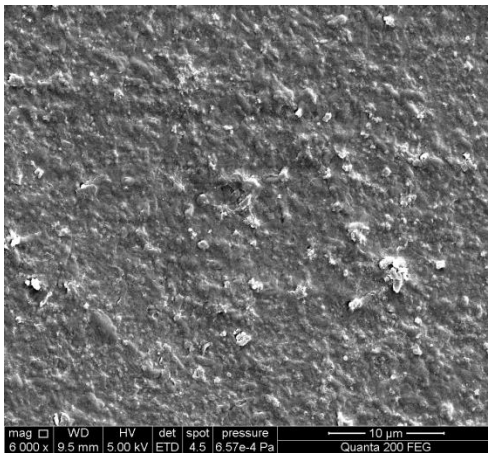
(ii)



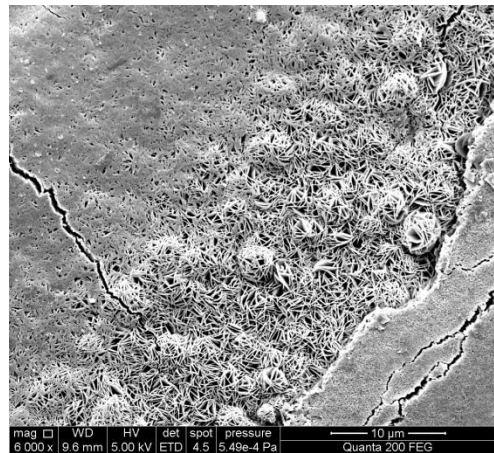
(iii)



(iv)



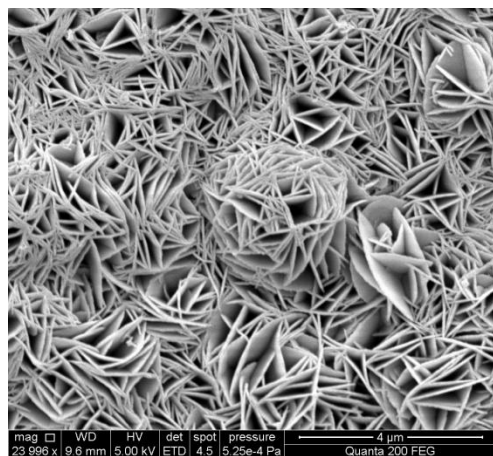
(v)



(vi)

Figure IV.5. SEM images for used BW membranes
 (i) BW1 pH 8 (ii) BW2 pH 8 (iii) BW1 pH 10 (iv) BW2 pH 10
 (v) BW1 pH 10+ (vi) BW2 pH 10+

Nevertheless, defined crystal shape was observed on BW2 membrane surface operated at pH 10 with antiscalant addition. It is suspected that antiscalant injection was not efficient to prevent scaling. SEM imaging was done in higher magnification of 24,000x for this membrane, as illustrated in Figure IV.6. Based on EDX analysis, it was found that Mg element exists in high number, while it is not part of membrane material. Thus, it can be concluded that the crystal may be magnesium hydroxide (MgOH). It is reported that magnesium hydroxide scaling is the limiting factor for the second pass of SWRO process. This may be true since alkali solution, particularly sodium hydroxide, is added to increase the pH in the second pass [38].



Element	Wt%	At%
C	18.25	25.43
O	42.10	46.41
Mg	33.56	24.84
Al	0.64	0.41
Si	0.37	0.23
S	5.09	2.67

Figure IV.6. SEM image with 24,000x magnification (left) and EDX analysis (right) for used BW2 pH 10+

Compared to other used BW membranes, used BW3 membrane showed relatively clean surface. As illustrated in Figure IV.7, sludge-like layer covered part of the membrane surface with only small amount of crystal deposits exist on the

membrane surface operated at pH 10 without antiscalant addition. It is suggested that the crystal is sodium hydroxide (NaCl), which is normal to exist as the left over from the filtration experiment.

