AMERICAN UNIVERSITY OF BEIRUT

AN OPTIMIZED PRETREATMENT APPROACH FOR SEAWATER REVERSE OSMOSIS PROCESSING

by
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Disclaimer

The idea of using the principle of the process of alkalizaion and softening as an optimized pretreatment for SWRO is initiated and developed by Prof. George Ayoub and consequently he is reserved all the rights and privileges pertaining to this idea.

AN ABSTRACT OF THE THESIS OF

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Increase in water consumption intensified water shortages all over the globe; therefore water is rapidly being perceived as a limited resource of high economic value. Seawater Desalination advancements in both thermal and membrane technologies rendered desalination as an important source of drinking water.

The application of RO for seawater desalination has intensified rapidly throughout the globe with the construction of large RO plants. Seawater Reverse Osmosis (SWRO) is a highly effective desalination process; however the main drawback that has been facing this process is fouling of RO membranes including: inorganic, organic, colloidal, and biological fouling.

The present study aims at reporting an investigation conducted on a SWRO conventional pretreatment process that optimizes the multi-process pretreatment that is practiced at present. Based on the principle of softening the process includes (coagulation-flocculation) using $Mg(OH)_2$ and $CaCO_3$, thus inducing simultaneous and quasi-complete control of the pollutants responsible for membrane fouling, as well as partial but appreciable removal of boron.

The results of the study showed that the sequences of conducting jar test experiments using optimal concentrations of NaOH and Na_2CO_3 as alkalizing agents and $Mg(OH)_2$ and $CaCO_3$ as coagulants at optimal temperatures recorded removal efficiencies as high as: 100 % for Ca, 99.6% for Mg, 100% for Si, 82% for B, 99% for Fe, 93% for VSS, and 58.4% for TOC, in addition to complete inactivation of total and fecal coliforms. Furthermore, sludge produced from the treatment process was studied and the sludge mass produced as a result of the process is about 7.9 kg/m^3.

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ABBREVIATIONS

AUB: The American University of Beirut

Ca: Calcium

CDI: Capacitance deionization

CEOP: Cake-Enhanced Osmotic Pressure

CI: Confidence Interval

ED: Electro Dialysis

EDL: Electric Double Layer

EPS: Extracellular Polymeric Substances

FO: Forward Osmosis

GHF: Gas Hydrates Freezing

HAA: Halo Acetic Acids

HDH: Humidification Dehumidification

ICIS: Independent Chemical Information System

MD: Membrane Distillation

MED: Multiple-Effect Distillation

MF: Micro Filtration

MFI: Modified Fouling Index

$Mg(OH)_2$: Magnesium Hydroxide

Mg: Magnesium

MSF: Multi-Stage Flash

Na_2CO_3: Sodium Carbonate

NaOH: Sodium Hydroxide

NF: Nano Filtration

NOM: Natural Organic Matter

R&D: Research and Development

RO: Reverse Osmosis

SDI: Silt Density Index

Si: Silica

SWRO: Seawater Reverse Osmosis

TBT: Top Brine Temperature

TDS: Total Dissolved Solids

THMs: TriHalomethanes

TOC: Total Organic Carbon

TSS: Total Suspended Solids

UF: Ultra Filtration

UV: Ultra Violet

VC: Vapor Compression

VDS: Volatile Dissolved Solids

VDW: Van der Waals

VSS: Volatile Suspended Solids

CHAPTER 1

INTRODUCTION

Water scarcity is rapidly increasing all over the globe, while such scarcity frequently occurs in arid regions, pollution of fresh water resources in addition to the extensive use of ground water aquifers and surface water has led to the deterioration of fresh water quality and quantity (Valavala et al., 2011). Water is increasingly perceived as a limiting resource of environmental and economic value. According to the U.S. Geological Survey 96.5% of Earth's water is located in seas and oceans and 1.7% of Earth's water is located in the ice caps. Approximately 0.8% is considered to be fresh water. The remaining percentage is made up of brackish water, slightly salty water found as surface water in estuaries and as groundwater in salty aquifers (Dunham, 2011). Therefore the only nearly inexhaustible sources of water are the oceans. The main drawback of ocean waters, however, is the high salinity. Over 17% of the earth's population is suffering from the lack of clean drinking water, and approximately 40 % of the population lives in regions with chronic water shortages (Service, 2006). The increase in water demand due to population, industrial, and agricultural growth increased water consumption intensifies the problem of water shortage, thus providing additional and new fresh water resources is essential.

Water conservation, reuse, and desalination (brackish and seawater) are gaining considerable attention from scientists, resource planners, policy-makers, and other stakeholders in addressing water supply reliability. These measures have been incorporated successfully in providing additional fresh water to communities relying on conventional water treatment and fresh water resources (Johns and Karajeh, 2004; Reahl, 2006; Sanza et al., 2007). Water reuse technologies have been utilized to provide water for industrial processing, irrigation, power plant cooling, and ground-water recharge. they have also been accepted as means for indirect drinking water production (Focazio et al., 2008; Fono et al., 2006; Sedlak et al., 2000). Desalination advancements in both thermal (during the past 60 years) and membrane desalination technologies (during the past 40 years) rendered desalination as an important source of drinking water (Gleick et al., 2006). Nowadays desalination is considered as a main source of fresh water in many countries in the Middle East and other regions of the world (El Saliby et al., 2009).

Desalination is the process of removing salts from water to produce fresh water with total dissolved solids (TDS)< 1000 mg/L, and is used for both seawater and brackish water (Sandia, 2003). Different countries have different drinking water standards for contaminants; this is also applicable to TDS. The WHO and the Gulf Drinking Water standards recommend a drinking water standard of 1000 mg/L TDS for drinking water. A TDS > 1000 mg/L in drinking water will adversely affect taste, color, corrosion propensity, and odor (Fritzmann et al., 2007). Most desalination facilities are designed to achieve a permeate TDS value of 500 mg/L or less (Petry et al., 2007)

Current commercial desalination technologies can be divided into thermal distillation (MSF and MED) and membrane separation (RO) with some hybrid plants integrating both thermal and membrane technologies (Hamed, 2006). There are other commercial technologies with less application such as vapor compression (VC) which is used with small size units and electro dialysis (ED) used in the treatment of water with lower salinities. Emerging technologies such as forward osmosis (FO), membrane distillation (MD), capacitance deionization (CDI), and gas hydrates (GH), freezing, humidification dehumidification (HDH) and solar stills are still undergoing a phase of research and development (R&D) (ESCWA, 2009). Global desalination capacity by process shown in Figure 1.1 illustrates the dominance of RO and thermal treatment over other technologies.

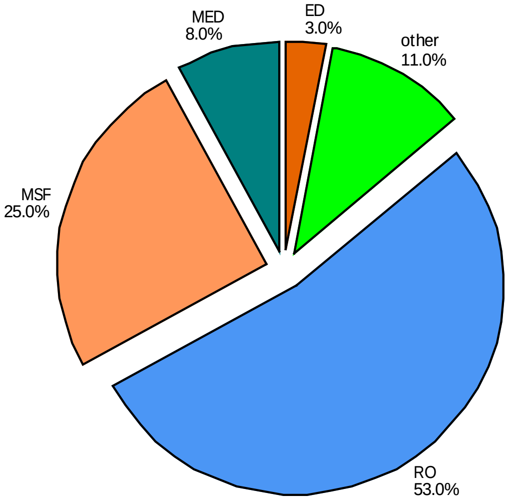


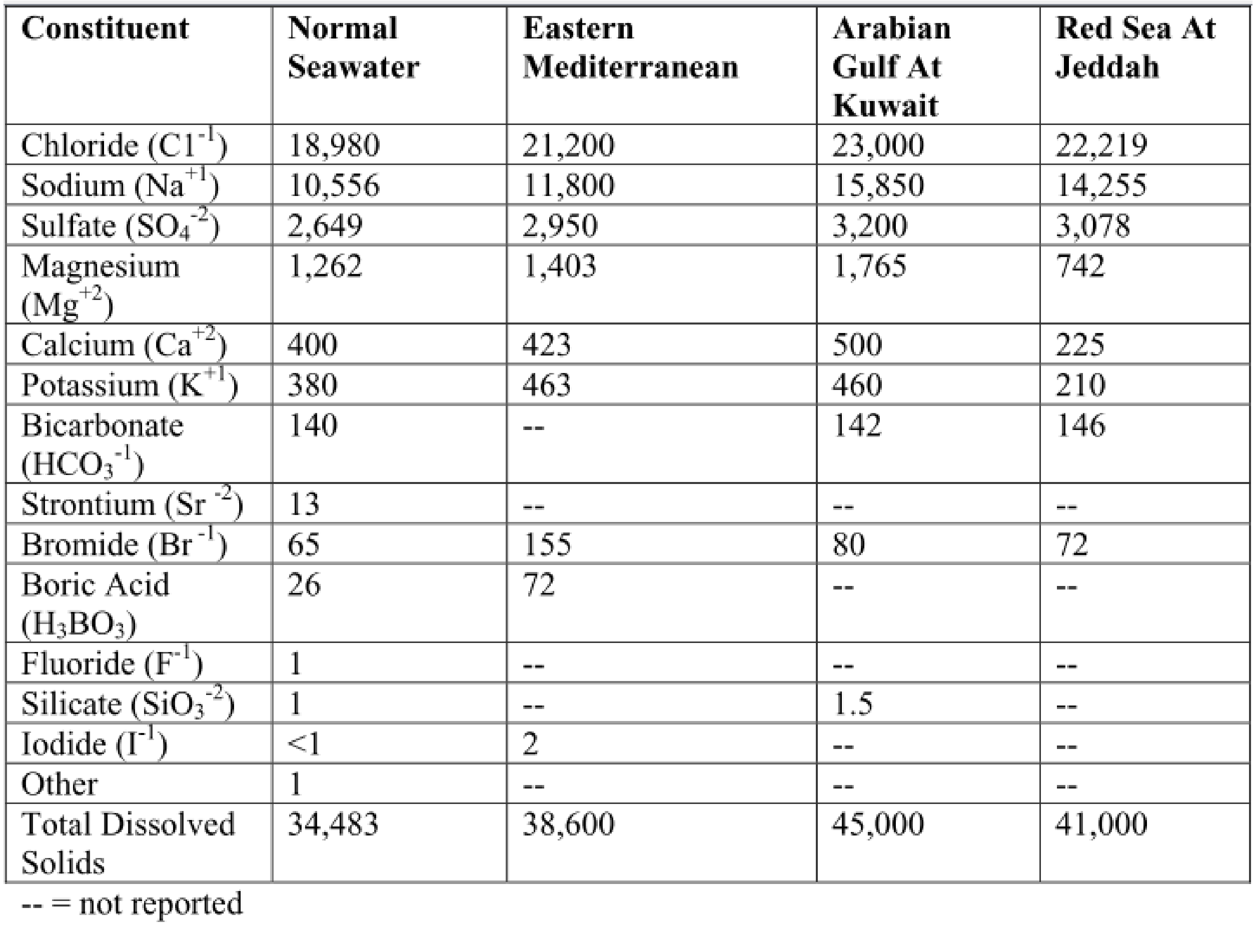
Figure 1.1 Global desalination capacities by process (ESCWA, 2009)

Heat energy is used in thermal desalination whereby salt is separated from water by evaporation and condensation, on the other hand RO desalination (membrane desalination) is the passage of water through a membrane retaining the majority of the salts (Fritzmann et al., 2007). Even though membrane technologies are thought to be the most developed of desalination technologies, the adoption of a desalination technology is influenced by the feed water characteristics, required permeate quality, labor cost, available area, energy cost, and local demand for electricity (Valavala et al., 2011). This explains the reason behind the huge market share of thermal technique in the Middle East region which basically is guided by low energy costs and large scale cogeneration plants (Mezher et al., 2011).

Both desalination techniques demonstrate advantages and disadvantages, seawater constituents can adversely affect the operation and outcome of any technique used. Thermal desalination plants are affected by scale formation, such as calcium carbonates/sulfates, and magnesium hydroxide, thus limiting the top brine temperature used in the plant (TBT) (Cooley et al., 2006). The use of membrane technologies also exhibits several limitations among which RO membranes are susceptible to membrane fouling associated with particulate matter and colloids, organic/inorganic compounds, and biological growth (Tran et al., 2007).

A successful application of desalination using any of the two processes requires a careful consideration of the composition of the water to be desalinated and the application of proper pretreatment in order to alleviate the extent of damage that might result from the presence of certain chemicals or pollutants in the raw water. Although the characteristics and composition of seawater tend to be stable, yet slight variations could exist due to environmental conditions that persist at the locations from where such waters might be tapped. Table 1.1 shows the ionic composition the seawater at different locations in the Middle East area.

Table 1. 1 Ionic composition of different seawater (mg/L) (Cotruvo, 2004)



Constituent	**Normal Seawater**	**Eastern Mediterranean**	**Arabian Gulf At Kuwait**	**Red Sea At Jeddah**
Chloride ($C1^{-1}$)	18,980	21,200	23,000	22,219
Sodium (Na^{+1})	10,556	11,800	15,850	14,255
Sulfate (SO_4^{-2})	2,649	2,950	3,200	3,078
Magnesium (Mg^{+2})	1,262	1,403	1,765	742
Calcium (Ca^{+2})	400	423	500	225
Potassium (K^{+1})	380	463	460	210
Bicarbonate (HCO_3^{-1})	140	--	142	146
Strontium (Sr^{-2})	13	--	--	--
Bromide (Br^{-1})	65	155	80	72
Boric Acid (H_3BO_3)	26	72	--	--
Fluoride (F^{-1})	1	--	--	--
Silicate (SiO_3^{-2})	1	--	1.5	--
Iodide (I^{-1})	<1	2	--	--
Other	1	--	--	--
Total Dissolved Solids	34,483	38,600	45,000	41,000

-- = not reported

SWRO desalination invariably requires the application of a proper pretreatment procedure with the aim of lowering the fouling propensity of the water on the RO membrane system (Morenski, 1992),and which in turn, is divided into two categories conventional and membrane pretreatment.

Conventional pretreatment typically involves acid addition, coagulant/flocculant addition, disinfection, filtration, dechlorination, pH adjustment, and adjustment of the solubility parameters to avoid precipitation of sparingly soluble salts on the membranes

(Isaias, 2001). However, a disadvantage attributed to conventional pretreatment is that certain colloids and suspended particles pass through conventional pretreatment and contribute to RO membrane fouling that is difficult to remove (and possibly irreversible) (Brehant et al., 2003). This has led to an increased tendency towards the use of larger pore size membranes (MF, UF, and NF) to pretreat RO feed water (Greenlee et al., 2009). Different pore sizes for the membrane pretreatment technologies is shown in Figure 1.2

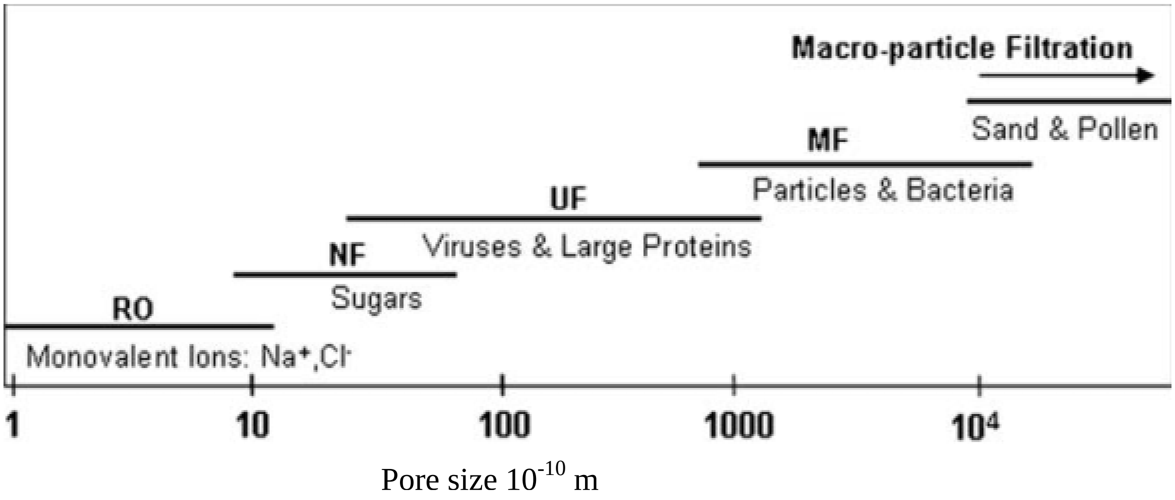


Figure 1.2 Range of nominal pore diameters for commercially available membranes (Perry & Green, 1997)

It is important to note that membrane pretreatment also requires chemical addition, mainly in coagulation-flocculation where Ferric chloride ($FeCl_3$) is mostly used. The coagulant is added upstream of the membrane pretreatment which could lead to the formation of a porous coagulated cake on the surface of the membrane (Brehant et al., 2003).

The search for more feasible substitutes is an ongoing process when it comes to SWRO. Previous studies reported the beneficial effect of seawater alkalization using NaOH in removing impurities from water along with some chemicals that invariably play a role in membrane fouling (Ayoub et al., 2000; El-Manharawy & Hafez, 2002).

The present study aims at reporting an investigation conducted on a SWRO conventional pretreatment process that optimizes the multi-process pretreatment that is practiced at present. If properly applied the process will simultaneously and almost quasi-completely control the removal of the pollutants responsible for membrane fouling including calcium, magnesium, iron, silica, bacteria, organic matter, oil and, when present, algal cells. Partial removal of boron will be effected as well. The need for the application of chlorine for disinfection is eliminated and the resulting sludge may be converted into economically sustainable products. The studied system can also be used for thermal desalination pretreatment. The complete removal of calcium eliminates the need for antiscalants addition to the treated water, thus allowing the use of a higher TBT which leads to a more efficient thermal desalination process.

CHAPTER 2

LITERATURE REVIEW

Desalination is a process which provides alternative sources of water. Even though desalination is becoming more widely accepted around the globe, limitations to the process are highly affecting the extent of its spread. Nearly all types of desalination systems exhibit weaknesses, for example, the most widely used desalination techniques such as RO desalination and MSF are highly affected by the contaminants present in the water intake (Greenlee et al., 2009). A major limitation in RO membrane desalination is the presence of components such as Ca, Mg, bacteria, organic matter, and silica which cause membrane fouling and deteriorate desalinated water quality (Belfer et al., 2001)

With thermal desalination (MSF and MSD), the presence of such components also affects the process, for example the presence of Ca and its precipitation at 120^{o}C have a scaling effect on the MSF treatment process, therefore limiting the TBT to 120^{o}C or imposing the need for the addition of chemical anti-scalents to the water, which are known to have a negative impact on water quality and force additional economic burden to the process (Hamed & Al-Otaibi, 2010).

As membrane fouling and thermal scaling occur, the need for pretreatment in SWRO and thermal desalination becomes unavoidable. Pretreatment is separated into conventional and membrane pretreatment (Pontié et al., 2005).

2.1 Membrane Fouling

Membrane fouling is the loss of membrane permeability due to the accumulation of solutes onto the surface of the membrane and/or into its pores. Fouling is one of the main disadvantages in membrane filtration processes (Kim et al., 2006). The term fouling is used for both reversible and irreversible solute absorption, nevertheless the major problem in RO membrane is the irreversible fouling which produces a flux decline that cannot be ceased via hydraulic membrane cleaning (Jones & O'Melia, 2000). There are various types of membrane fouling, often divided as inorganic scaling, colloidal deposition, organic adsorption, and biofouling. The main contributors to RO membrane fouling are colloidal particles and dissolved organic matters (Yu el al., 2010). Si, Al, Fe, Ca and Mg were found as the major inorganic foulants deposited on the RO membranes (Yang et al., 2010). Humic and non-humic NOM is the cause of organic fouling (Lee et al., 2005). Fouling reduces permeate retrieval percentage and causes the deterioration of desalinated water quality. The frequent replacement and chemical cleaning of membranes as a result of fouling increases the operating cost, and ultimately shortens the lifespan of pressure membrane systems. This imposes a large economic burden on RO membrane plant operation thus limiting the capacity of such systems to replace conventional treatment systems (Lee et al., 2004; Ridgway, 2003).

Membrane fouling remains to be the largest obstacle facing the RO desalination industry and membrane desalination research, which aims at enhancing and maintaining the membrane flux without sacrificing desalination efficiency (Hoek et al., 2001; Vrouwenvelder et al., 2006). Membrane fouling is conventionally measured using two indexes the silt density index (SDI) and the modified fouling index (MFI) (Hong et al., 2009)

The types of fouling in this review will be divided into 4 major categories as proposed by Vrouwenvelder et al. (2006) and Flemming (1997):

1. Crystalline/ inorganic material: Crystalline Si, Mg, Ca, etc.
2. Organic material: humic substances and oils
3. Colloidal/ particulate: Clay, humic substances, Si, debris
4. Biological: microorganisms forming biofilms on the membrane (Coulombwall & Flemming, 1997).

According to Chong et al. (2007) the osmotic-resistance filtration model best describes the fouling effect on flux with the following equations:

$$J_0 = \frac{\Delta P - M_0 \Delta \prod_b}{\mu R_m}$$

$$J_f = \frac{\Delta P - M_f \, \Delta \prod_b}{\mu (R_m + R_{f)}}$$

Where J_o is the water flux of a clean membrane, J_f is the water flux of a fouled membrane, ΔP is the trans-membrane pressure $\Delta\Pi_b$ is the osmotic pressure difference between the bulk feed water and the permeate, μ is the feed water viscosity, R_m is membrane hydraulic resistance, and R_f is additional hydraulic resistance caused by the cake layer, M_0 and M_f are the concentration polarization (CP) modulus for the clean membrane and that for the fouled membrane (Chong et al., 2007; Hoek et al., 2001). General membrane fouling processes caused by different types of foulants are shown in Figure 2.1

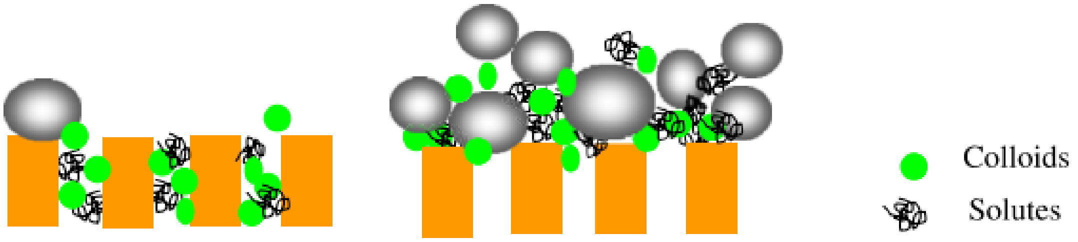


Figure 2.1 Membrane fouling process pore blocking and cake layer adapted from Meng et al., 2009

2.1.1 Inorganic Fouling

The abundance of Mg and Ca compounds in seawater composition makes inorganic fouling an expected encounter in SWRO. Research conducted by Ognier et al. (2002) reported that severe $CaCO_3$ fouling in an RO membrane rendered the membrane inoperable, they also stated that high alkalinity caused $CaCO_3$ precipitation. Inorganic fouling can occur easily when an inorganic membrane is used, due to the strong cohesion between inorganic molecules and the inorganic surface of the membrane (Kang et al., 2002).

Inorganic cake layer formation at the membrane surface is the result of the coupling of inorganic foulants with inorganic precipitates. The inorganic matter which contribute to the cake formation are mostly Mg, Al, Fe, Ca, and Si (Wang et al., 2008). The contribution of inorganic foulants to the overall fouling process was found to be more significant than that of biopolymers (Lyko et al., 2007), due to the fact that inorganic scaling is not easily eliminated by chemical cleansing of the RO membrane (You et al., 2006).

2.1.1.1 Inorganic fouling mechanism

Inorganic fouling can occur in two ways both of which are considered to be precipitative: biological precipitation and chemical precipitation (Meng et al., 2009). Meng et al. (2009) reported chemical precipitation as a result of increase in concentration polarization in the presence of cations and anions such as Ca^{2+} , Mg^{2+}, Al^{3+}, Fe^{3+}, CO_3^{2-}, SO_4^{2-}, PO_4^{3-}, and OH^- . It is also reported that one of the major sources of inorganic fouling are carbonates, the carbonates of metals such as Ca, Mg, and Fe can increase the potential of membrane scaling (You et al., 2005).

On the other hand biological precipitation is the quick reaction of metals with ionizable groups such as COO^-, CO_3^{2-}, SO_4^{2-}, PO_4^{3-}, and OH^- (Meng et al., 2009). The formation of complexes and bio-cake layers or gel layers were also reported in the presence of calcium and acidic functional groups (R–COOH) (Costa et al., 2006). The presence of metal ions and their interaction with cells and biopolymers leads to the formation of a fouling precipitate that produces a denser cake layer which imposes flux difficulties (Meng et al., 2009). Both Inorganic fouling and the formation of bio-cake layer mechanisms are presented in Figure 2.2.