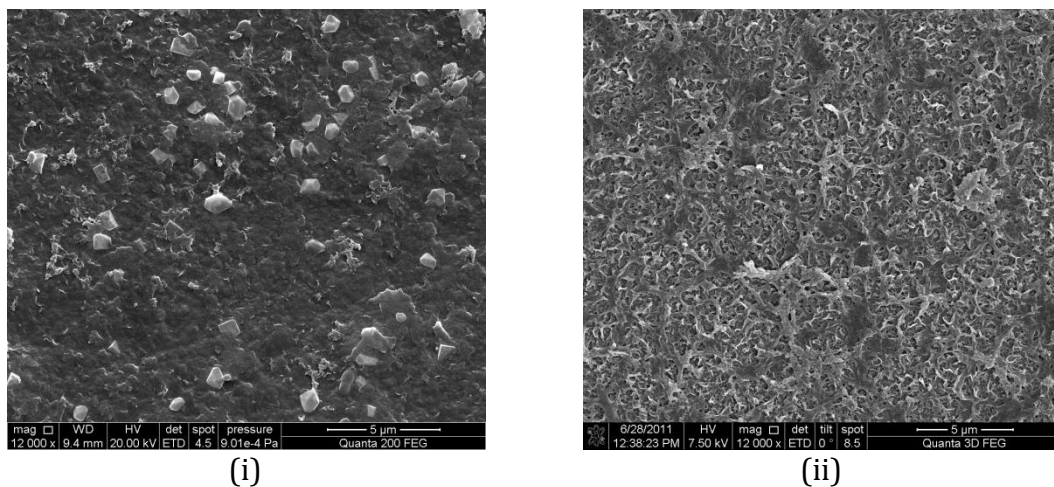


Figure IV.7. SEM images for used BW3 membranes
(i) pH 10 (ii) pH 10+

Even though permeate flux was not recorded during the filtration experiment, it was observed during obtaining samples that SW2 showed higher flux than SW1. Also BW2 showed higher flux than BW1. This may be because SW2 and BW2 are thinner than SW1 and BW1 membranes, thus less resistance for permeate to flow through the membranes. In addition, SW2 and BW2 membranes might have greater permeability than SW1 and BW1 membranes. It is known that having high flux leads to more potential scaling on membrane surface [38]. Thus, there is a certain point that SWRO plants can operate safely without scaling occurred. This might be a reason for having more deposits on SW2 and BW2 membranes. There was an exception, however, for BW operated at pH 10+ where BW1 was found to have

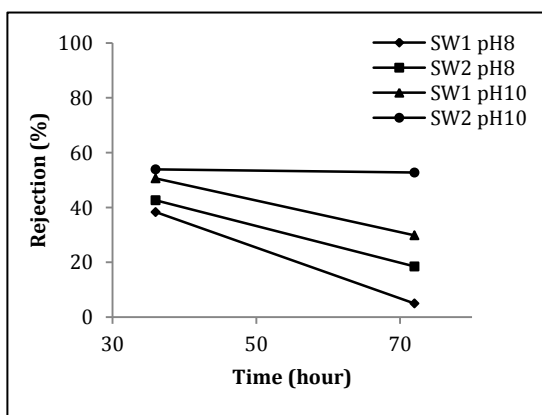
higher flux than BW2. It is suspected that this was due to heavy scaling on BW2 membrane surface, adding more resistance for permeate to flow through the membrane.