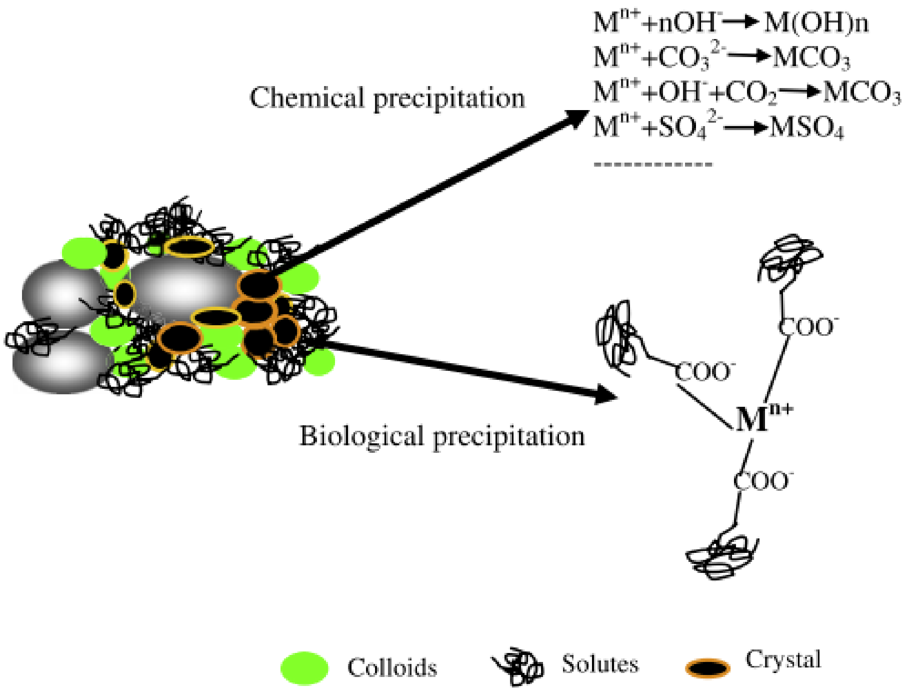


Figure 2. 2 Schematic illustration of the formation of inorganic fouling adabted from Meng et al., 2009

2.1.1.2 Treatment of inorganic fouling

The relation of metals removal via coagulation-flocculation with Mg and the settling of $Mg(OH)_2$ flocs have been previously assessed, and heavy metals were successfully removed via settling due to the presence of MgSiOH floc (Ayoub et al., 2001; Semerjian & Ayoub, 2003). Raising the pH, in the presence of magnesium in seawater will cause the formation of $Mg(OH)_2$ which will in turn settle out. The presence of $Mg(OH)_2$ floc which are normally formed at high pH values of about 11, should result in iron removal from the permeate, with iron being one of the membrane fouling components (Ayoub et al., 2000).

Iron is present in water in two forms, ferric and ferrous. Ferric iron is basically ferrous iron which has been oxidized; this form of iron is easily removed via filtration. On the other hand ferrous iron is more water soluble and cannot be removed easily. There are a variety of ways for removing ferrous iron, these methods fall into two categories: ion exchange and oxidation/filtration (Okoniewska et al., 2007)). The mixing process will result in oxidizing ferrous into ferric iron thus facilitating the removal of iron from the sample. Iron in seawater is invariably present in the ferric form.

Mg and Ca carbonates represent hardness in a water sample. Upon increasing the pH of a seawater sample flocs are formed. Depending on the specific alkalizing agent used, different types of flocs such as $Mg(OH)_2$ and $CaCO_3$ are normally formed (Semerjian & Ayoub, 2003)

The mechanisms of precipitation of inorganics are explained as recorded by Culp et al. (1987) are:

$$Ca(OH)_2 + H_2CO_3 \leftrightarrow CaCO_3 \downarrow + 2H_2O$$

$$Ca(OH)_2 + Ca(HCO_3)_2 \leftrightarrow 2CaCO_3 \downarrow + 2H_2O$$

$$3Ca(OH)_2 + 2PO_4^{-3} \leftrightarrow Ca_3(PO_4)_2 \downarrow + 6OH^-$$

$$4Ca(OH)_2 + 3PO_4^{-3} + H_2O \leftrightarrow Ca_4H(PO_4)_3 \downarrow +9OH^-$$

Raising the pH by using NaOH (providing OH- ions) to a value greater than 10.5 in the presence of Mg^{2+} ions will result in the following reaction (Stumm & Morgan, 1981; Ayoub et al., 1999)

$$Mg^{2+} + 2OH^- \rightarrow Mg(OH)_2 \downarrow$$

When alkalized by either NaOH, or $Ca(OH)_2$ magnesium sulfate and magnesium chloride found in seawater will react to produce $Mg(OH)_2$, following the reactions (Ayoub et al., 1999):

$$MgSO_4 + Ca(OH)_2 \rightarrow Mg(OH)_2 \downarrow +CaSO_4$$

$$MgCl_2 + Ca(OH)_2 \rightarrow Mg(OH)_2 \downarrow +CaCl_2$$

$$MgSO_4 + 2NaOH \rightarrow Mg(OH)_2 \downarrow +Na_2SO_4$$

$$MgCl_2 + 2NaOH \rightarrow Mg(OH)_2 \downarrow +2NaCl$$

The coagulation-flocculation procedure is based on the theory of LMC (Lime Magnesium Carbonate) process softening, in sea water it causes the production of magnesium hydroxide and calcium carbonate which precipitate (Mavis & Checkovich, 1975)

In addition to pretreatment using coagulation-flocculation, chemical cleaning agents such as EDTA are used to clean the membrane. EDTA initiates ligand exchange reaction in the presence of Ca^{2+} which might efficiently remove inorganics (Ahmed Al-amoudi & Lovitt, 2007).

2.1.2 Organic Fouling

Organic matter is present in nearly all sources of natural water. Organic matter includes bi-polymers such as proteins and polysaccharides, and natural organic matter (NOM) (Li & Elimelech, 2006; Kim et al., 2008). According to Kim et al. (2008):

> “Natural organic matter (NOM) is of concern in water treatment, because it serves as the precursor for the formation of chlorinated disinfection by-products (DBPs), it competes with synthetic organics for adsorption sites on activated carbon, and it is a major foulant when water is treated by membrane filtration”.

Humic substances are refractory anionic macromolecules and are considered to be the major fraction of NOM in the environment. According to Aiken (1985) humic substance contains both aromatic and aliphatic components with primarily carboxylic and phenolic functional groups. Therefore NOMs are negatively charged in neutral pH conditions (Hong & Elimelech, 1997).

Organic fouling could cause either reversible or irreversible fouling. Flux decline is the major effect of NOM fouling on the RO membrane. Chemical cleaning is considered to be a solution for reversible flux decline, the addition of specified dosages can restore the flux lost (Al-Amoudi & Farooque, 2005). On the other hand chemical dosing will not completely restore the flux in case of irreversible fouling (Roudman & DiGiano, 2000) due to the presence of colloidal organic matter and the increase in concentration polarization (Al-Amoudi, 2010). Fouling caused by NOM can also be divided into external surface fouling (build-up of a cake/gel-like layer on the upstream face of membrane) and pore blocking fouling (Knyazkova & Maynarovich, 1999), an illustration of the two types is presented in Figure 2.1. Organic fouling by NOM is affected by ionic strength (solution chemistry), pH, membrane surface, permeate flux and operating pressure (Al-Amoudi, 2010). General effects on NOM fouling in membrane treatment is illustrated in Figure 2.3

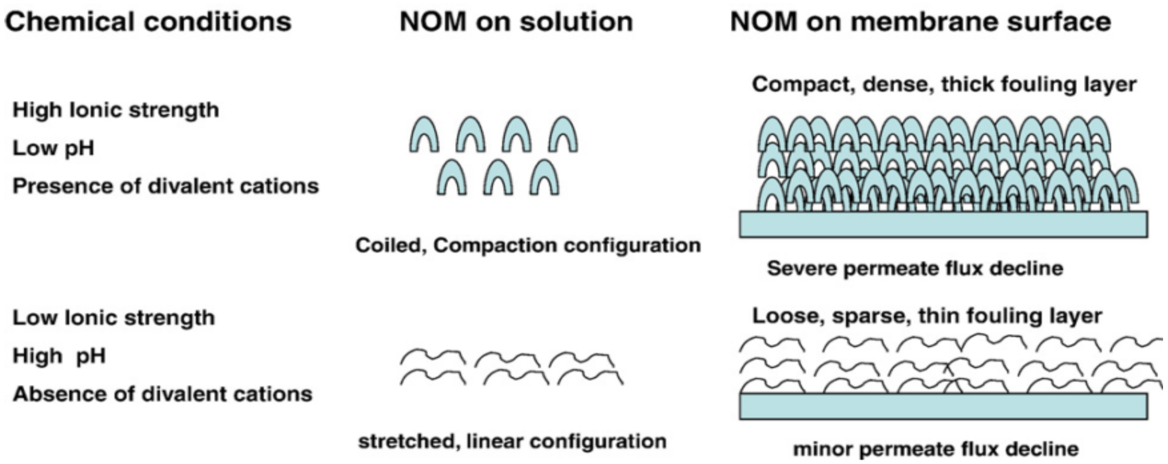


Figure 2.3 Schematic description of the effect of solution chemistry on the conformation of NOM macromolecules in the solution and on the membrane surface, and the resulting effect on membrane permeate flux. (Al-Amoudi, 2010)

Numerous studies were conducted to establish the effect of pH on NOM the results of which indicate that NOM is denser at low pH as a result of the reduction of electrostatic repulsion between the membrane surface charge and NOM (Childress &

Elimelech, 1996; Hong & Elimelech, 1997). According to studies made by Childress & Deshmukh (1998) and Jucker & Clark (1994) humic acid adsorption to the membrane occurs at low pH where electrostatic repulsion is lower, thus escalading NOM fouling potential.

Divalent cations also exhibit a significant effects on NOM fouling; several researchers stated that as the Ca^{2+} concentration increases in the presence of NOM the water flux decreases dramatically as a consequence of the reduction reaction of the NOM and the surface charge of membrane (Hong & Elimelech, 1997). Flux drops were not nearly as extensive in the presence of monovalent ions such as Na^{+} (Jarusutthirak et al., 2007).

It was also reported that membrane organic fouling potential and its effects on flux loss is strongly dependent on Ca^{2+} concentration. Lee et al. (2005), Hong & Elimelech. (1997), and Schafer et al. (1998) offered an explanation to the Ca^{2+} and NOM relation, whereby divalent cations interact with humic carboxyl functional groups and reduce the charge and the electrostatic repulsion between humic macromolecules, also according to Al-Amoudi (2010):

> “Divalent cations may also bridge two free functional groups of humic acid. As a result, humic matter deposition onto the membrane surface increases and a more densely packed fouling layer forms”

Other factors also interfere with NOM fouling, for example membrane characteristics such as surface material and roughness can increase fouling rate of attachment to the membrane (Childress & Elimelech, 1996; Herzberg & Elimelech, 2007;

Lee et al., 2005). Schafer et al. (1998) also stated that increasing operating pressure had a strong effect on increasing NOM deposition in the presence of divalent ions and humic acid.

Al-Amoudi (2010) summarized the methods used in NOM treatment by the following:

1. Changing operating conditions (in terms of flux, pressure, etc.)
2. Modifying the membrane (surface, type)
3. Antifoulants addition to the feed water (Roux, 2005)

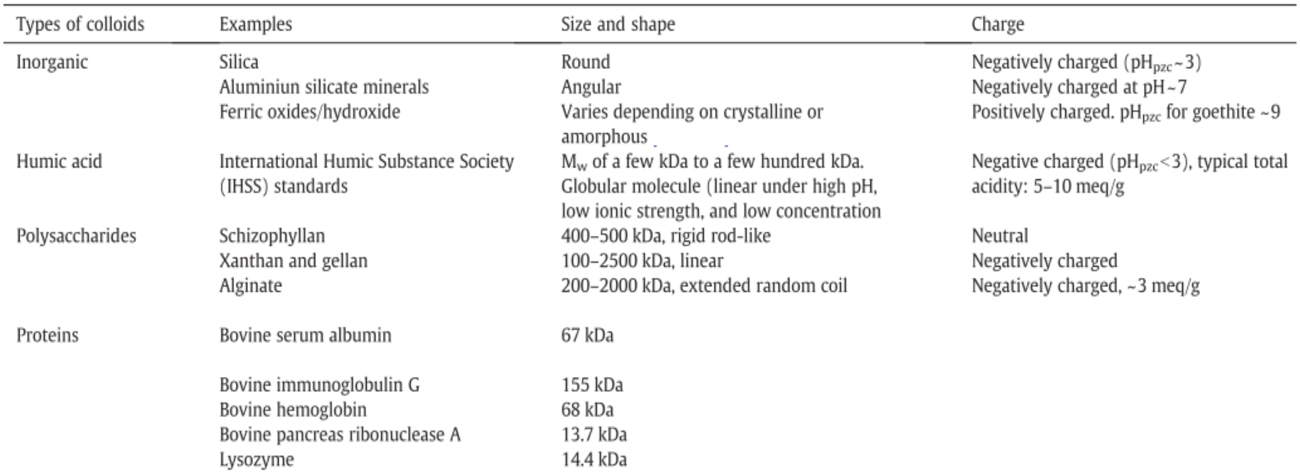
It is to be noted that NOM could be reduced by these methods but not prevented.

2.1.3 Colloidal Fouling

Despite developments in research on RO fouling the mechanisms involved in colloidal fouling are still not entirely clear (Paul & Abanmy, 1990; Tang et al., 2011). Due to the size of colloids, which range between 1-1000 nm, such particles are capable of severely fouling RO membranes (Bacchin et al., 2006). Colloids can be both organic or inorganic at the stated size range, where major inorganic colloids present in RO membrane fouling include aluminum silicate, silica, iron oxides/hydroxides, and elemental sulfur (Ning et al., 2005; Tran et al., 2007), while organic colloids include polysaccharides, proteins, and natural organic matter (Tran et al., 2007). Also present are microorganism cells and cell debris which are classified as bio-colloids (Tang et al., 2011). Table 2.1

presents the types and properties of colloids including their size, shape, and charge which affect their fouling mechanism.

Table 2.1 Abundant colloids and their properties (Tang et al., 2011)



Types of colloids	Examples	Size and shape	Charge
Inorganic	Silica	Round	Negatively charged (pH_{pzc} ~ 3)
	Aluminiun silicate minerals	Angular	Negatively charged at pH ~ 7
	Ferric oxides/hydroxide	Varies depending on crystalline or amorphous	Positively charged. pH_{pzc} for goethite ~9
Humic acid	International Humic Substance Society (IHSS) standards	M_w of a few kDa to a few hundred kDa. Globular molecule (linear under high pH, low ionic strength, and low concentration	Negative charged ($pH_{pzc} < 3$), typical total acidity: 5–10 meq/g
Polysaccharides	Schizophyllan	400–500 kDa, rigid rod-like	Neutral
	Xanthan and gellan	100–2500 kDa, linear	Negatively charged
	Alginate	200–2000 kDa, extended random coil	Negatively charged, ~3 meq/g
Proteins	Bovine serum albumin	67 kDa	
	Bovine immunoglobulin G	155 kDa	
	Bovine hemoglobin	68 kDa	
	Bovine pancreas ribonuclease A	13.7 kDa	
	Lysozyme	14.4 kDa	

2.1.3.1 Colloidal interactions

Colloidal interactions are best represented by the Derjaguin–Landau–Verwey–Overbeek theory (DLVO). It defines colloidal interaction as a function of both electrostatic forces also known as electrical double layer (EDL), and Van der Waals force (Gregory, 2006). Colloidal interactions can be dominated by acid base interaction forces at high ionic strength (e.g., in seawater) where the electrostatic interactions and VDW forces are minimized (Kuhnl et al., 2010).

2.1.3.2 Colloidal fouling mechanisms

According to Valavala et al., 2011:

> “Suspended and colloidal particles foul a membrane by coagulating together and forming a cake-like layer on the membrane surface, while dissolved organics interact directly with the membrane surface and with each other to cause fouling”.

Colloidal fouling potential is highly increased in the presence of inorganic and organic matter. Colloids can form a layer on the RO membrane “cake layer”. Other colloids, mainly those with strong colloidal interaction (like polysaccharides in the presence of Ca, tend to cause excessive fouling via the formation of a large three dimensional cross linked layer (gel layer) (Buffle et al., 1998; Wang & Waite, 2008). The formation of a deposit layer on the RO membrane surface will affect membrane flux in two ways. The first is by reducing membrane permeability, and thus forcing a higher pressure input to maintain a constant permeate flux (Ang et al., 2006; Palecek & Zydney, 1994). The second is the effect imposed by the porous layer of the cake created due to colloidal fouling, a phenomenon known as cake-enhanced osmotic pressure (CEOP), which increases concentration polarization inside the cake layer and significantly increases the solute concentration at the membrane surface. Thus CEOP tends to reduce flux at constant pressure or vice versa (Hoek et al., 2001). Colloidal cake formation can be affected by many factors, and according to Tang et al. (2011) the factors can be summarized in three groups shown in Figure 2.4.

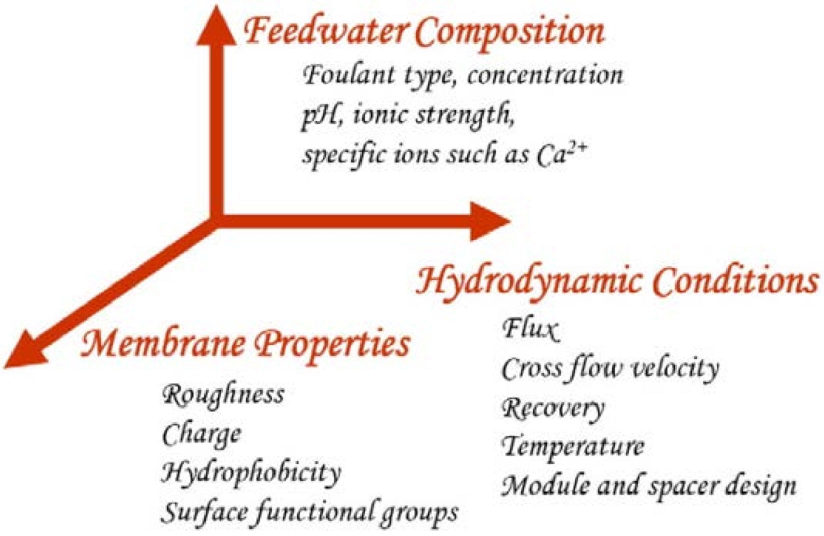


Figure 2.4 Factors affecting colloidal fouling on membrane (Tang et al., 2011)

Feed water composition is important in determining the fouling potential, different water intakes exhibit different types of foulants, and at different concentrations, solution chemistry, pH, and ionic strength can drastically affect the properties of colloidal particle present in the intake. Many of the important colloidal physiochemical properties can be drastically affected by solution chemistry (Buffle et al., 1998; Buffle & Leppard, 1995; Tang et al., 2007). A study reported by Buffle et al. (1995) also concluded that:

> “The surface charge of colloids can also be altered due to the specific interaction between some functional groups and ionic species”.

The second factor is the membrane itself, the properties of membranes differ according to manufacturers’ preferences, surface roughness, charge properties, and hydrophobicity (Zhu & Elimelech, 1995).

In addition, studies reported by Lee et al. (2010) and, Wilf and Alt. (2000) stated that:

> “Smooth, low surface charge, and more hydrophilic membranes tend to show better anti-fouling properties at the initial stage of membrane fouling. Nevertheless, under severe fouling, this is not observed due to the fact that fouling may be dominated by deposited foulants and foulant interaction instead”

The third factor controlling colloidal fouling mechanisms is the plant operating conditions; variations in flux and cross flow velocity will impact the fouling mechanism. Severe fouling can occur at higher membrane flux and/or lower cross flow. The cross flow affects the mass transfer rate over the membrane surface (Goosen et al., 2004). A higher cross flow will limit membrane fouling potential due to colloidal particles by reducing the boundary layer thickness and concentration polarization (Goosen et al., 2004). Temperature variation can also significantly affect colloidal fouling (Tang et al., 2011). A scheme of colloidal fouling on the RO membrane surface is shown in Figure 2.5.

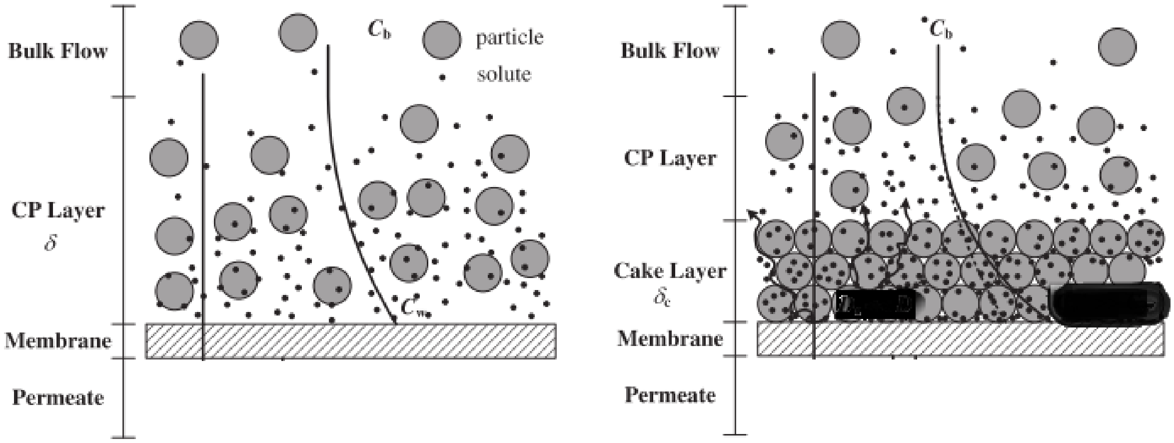


Figure 2.5 Concentration polarization and CEOP (a) before membrane is fouled and (b) after membrane is fouled (Hong & Elimelech, 1997)

<u>2.1.3.3 Colloidal fouling treatment</u>

Media filtration is a method by which some colloids are removed from feed water; however colloids that can highly impact the operation are finely dispersed solid particles or liquid droplets that escape filtration by sand, multimedia and 5 or 1 micron guard filters (Ning et al., 2005; Ning & Troyer, 2007). The control and removal of colloidal silicates and colloidal sulfate through chemical addition (disinfectants and anticoagulants) proved to be effective, in addition to various methods involving flux and cross flow control as explained by Tan et al. (2011). The removal of colloidal silica and colloidal organic matter will be discussed in their respective sections. Some treatment methods employed in removing colloids are:

1. Disinfection (to eliminate Bio colloids) (Paul & Abanmy, 1990)
2. Membrane cleaning

3. Coagulation-flocculation with aluminum sulphate and ferric chloride (Koohestanian et al., 2008)

The coagulation-flocculation reactions as reported by Koohestanion et al. (2008) are:

$Al_2(SO_4)_3 + 3\ Ca(HCO_3)_2 \leftrightarrow 2\ Al(OH)_3\ (\downarrow) + 3\ CaSO_4 + 6\ CO_2$

$Al_2(SO_4)_3 + Na_2CO_3 + H_2O \leftrightarrow 2Al(OH)_3\ (\downarrow) + 3\ Na_2SO_4 + 3\ CO_2$

$Al_2(SO_4)_3 + 6NaOH \leftrightarrow 2Al(OH)_3\ (\downarrow) + 3\ Na_2SO_4$

$Al_2(SO_4)_3 + 6\ H_2O \leftrightarrow 2Al(OH)_3\ (\downarrow) + H_2SO_4$

$2FeCl_3 + 6HCO_3 \leftrightarrow 2Fe(OH)_3\ (\downarrow) + 6Cl^- + 6CO_2$

2.1.4 Biological Fouling

Biofouling is the formation of biofilm on the RO membrane surface as a result of bacterial attachment to the membrane. Once the bacteria are attached, they grow, multiply, and relocate leading to severe biofilm formation, which decreases membrane performance (Lee & Kim, 2011). This type of fouling cannot be removed through pretreatment alone, due to the nature of bacteria. If 99.99% of all bacteria were removed in the pretreatment stage a few surviving cells entering the system will adhere to membrane surfaces, and multiply at the expense of biodegradable substances dissolved in the feed water (Matin et al., 2011). Biofouling has already infected 70% of the seawater RO membrane installations (Khedr, 2011). It was found that such fouling occurs even after water intake pretreatment and the addition of Cl disinfectant (Flemming et al., 1997)

2.1.4.1 Biofilm growth and development

Microorganisms present in feed water adhere to the membrane surface, the nutrients in the water intake aid in their growth. The microorganisms secrete extracellular polymeric substances (EPS) to form biofilms (Flemming, 2002). Biofilm's physical and physiological properties are reliant on the EPS and the nature of bacterial cells respectively (Beer & Stoodley, 2006). Events through biofilm formation occur as explained by Matin el al., (2011) are presented in Figure 2.6.