IV.2 Effect of pH on boron removal

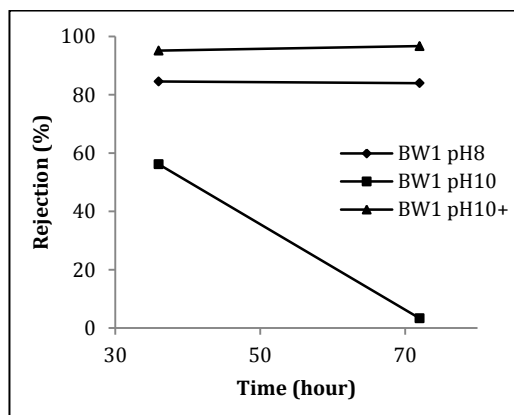
During three days operation, boron rejection with SW membranes decreased except for SW2 membrane at pH 10, which showed relatively constant rejection. Both SW1 and SW2 performed better in terms of boron rejection at pH 10, as expected. However, boron rejection by SW2 is better than that of SW1. The highest boron rejection (54%) is achieved by SW2 membrane at pH 10, which is able to remove boron from 5.2 to 2.4 mg/l. It is important to note that boron concentration in permeate commonly achieved by first pass in commercial scale plants is lower than the value obtained in this bench scale unit as it runs at lower normalized operating conditions. Thus, very low permeate flow rate was obtained and same as boron rejection. Hence, high boron concentration in permeate was obtained.

As can be seen in Figure IV.8, the results for SW membranes were also applicable for the BW membranes. The highest achievable boron rejection of 96.7% was obtained by BW1 at pH 10+, leaving 0.09 mg/l of boron in permeate. Two other membranes operating at pH 10+ were also able to fulfill boron requirement of 0.5 mg/l or lower in permeate. Operating at pH 10+ has been a choice for second pass SWRO plant and used for decades [8]. Operating at pH 10 without antiscalant may be feasible since boron concentration in permeates were below the guideline value of 0.5 mg/l.

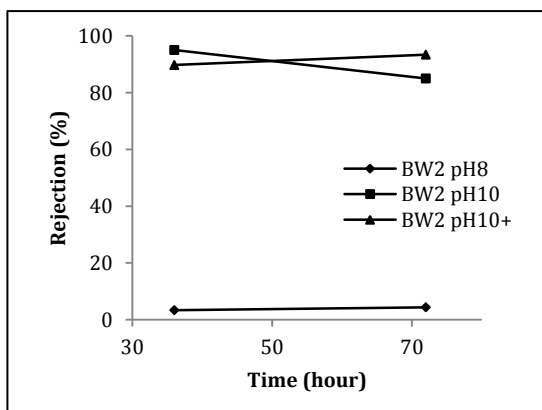
However, at the end of experiments boron rejection substantially decreased. Lower boron removal was attributed to the super saturation effect which may cause not only concentration polarization but also the change in membrane surface characteristics or adsorption of counter ions. This could be true since in alkaline condition, some salts start to precipitate [36]. In general, BW membranes performance at pH 10+ was better than that of pH 10.



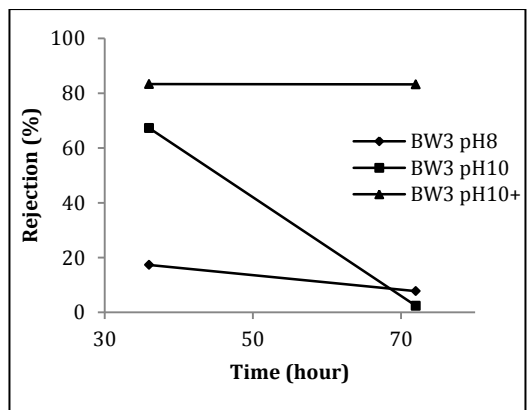
(i)



(ii)



(iii)



(iv)

Figure IV.8. Boron rejection for various membranes at different pH
(i) SW membranes (ii) BW1 (iii) BW2 (iv) BW3

Operation at pH 8 gave low boron rejection, leaving more than 1 mg/l of boron in permeate, except for BW1 which performed excellent boron rejection. Among three BW membrane samples, BW1 shows the best performance at pH 8 and pH 10+, while BW2 is excellent when it is operated at pH 10. Boron rejection comparison among BW membranes is depicted in Figure IV.9.