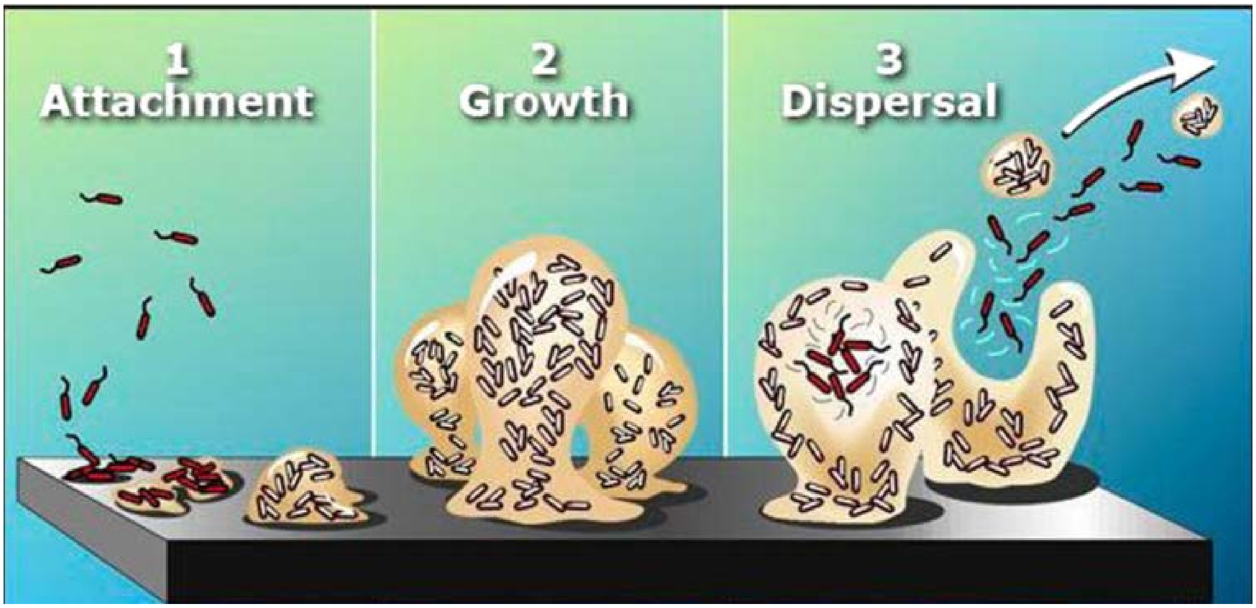


Figure 2.6 Sequence of events leading to the formation of a Biofilm (Matin el al., 2011)

The cell detachment stage is the last stage of biofilm formation, during this stage microbial cells disperse from the population and subpopulations of detached mature biofilm cells reinitiate biofilm formation on new sites (Romeo, 2006; Davies & Marques, 2009). Afterwards the biofilm begins its development process on the membrane surface; the three general phases of biofilm development on the membrane surface are shown in Figure 2.7.

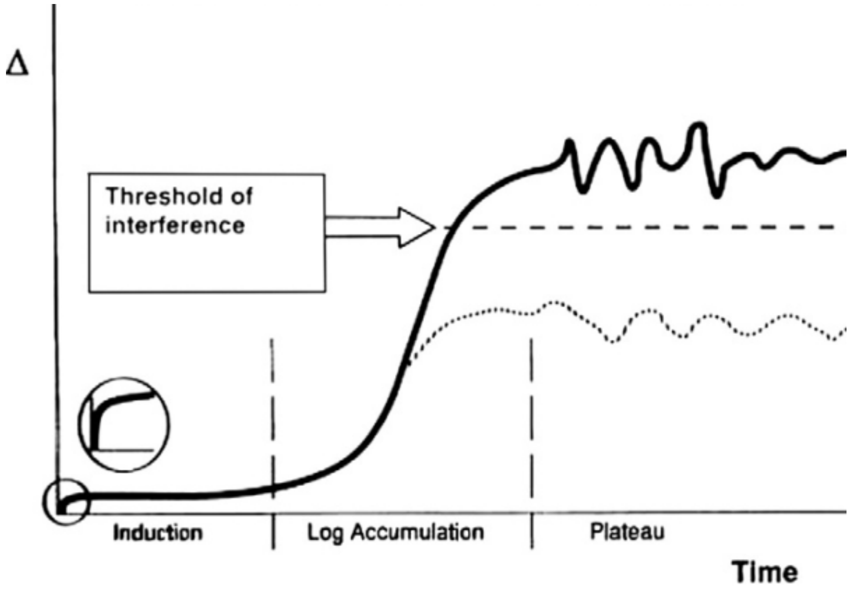


Figure 2.7 Time-dependent development of biofilm accumulation: Δ, biofilm growth parameter (thickness, weight, etc.); inset, primary colonization; threshold of interference, arbitrary extent of biofilm development above which the biofilm interferes with the performance of a membrane system Adopted from Flemming (1997)

According to Matin et al, (2011):

> “The induction phase is characterized by an initial rapid primary colonization followed by a primary plateau, during this phase adhesion is essentially proportional

> to the cell density in the water phase and occurs owing to weak physicochemical interactions. The second phase is the logarithmical growth phase, when cell growth on the surface contributes more to biofilm accumulation than does the adhesion of cells suspended in solution (water intake). Afterwards, the biofilm growth (adhesion and multiplication) is in balance with cell detachment and cellular senescence. This stage is known as the plateau phase and is mainly controlled by nutrient concentration and the resultant growth rate, the mechanical stability of biofilm, and the effective shear forces. When this phase is reached, the original surface properties of the membrane are masked by the biofilm”

Once biofilm formation causes unacceptable operational problems, it is classified as biofouling (Characklis & Marshall, 1990). Serious operational problems caused by biofilm accumulation are:

1. Increase in normalized pressure drop (NPD) around 15–30%
2. Decrease in normalized flux while operating at constant temperature and pressure exceeds 10% of the start-up values (Vrouwenvelder et al., 2008)

2.1.4.2 Effects on RO membrane process

Biofilm has the capacity to act as a secondary membrane when attached to the surface of RO membrane leading to permeate flux decline, thus forcing a boost in system pressure to compensate for the lost flux. Such compensation will increase energy consumption especially in large separation facilities of more than 4×10^6 L/day capacity where high electrical pumping costs are needed to maintain operating pressures and constant product output (Matin et al., 2011).

Biofouling of the RO membrane can be separated into two mechanisms (Herzberg & Elimelech, 2007):

1. Bacterial cells hinder the back diffusion of salt, which results in elevated osmotic pressure on the membrane surface (increase in TMP), and hence a decline in permeate flux
2. EPS contributes to the decrease in flux by increasing hydraulic resistance to permeate flow.

Biofilm also contributes to concentration polarization phenomena, which is the accumulation of dissolved substances retained by the membrane at the reject side, due to the reduction of turbulent mixing at the membrane surface. As a result, solute transport through the membrane increases, and salt rejection of the operation decreases in response to greater ionic activity in the boundary layer (Matin et al., 2011).

2.1.4.3 Biofouling treatment methods

Biofouling can occur at any given time even during membrane transfer, storage and maintenance operations, therefore control and prevention of such fouling are necessary. Pretreatment (conventional/membrane) reduces biofouling potential, however to a limited extent (Kumar et al., 2006). Membrane pretreatment can obtain a lower SDI thus it can be more effective than conventional pretreatment in inhibiting biofouling (Teng et al., 2003).

The most common method of treatment when it comes to biofouling is the continuous dosage of chemicals which are able to deactivate microorganisms (Ridgway, 1998; Kim el al., 2009). All SWRO pretreatment plants contain a disinfection stage to insure the efficient removal of bacteria regardless of whether the SWRO plant is conventional or non-conventional (Bae et al., 2011). The disinfection stage in SWRO plants is somewhat space consuming, in addition to the chemicals used, such as Cl, and O_3, induce an added cost to the pretreatment procedure (Ebrahim et al., 2001; Abdel-Jawad and Ebrahim, 2002; Al-Sheikh, 1997).

Chlorine has been dominantly used for disinfection purposes in SWRO. Biofilm growth was not recorded when using chlorinated water containing a residual of 0.04– 0.05 mg/L free chlorine (Lund & Ormerod, 1995). Chemical used in disinfection processes include free chlorine (i.e. HOCl, OCl^-), chloramines (NH_2 Cl), and chlorine dioxide (ClO_2) (Bartels et al., 2005; Petrucci & Rosellini, 2005).

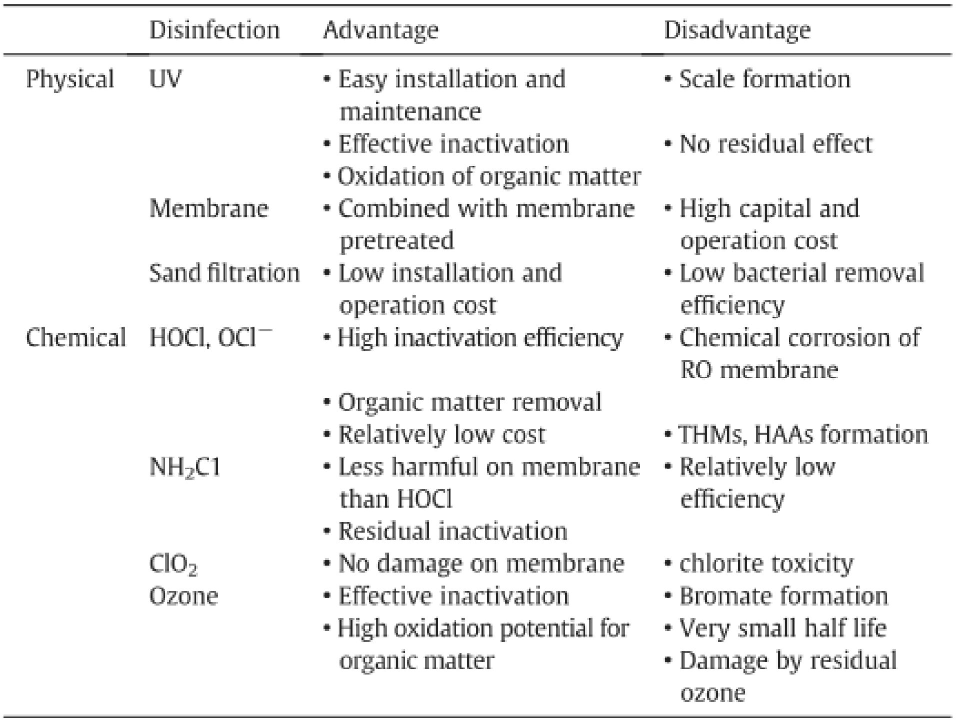
The strong oxidation potential of chlorine can cause deterioration of the RO membrane due to chemical attack of the amide functional group present on the RO membrane surface (Kang et al., 2007). The addition of chlorine to water containing organic matter results in the generation of carcinogenic by-products such as trihalomethanes (THMs) and halo acetic acids (HAA) (Sorlini & Collivignarelli, 2005). Chlorination/de-chlorination processes are known to occasionally enhance severe biofouling (Applegate el al., 1989; Moch et al., 1995)

A more effective chemical to be used in SWRO is ozone which is a strong oxidant as well. It has been shown to be effective against biofilms with reduced production of toxic byproducts. However, the cost for ozone generation is high compared to that of chlorine (Koyuncu et al., 2006). Another major disadvantage of ozone usage is the generation of bromine compounds that are carcinogenic and cause membrane surface deterioration (Perrins et al., 2006; Tyrovola & Diamadopoulos, 2005).

Photochemical inactivation via UV radiation has recently seen a rebirth in usage, it is independent of pH and does not produce disinfection byproducts (Li et al,. 2009; Oh et al., 2007). It should also be noted that both, high and low pH values, result in the inactivation of bactieral and viral content in water (Zebger et al., 2003; Rincón and Pulgarin, 2004; Lechevallier et al., 1988).

In conclusion all treatment methods adopted for biofouling prevention exhibit advantages and disadvantages, Table 2.2 presents a summary of the methods used and outlines the advantages and disadvantages of each of the methods.

Table 2.2 Comparison chart for disinfectants used for bio-fouling control of SWRO membranes. (Kim et al. 2009)



	Disinfection	Advantage	Disadvantage
Physical	UV	• Easy installation and maintenance • Effective inactivation • Oxidation of organic matter	• Scale formation • No residual effect
	Membrane	• Combined with membrane pretreated	• High capital and operation cost
	Sand filtration	• Low installation and operation cost	• Low bacterial removal efficiency
Chemical	HOCl, OCl^{-}	• High inactivation efficiency • Organic matter removal • Relatively low cost	• Chemical corrosion of RO membrane • THMs, HAAs formation
	NH_2C1	• Less harmful on membrane than HOCl • Residual inactivation	• Relatively low efficiency
	ClO_2	• No damage on membrane	• chlorite toxicity
	Ozone	• Effective inactivation • High oxidation potential for organic matter	• Bromate formation • Very small half life • Damage by residual ozone

Membrane cleaning is considered to be another form of treatment which reverses much of the decline in membrane performance (Madaeni et al., 2001; Sadhwani & Vesa, 2001). In general, around 5–20% of the operating cost lies in the cost of cleaning.

Recent developments used membrane surface modification technology to prevent the formation stage or the development stage of bacterial formation. This method employs the usage of nanomaterials with strong antimicrobial properties such as:

1. Chitosan (Qi et al., 2004)
2. Silver nanoparticles (Morones et al., 2005)

3. Photocatalytic TiO_2 (Cho et al., 2005)
4. Aqueous fullerene nanoparticles (Lyon et al., 2006)
5. Carbon nanotubes (Kang et al., 2007)

However, the cost of such material is much higher than that of chemicals used in the chemical disinfection process.

2.2 Silica

Si is considered to be one of the earth’s most abundant minerals, and is present in two forms crystalline and amorphous(Sheikholeslami & Tan, 1999). The dissolution reaction of silica in water as reported by Sheikholeslami and Bright (2002):

$$SiO_2 + 2\ H_2O \rightarrow Si(OH)_4$$

$Si(OH)_4$ is mostly unionized and highly soluble in water at neutral pH levels and contains one Si ion. Therefore it is said to be in a monomeric state as mono silicic acid (Sheikholeslami et al., 2002). Si has the potential to contribute to two types of fouling in the RO membrane, the first is precipitation fouling also referred to as silica scaling and it occurs when dissolved silica exceeds its solubility limits and precipitates with other molecule. The second type is colloidal accumulation of Si in bulk solution. Both events of fouling lead to the dehydration of Si and the molecule becomes hard like cement (Sheikholeslami & Tan, 1999). This leads to the increase of operation cost of the RO desalination plant, due to both energy consumption as a result of using a higher osmotic pressure, and decrease in membrane lifespan. The presence of other species in feed water such as calcium, magnesium, iron, and manganese can exacerbate the impact of Si related fouling in RO membrane. Seawater contain a significant amounts of Mg, Ca, and colloids which makes the SWRO membrane easily vulnerable to such fouling (Sheikholeslami & Bright, 2002).

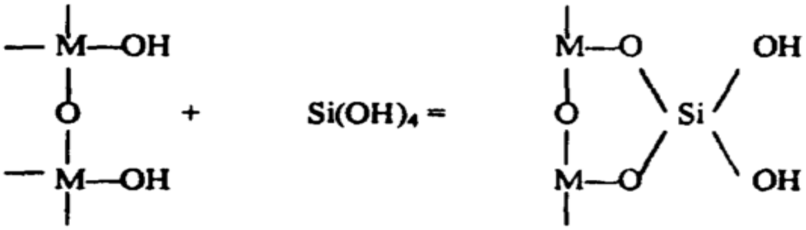
2.2.1 Silica removal methods

The removal of both colloidal and dissolved silica from water can be achieved by precipitating with soluble metals in an alkaline environment. This procedure leads to the formation of insoluble hydroxides. The addition of $Mg(OH)_2$ as an insoluble hydroxide also efficiently removes silica from water (Sheikholeslami & Bright, 2002). In earlier laboratory studies the removal of silica was assessed and efficient removal was recorded via adsorption and precipitation by hydroxides of aluminum, iron, manganese and magnesium (Iler, 1979). Dissolved silica is normally absorbed onto the surface of the insoluble hydroxides, however a pH of 9.0 or higher is required (Faust & Osman, 1983). The most widely used process for silica removal is the lime-soda softening process where calcium, magnesium and alkalinity concentrations are reduced, and silica will be adsorbed with the precipitation of magnesium hydroxide (Sheikholeslami et al., 2002). Formation of $Mg(OH)_2$ during lime soda softening is the major contributor for silica removal (Sheikholeslami et al., 2001) and the reactions are as follows:

$Mg(HCO_3)_2 + Ca(OH)_2 \rightarrow CaCO_3 (\downarrow) + MgCO_3 + 2H_2O$

$MgCO_3 + Ca(OH)_2 \rightarrow CaCO_3 (\downarrow) + Mg(OH)_2 (\downarrow)$

After the formation of insoluble $Mg(OH)_2$, $Si(OH)_4$ attaches to agglomerates with the floc formed just as it would with any solid surface which has OH groups it can react with (Sheikholeslami & Tan, 1999).



Soluble silica may also be removed by magnesium bicarbonate hardness as well, following the reaction:

$Mg(HCO_3)_2 + 2\ H_2SiO_4 \rightarrow MgSi_3O_6(OH)_2 + 6H_2O + 2CO_2$

However, the most likely mechanism to the removal of Si is simple adsorption onto the surface of $Mg(OH)_2$ flocs. Due to the hydrophilic nature of colloidal silica, coagulation process assists in its removal. Alumina could acts as a catalyst, where small quantities of Al^{+3} will be needed to remove colloidal silica as aluminosilicate following the equation by Sheikholeslami et al. (2001).

Removal of silica as aluminosilicate is expressed by the following reaction:

$Na^+ + Al^{+3} + 3H_4SiO_4 \rightarrow NaAlSi_3O_8$ (albite) $+4H_2O + 4H^+$

The optimum pH range in this case is around 4.1--4.7 (Okamoto et al., 1996).

2.3 Pretreatment

The objectives for pretreatment of water destined for RO processing are set to eliminate the impurities that might have fouling impact on the RO membrane (Maa et al., 2007). Reverse osmosis membranes are very sensitive to foulants such as Si, Colloids, organic matter, bacteria, Ca, and Mg (Bonnely et al., 2004), thus pretreatment is a necessary step before SWRO. Performance of an RO system and its life span will only be as good as the quality of feed water it is receiving (Ebrahim et al., 2001; Al-Sheikh, 1997). Pretreatment includes a variety of methods (conventional/membrane) incorporated to alter the components of seawater thus improving the SWRO overall process (Valavala et al., 2011). Overall simplified scheme of current pretreatment methods is illustrated in Figure 2.8.

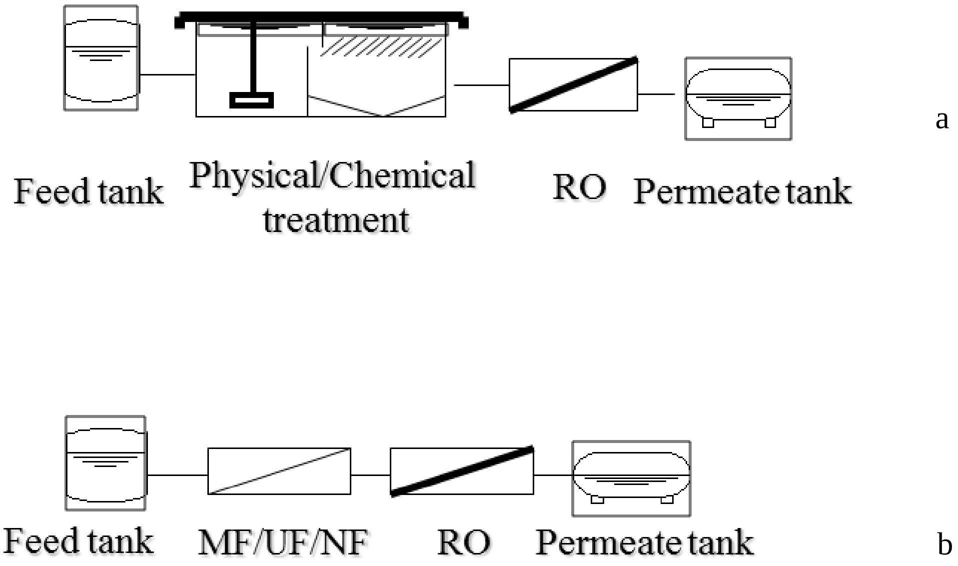


Figure 2. 8 a. Conventional pretreatment and b. membrane pretreatment

2.3.1 Conventional pretreatment

Conventional pretreatment typically consists of acid addition, coagulant addition, disinfection, media filtration, and cartridge filtration, and activated carbon adsorption (Greenlee et al., 2009). The first chemical additions, including acid, coagulant, and flocculent, prepare the feed water for granular media filtration (Isaias, 2001). Acid treatment reduces the pH of the feed water (typical pH range 5–7), which increases the solubility of calcium carbonate, the key potential precipitate in many feed waters. The most common acid used to lower feed water pH is sulfuric acid (H_2SO_4) (Bonnely et al., 2004).

Curtovo (2004) reported the steps of conventional pretreatment and stated that:

> “Suspended solids are removed by filtration, pH adjustments (lowering) are made to protect the membrane and control precipitation of salts; antiscaling inhibitors are

> added to control calcium carbonates and sulfates. A disinfectant is added to control biofouling of the membrane. Disinfection can involve chlorine species, ozone or UV light and other agents. Marine organisms, algae and bacteria must be eliminated, and if ozone or chlorine are used they should be neutralized prior to contact with the membrane”

Coagulation is known to be an efficient process of removing colloids and particulate matter. However, studies proved that the type of coagulant used can have a negative effect on the RO membrane, examples of such coagulants are aluminum sulfate and ferric chloride (Gabelich et al., 2002). Conventional pretreatment is costly, space-consuming, and the filtrate quality and quantity are usually not steady (Abdel-Jawad & Ebrahim, 2002). According to Abdel-Jawad & Ebrahim (2002) beach well intake system can be considered an alternative to some pretreatment stages due to the different water composition and the absence of some foulants. Even though beachwell pretreatment is considered to be more economically feasible than conventional pretreatment for SWRO it is a complex system that requires drilling and space consumption.

2.3.2 Membrane pretreatment

Irreversible RO membrane fouling was reported in many SWRO desalination plants even in the presence of conventional pretreatment (Ebrahim et al., 2001; Abdel-Jawad & Ebrahim, 2002), due to the passage of colloids and suspended particles through such treatment systems (Brehant et al., 2002), this resulted in an increased tendency towards membrane pretreatment. Membrane pretreatment involves the use of lager pore size membrane such as UF/MF/and NF, and the selection of a specific membrane for pretreatment is dependent on the associated contaminant removal issues in comparison to the intended feed water chemistry (Valavala et al., 2011)

NF membranes have the smallest pore size of all three and can operate under higher flux, whereas MF removes large particulate matter at higher flux, and NF removes dissolved contaminants as well as particulate and colloidal material (Greenlee et al., 2009)

A study conducted by Durham et al. (2001) compared the effectiveness of membrane filtration (MF/UF) to that of conventional systems, the advantages related to the former system as reported by the study were:

1. The chemistry of the water intake, whereby the quality of the MF/UF product water was found to be independent of feed quality
2. The capacity of the system and the space available
3. The amount of cleaning or maintenance required for the pretreatment system
4. The reliability, capital and operating costs of the NF or RO system reaching an SDI<2 (Tiwari et al. 2006; Vedavyasan, 2007), in addition the turbidity of the pretreated water can be lowered to less than 0.05 NTU (Bartels, Franks, Rybar, Schierach, & Wilf, 2006; Pearce, 2008).

When comparing NTU and SDI values to that of conventional system which employ the use of pressurized media filtration, the latter reduced SDI by a factor of 2 (Morenski, 1992) and turbidity was recorded to be around 0.1 NTU (Bonnelye et al., 2004).

The major drawback of using membrane pretreatment is that (UF/MF/NF) membranes can become fouled themselves with reversible and irreversible surface and pore fouling (Greenlee et al., 2009). Seawater contains a tremendous amount of salts which also poses a threat to NF membranes operation which is vulnerable to salt precipitation and membrane scaling, due to the much smaller pore sizes (Le Gouellec & Elimelech, 2002).

The fact that membrane pretreatment technologies are exposed to fouling just as intensely as the RO membrane itself, coagulation with $FeCl_3$ or Al_3SO_4 has been successfully used in line with MF, UF, and NF membranes (Brehant et al., 2003).

Glueckstern & Priel (2005) and Henthorne (2007) estimated the cost of pretreatment using conventional and membrane technologies to be 0.57 and 0.55 $\$/m^3$ respectively.