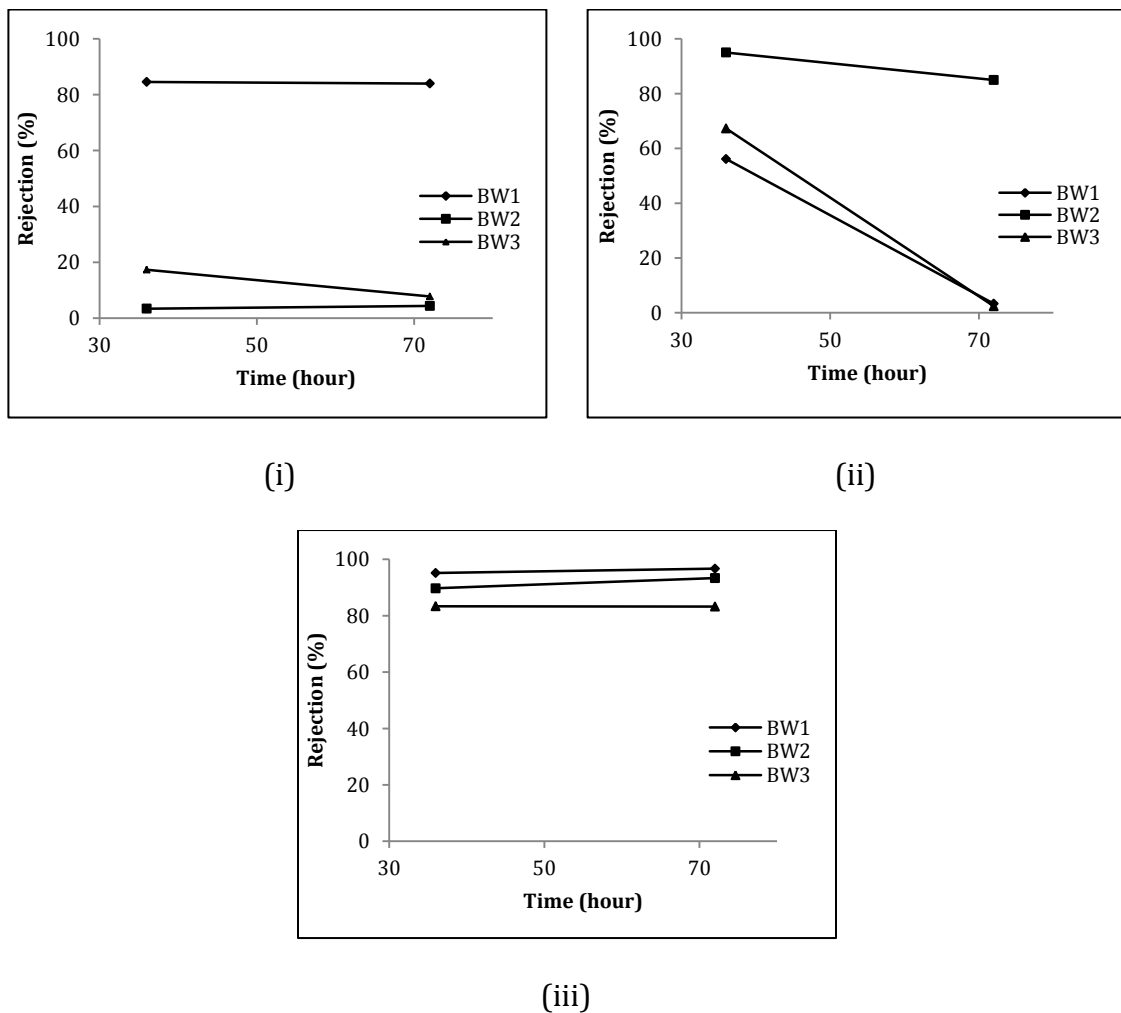


Figure IV.9. Boron rejection for various BW membranes
(i) pH 8 (ii) pH 10 (iii) pH 10+