2.4 Boron

High concentrations of the elemental boron in seawater resources make them unsuitable for human consumption and for irrigation purposes (SÜTÇÜ, 2005). Boron is never found in the elemental form in nature, it exists as a mixture of the 10B (19.78%) and 11B (80.22%) isotopes (Butterwick et al., 1989). Typically, low-saline ground water and rivers contain low concentrations of boron (<0.1 mg/l) (Neal et al., 1998; Wyness et al., 2003), whereas saline water may show concentrations as high as tens of mg/l. Sea water typically has the concentration of 4.7 mg/l (Weinthal & Parag, 2005). Boron is widely distributed in the environment, occurring naturally or from anthropogenic contamination, mainly under the form of boric acid or borate salts (Simonnot et al., 2000). Because bonds in borate and boric acid are characterized by different vibrational frequencies, boric acid is isotopically heavier than borate by 27.2% (Klochko et al., 2006). Figure 2.9 adopted from Allen et al. (2011), shows speciation (Figure 2.9 a) and isotopic composition (Figure 2.9 b) of dissolved borate in seawater where both change with pH. Toxicological studies that focused on high concentration oral exposure of laboratory animals showed that boron toxicity could lead to reduced fertility and sterility (Mastromatteo & Sullivan, 1994). The only proven effects of acute exposure on humans were short-term irritation of the upper respiratory tract (Weinthal & Parag, 2005). An influence of boron intake on certain human key enzymes, however, cannot be excluded (Huel et al., 2004)

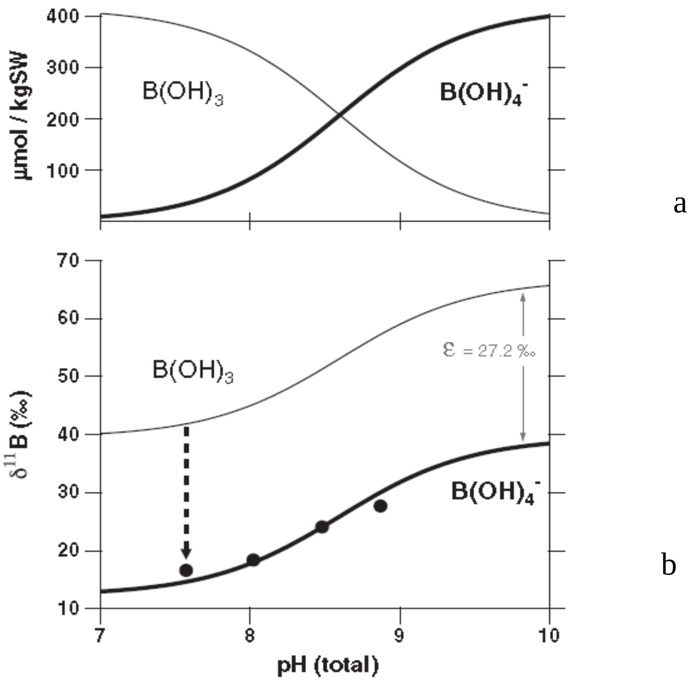


Figure 2. 9 a. Speciation and b. Isotopic composition of dissolved borate in seawater both change with pH (Allen el al., 2011)

In 1998 WHO guidelines for drinking water quality proposed a 0.3 mg/l, however in 2011 WHO increased the standard for boron concentration in drinking water to 2.4 mg/l (WHO, 2011). In addition CCME (The Canadian Council of Ministers of the Environment) guidelines for boron concentrations are shown in Table 2.3

Table 2. 3 CCME Recommended guidelines

Type of Water	Recommended Boron Concentration
Drinking water	5.0 mg/L
Fresh water aquatic life	1.2 mg/L
Marine aquatic life	1.2 mg/L
Wildlife	5.0 mg/L

Irrigation	Depends upon crop
Livestock watering	5.0 mg/L

2.4.1 Boron removal methods

Boron removal is one of the most challenging issues in SWRO, due to its existence in the uncharged non-ionic form in seawater (Magara et al., 1998). To alter such a state of boron and enhance its rejection on the RO membrane, a rise in pH is needed however increasing the pH will cause precipitation and scaling of the membrane (Valavala et al., 2011). To avoid multiple membrane passes, a number of boron removal processes have been reported by different researchers the major ones of which include:

1. Coagulation Flocculation mainly perceptive softening (Parks & Edwards, 2007)
2. Adsorption with oxides such as magnesium oxides (Soto & Mar, 2006)
3. Reverse osmosis (Glueckstern, 2003)
4. Ion exchange (Hilal et al., 2011)
5. Adsorption membrane filtration (AMF) (Kabay et al., 2006)
6. Activated carbon and microfiltration
7. Liquid-Liquid extraction
8. Electrodialysis
9. Mg–Al (NO3) layered double hydroxide (Kentjono et al. 2010)

Parks and Edwards (2007) demonstrated that 30 % of geothermal waste boron could be removed from water containing 135 mg/L silicon with the addition of MgO. Having an Mg:Si ratio of lower than 5:1 induces the formation of MgSi compound**.**

CHAPTER 3

MATERIALS AND METHODS

3.1 Seawater

The research at hand involved frequent sampling, testing and analyzing of seawater obtained from the AUB beach, Beirut, Lebanon for RO foulants removal. The sampling location was chosen based on its proximity to the research laboratory, ease of access, and the fact that multiple analyses conducted at the Environmental Engineering Research Center at AUB showed that its quality is consistent with that of the seawater along the Eastern Mediterranean. Samples were collected, stored at 24 degrees Celsius, and analyzed for the following parameters: TDS, TSS, VSS, TOC, Ca, Mg, total and fecal coliforms, turbidity, iron, sodium ions, pH, temperature, and boron (B).

The duration of the experimental research was about 8 months, starting from January 2012 and ending August 2012. Table 3.1 presents the characteristics of the collected seawater used in the experimental study.

Table 3.1 characteristics of the collected seawater used in the experimental study

Parameter	**Unit**	**Number of observation****	**Mean ± standard deviation**	**Range**

pH	pH units	26	8.02 ± 0.1	7.82-8.15
TDS	mg/L	4	37701±718	37701-38500
TSS	mg/L	4	217.750 ± 10	198-220
VSS	mg/L	4	49.547± 1.98	46.67-58.00
TOC	mg/L	4	5.285 ±0.106	4.58-5.2
Mg	mg/L	20	1535.8 ± 55	1460-1623
Ca	mg/L	20	521 ± 9.2	502-530
Sodium	mg/L	5	11683 ± 81	11600-11792
Boron	mg/L	10	5.1 ± 0.3	4.8-5.6
Turbidity	NTU	4	3.2 ± 0.1	3.0-3.4
Iron	mg/L	7	0.29 ± 0.03	0.23-0.31
Silica (as Si)	mg/L	10	1.5 ± 0.05	1.4-1.7
Silica (as SiO_2)	mg/L	10	3.0± 0.02	2.9-3.4
Total Coliforms	CFU	6	0	N/A
Fecal Coliforms	CFU	6	0	N/A

*N/A: Not applicable

**Number of observations represents the number of times the test was conducted on different samples

Samples of 40 liters were collected on each sampling run on a bimonthly bases and when needed, were tested frequently for the parameters, shown in table 3.1, prior to conducting the experiments in order to insure that the water quality is not altered or affected by storage in the laboratory. To prevent any contamination of the collected samples, the 20 liter containers were cleaned properly in the laboratory prior to sampling, furthermore the containers were rinsed twice with seawater on the site before collecting samples. Figure 3.1 shows the containers used in collecting seawater sample.

Figure 3.1 20 liter containers used in collecting seawater samples

3.2 Optimal Alkalizing Agent

The experiment involved assessing the efficiency of alkalizing agents such as lime slurry, caustic soda, and soda ash in producing $Mg(OH)_2$ and $CaCO_3$ coagulants. $CaCO_3$ coagulant is formed at pH 8-9, while $Mg(OH)_2$ starts forming at pH 9.5 and formation becomes more significant at pH 10.5, with optimal reaction occurring at pH 11-11.5 (Semerjian & Ayoub, 2003). Efficiencies in removal of calcium, magnesium, and boron were analyzed to select the best alkalizing agent.

3.2.1 Calcium Oxide

Using calcium hydroxide as a source of OH^- ions for water softening has been assessed by many researchers (Ayoub et al., 1999; Semerjian & Ayoub, 2003). Freshly prepared 5% w/v slurry of $Ca(OH)_2$ was used in preparing a titration curve showing the pH variation as a function of the amount of $Ca(OH)_2$ added, and also was used as an alkalizing agent in preliminary experiments. Titration curve of $Ca(OH)_2$ in 1 liter sample seawater is presented in Figure 3.2

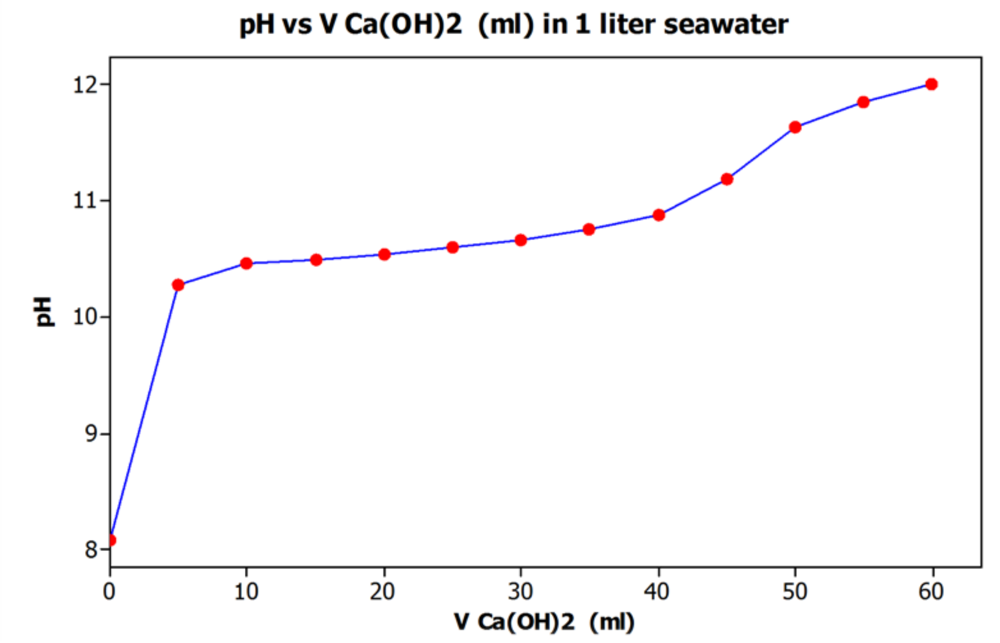


Figure 3.2 Titration curve of 5 % $Ca(OH)_2$ in 1 liter seawater

The addition of CaO induces a feasible reaction with water leading to the formation of hydrated lime:

$$CaO + H_2O \rightarrow Ca(OH)_2$$

Hydrated lime reacts with some constituents of seawater such as Mg carbonates, and Ca carbonates following the reactions (Liao & Randtke, 1986; Vahedi & Gorczyca, 2011):

$$CO_{2(aqueous)} + Ca(OH)_2 \rightarrow CaCO_3 \downarrow + H_2O$$

$$Ca(HCO_3)_2 + Ca(OH)_2 \rightarrow 2CaCO_3 \downarrow + H_2O$$

$$Mg(HCO_3)_2 + Ca(OH)_2 \rightarrow CaCO_3 \downarrow + MgCO_3 + 2H_2O$$

$$MgCO_3 + Ca(OH)_2 \rightarrow CaCO_3 \downarrow + Mg(OH)_2 \downarrow$$

$$MgSO_4 + Ca(OH)_2 \rightarrow Mg(OH)_2 \downarrow + CaSO_4$$

Aqueous CO_2 does not contribute to the hardness, but it reacts with the lime, and therefore uses up some $Ca(OH)_2$. The effect of $Ca(OH)_2$ addition to the sampled seawater on removal of Ca, Mg and B is presented in table 3.2.

Table 3.2 Effect of 5% $Ca(OH)_2$ on % removals of Ca, Mg, and B. *

Parameter	Number of observations	Mean ± Standard deviation
Sample Temperature ^oC	4	21.2 ± 0.05
pH	4	11.1 ± 0.09
Ca % removal	4	20 ± 1.2

Mg % removal	4	65 ± 3.8
B % removal	4	30 ± 0.8

* Volume of $Ca(OH)_2$ used to achieve pH 11 = 80 ml per 2 liters of seawater

3.2.2 Caustic Soda

NaOH is as excellent source of OH^- for seawater alkalization (Tebbutt, 1998; Scholz, 2006; Ratnayaka et al., 2009). The effect of NaOH on seawater softening was studied by El-Manharawy and Hafez (2002), the experiment lead to the classification of NaOH as an alkalizing agent with a high potential for removal of hard chemical species found in water, in addition to bacterial disinfection. A titration curve, using 5 N NaOH in 1 liter of sampled seawater was prepared and is presented in Figure 3.3.