Previous studies [15, 17, 19, 20, 23, 34] have shown that boron rejection by RO membranes improved as pH increased. At natural seawater pH, large portion boron exists as non dissociated boric acid. As the pH increases, more boric acid dissociated to negative charge borate ion. In addition, membrane surface charge is also more negative at high pH value. By these facts, it is expected that charge repulsion between negative charge borate ion and negative membrane surface charge enhanced boron rejection. Also, increased charge repulsion at higher pH contributed to diffusive transport decrease of boron through the membranes and reduce solute-solvent coupling [17]. Thus, boron concentration in permeate was lower. Moreover, borate ion is more hydrated. Thus, it has bigger size than boric acid. In this regard, size exclusion mechanism also increased boron rejection at high pH [10, 15, 34]. Another reason of low rejection of boric acid is because it is relatively easy to diffuse through the membranes by hydrogen bonds formation with membrane active group [10, 14, 23, 24].

IV.3 Correlation between boron and Total Dissolved Salts (TDS) rejection

Salts rejection, represented as TDS, was also measured to get the correlation between boron and salts rejection. As has been discussed in the previous section, it was suggested that boron rejection increased at pH 10. However, this could not be generalized for salts rejection, which also did not have proportional correlation with boron rejection [17]. As depicted in Figure IV.10 (i), salts rejections by SW membranes were relatively constant during three days operation. Operating SW2 at pH 10 gave positive impact on both boron and salts rejections. Salts rejection

achieved in this experiment was much lower than commonly achieved by first pass in commercial scale plants due to lower normalized operating conditions. Thus, very low permeate flow rate and low salts rejection were obtained.

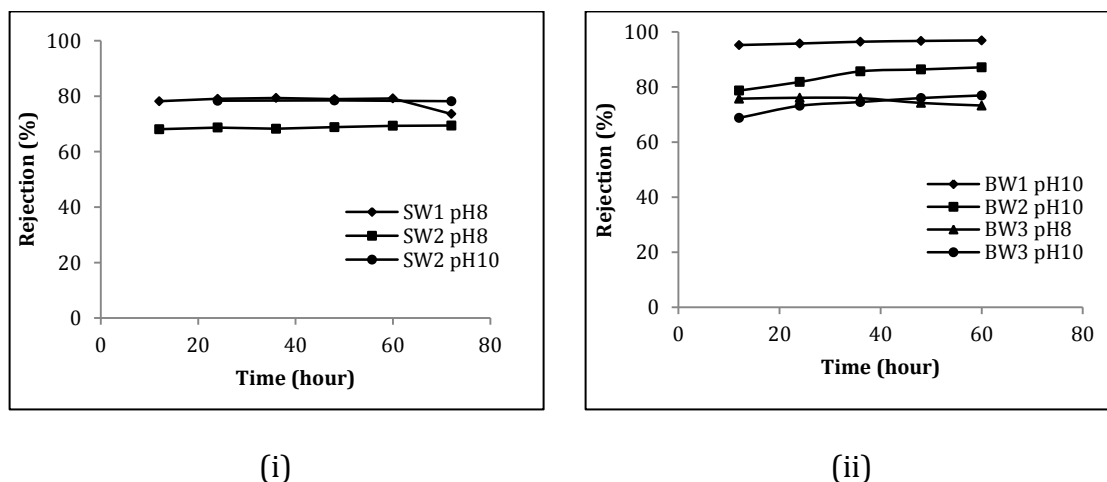


Figure IV.10. Salts rejection for various membranes
(i) SW membranes (ii) BW membranes

Figure IV.10 (ii) depicts the TDS rejection for BW membranes at representative operating pH. Salts rejection by all BW membranes were also relatively constant in three days operation. It is suggested that longer experiment time would be required to see the variation on ions rejections. Operating at different pH gave relatively the same TDS rejection. The average TDS rejection for BW1 membrane was 96%, leaving the TDS concentration in permeates of around 45 mg/l. The average TDS rejection for BW2 membrane was 85%, leaving the TDS concentration in permeates of around 160 mg/l. It can be said that BW2 performed worse TDS rejection than BW1. This was due to the concentration polarization might occur on BW2

membrane surface, causing more concentrated feed on the area close to the membrane surface. This could be proven by SEM imaging which showed more deposits on BW2 membrane surface. The average TDS rejection for BW3 membrane was 75%, leaving the TDS concentration in permeates of around 190 mg/l. All membranes were able to achieve lower than TDS guideline for drinking water of 500 mg/l [28]. BW3 membranes had lower rejection compared to other membranes. This is due to lower operating pressure for BW3 membranes, as they are specified as low energy membranes. On the other hand, as has been discussed in the previous section, boron rejection by BW membranes was enhanced by elevating the pH. Thus, it can be concluded that salts rejection does not have proportional correlation to boron rejection. In other words, the salts rejection would not be indicative of boron rejection. Among three BW membranes, BW1 showed the best TDS rejection.

CHAPTER V: CONCLUSIONS AND RECOMMENDATIONS

V.1 Conclusions

Bench scale experiment conducted with five commercial RO membranes with varying operating conditions suggested that boron rejection is substantially affected by pH due to dissociation of boric acid to negatively charged borate ions. In addition, membranes showed more negative surface charge at elevated pH. Thus, charge repulsion is expected to enhance boron rejection at high pH. Moreover, borate ions have bigger size and hydrated at alkaline condition. Membrane zeta potential increases as the concentration of electrolyte increases. Among membrane samples, BW2 has the most negative zeta potential. This might be due to the fact that this membrane is specified for boron removal in the second pass RO system.

Operating single pass RO system seems to be promising to reduce energy and chemical consumption cost. However, this study found that single pass RO system, with and without elevating the pH, may not be possible to apply because of two reasons. First, permeate quality in term of boron, does not fulfill WHO and local Saudi Arabia regulations of 0.5 mg/l. Second, there is severe scaling happened if operated in alkaline condition since Ca and Mg concentrations are still high to cause precipitation. For SW membranes, boron rejection by SW2 membrane was better than SW1 membrane. For BW membranes, however, the conclusion cannot be generalized.

Besides having high boron rejection, BW2 operated at pH 10 was also able to achieve high TDS rejection. This makes it promising to be applied in second pass SWRO process. BW3 was able to achieve regulated boron concentration in permeate at pH 10. The TDS rejection by this membrane was also satisfied the regulated value. Thus, it may be taken into consideration that BW3 membrane may be used in the second pass RO system with lower required pressure, i.e. lower energy consumption.

SW1 and BW1 membranes are specified as high boron rejection. However, the results showed that their boron rejections were better at elevated pH 10+. Thus, the role of high rejection membranes is questioned. Further investigations on these regards need to be performed. SEM imaging showed that there were deposits on the membrane surface with only three days operation, although heavy deposits were not found on all membranes.

V.2 Recommendations

Based on the conducted study, it may be taken into consideration that BW3 membrane is recommended to be used at pH10, since it gave satisfied both boron and TDS rejection, but consume lower energy as it was operated at 1/3 lower operating pressure than other BW membranes. However, longer test period should be performed to have clearer idea of overall membrane performance. Moreover, operating at pH 10 without antiscalant injection maybe feasible for BW2 membrane,

but it is also still to be tested in longer operation time to see more effect on scaling potential.

Regardless all the studies which have been conducted to achieve boron removal, the one pass SWRO process will become efficient if the new WHO boron guideline value of 2.4 mg/l is applied widely and followed by countries which still have stringent guidelines for drinking water purposes. In this scheme, single pass will be able to provide satisfy water quality resulting in lower energy and chemical consumption, also more environmentally friendly, which is the case in most of the countries which align their boron guidelines with Europe Union (EU) standard (1 mg/l) or even higher. Second pass RO may still remain necessary if low boron concentration is required for other purposes, such as agriculture.

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