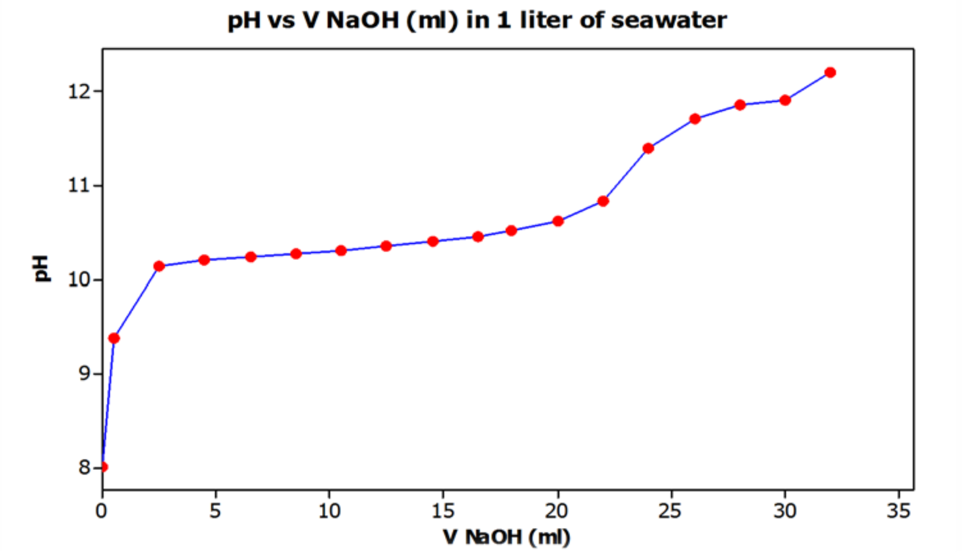


Figure 3.3 Titration curve of 5 N NaOH in 1 liter of seawater

As is the case with lime softening, carbon dioxide reacts with the caustic soda to make sodium carbonate and water, the reactions resulting from the addition of NaOH in water softening are as follows (Tebbutt, 1998; Scholz, 2006; Ratnayaka et al., 2009):

$$CO_2 + 2\ NaOH \rightarrow Na_2CO_3 + H_2O$$

$$Ca(HCO_3)_2 + 2\ NaOH \rightarrow CaCO_3 \downarrow + Na_2CO_3 + 2H_2O$$

$$Mg(HCO_3)_2 + 4NaOH \rightarrow Mg(OH)_2 \downarrow + 2Na_2CO_3 + 2H_2O$$

$$MgSO_4 + 2NaOH \rightarrow Mg(OH)_2 \downarrow + Na_2SO_4$$

The effect of NaOH addition to the sampled seawater on the removal of Ca, Mg and B is presented in table 3.3.

Table 3.3 Effect of 5 N NaOH on removal of Ca, Mg, and B. *

Parameter	Number of observations	Mean ± Standard deviation
Sample Temperature	4	22.4 ± 0.1 °C
pH	4	11.2 ±0.12
Ca % removal	4	67 ± 2 %
Mg % removal	4	84.2 ± 1.89 %
B % removal	4	21 ± 1.2 %

* Volume of NaOH used to achive pH 11 = 59 ml per sample of 2 liters of seawater.

3.2.3 Soda Ash

The use of Na_2CO_3 in water softening was assessed as a part of lime-soda softening (Tebbutt, 1998). The major contribution of Na_2CO_3 is the reaction with $CaSO_4$:

$$CaSO_4 + Na_2CO_3 \rightarrow CaCO_3 \downarrow + Na_2SO_4$$

Titration curve of 10% Na_2CO_3 (1.85 N) with 1 liter seawater is shown in Figure 3.4. To determine the effect of Na_2CO_3 on the removal of Mg and Ca, tests were conducted at pH 10, with results presented in Table 3.4.

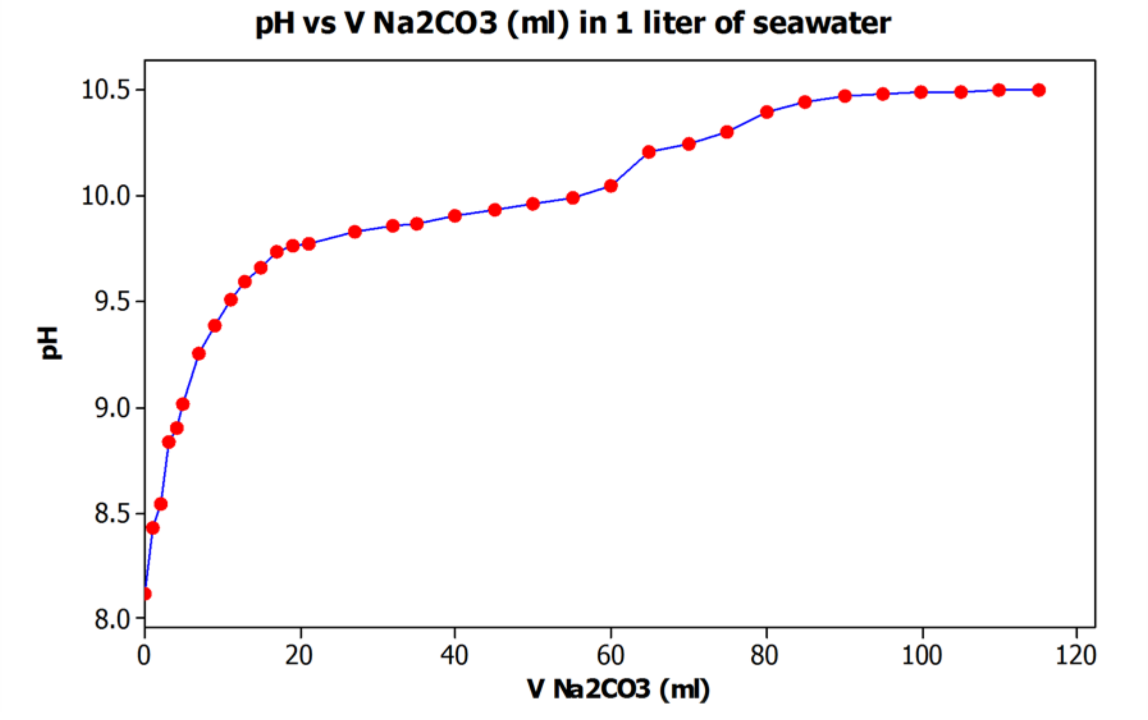


Figure 3.4 Titration curve of 10 % Na_2CO_3 with 1 liter seawater

Table 3.4 Effect of 10% Na_2CO_3 on removals of Mg, Ca, and B

Parameter	Number of observations	Mean ± Standard deviation
Sample Temperature	4	21 ± 0.04 ^oC
pH	4	9.95 ± 0.1
Ca % removal	4	90 ± 2.5 %
Mg % removal	4	15 ± 4.55 %
B % removal	4	28 ± 1 %

3.2.4 Combined Na_2CO_3 and NaOH

A complementary series of experiments using different combinations of 5N NaOH and 10% Na_2CO_3 in the coagulation-flocculation setup was conducted in order to determine the combined effects of both chemicals on the removal efficiency of Ca and Mg. No reaction will take place between caustic soda and soda ash.

Removal efficiencies based on using a combination of the two chemicals were evaluated and results are presented in Tables 3.5-3.7. Based on a review of the literature, it was assumed that the optimal pH for testing the effectiveness of the alkalizing solution is ≈ 11.

Table 3.5 NaOH:Na_2CO_3 of 2:1 solution removal efficiencies*

Parameter	Number of observations	Mean ± Standard deviation
Sample Temperature	4	25± 0.09 ^oC
pH	4	11.18 ±0.15
Ca % removal	4	≈100 %

Mg % removal	4	99.7% ± 0.008 %
B % removal	4	75 ± 3 %

*Volume of solution added = 75 ml

Table 3.6 NaOH:Na_2CO_3 of 1:1 solution removal efficiencies*

Parameter	**Number of observations**	**Mean ± Standard deviation**
Sample Temperature	4	22.1 ± 0.1 ^oC
pH	4	11.21 ±0.12
Ca % removal	4	≈100 %
Mg % removal	4	99.82 ± 0.0042 %
B % removal	4	41 ± 0.8 %

*Volume of solution added = 100 ml

Table 3.7 NaOH:Na_2CO_3 of 5:2 solution removal efficiencies*

Parameter	**Number of observations**	**Mean ± Standard deviation**
Sample Temperature	3	21.54 ± 0.02 ^oC
pH	3	10.9 ±0.12
Ca % removal	3	95 ± 0.077 %
Mg % removal	3	96.4 ± 0.056 %
B % removal	3	60 ± 3 %

*Volume of solution added = 70 ml

Comparing tables 3.5 and 3.7 the additional 5 ml of Na_2CO_3 had a significant effect on increasing the parametric removals. Therefore it was concluded that 2:1 NaOH to Na_2CO_3 is the optimal alkalizing solution to carry out the experiment. Titration curve of the 2:1 solution is presented in figure 3.5.

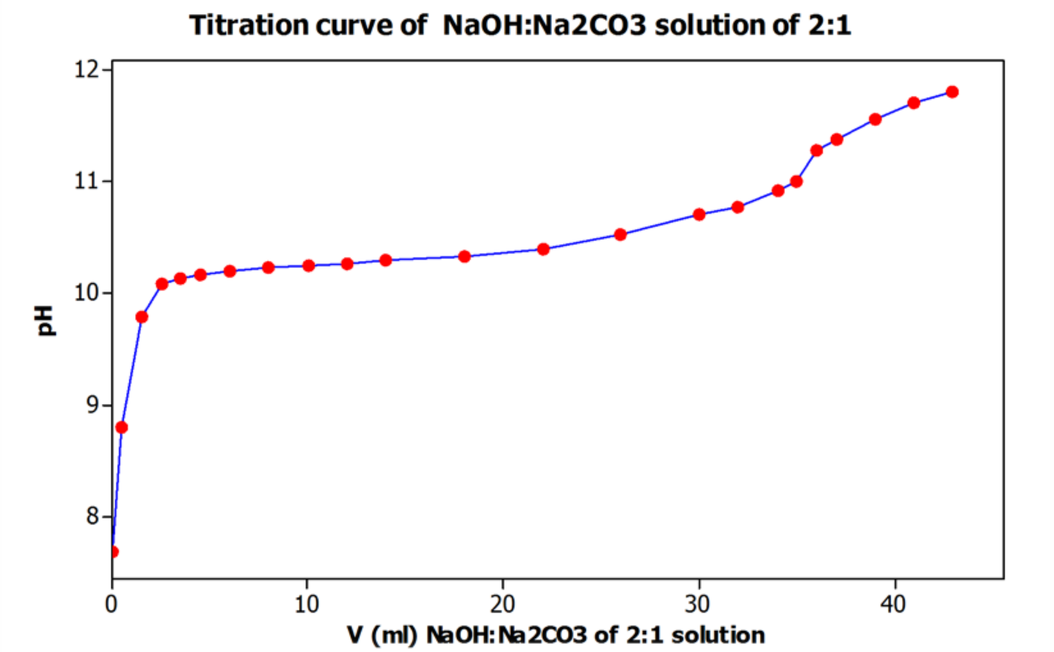


Figure 3.5 Titration curve of 2:1 NaOH:Na_2CO_3 solution

3.3 Experimental setup

Experiments were conducted under controlled laboratory conditions using a standard jar test apparatus (model 300) obtained from Phipps and Bird, Inc. (Richmond, Virginia). This apparatus, more commonly used for coagulation and flocculation tests, has multiple stainless steel paddles and stirrers.

The drive motor is equipped with a variable speed control to operate the paddles at a speed that varies between 1 – 100 rpms. The jars, shown in Figure 3.7, are made of acrylic plastic and have dimensions of 115 x 115 x 250 mm. The jars are fitted with a sampling port located at the 10cm from the bottom level so that test samples can be drawn without disturbing the settled solids.

Figure 3.6 Phipps & Bird model 300 standard jar test apparatus

Figure 3.7 2 Liter jar

3.4 Spiking

Seawater constituents shown in Table 3.1 are considered to be typical. However, in many desalination plants, seawater intakes were reported to be contaminated with bacteria (total and fecal coliforms), iron, and silica which alter the characteristics of the seawater. To prove the efficiency of the alkalization process at hand, the effect of such contaminants need to be taken into consideration. Therefore, additional experiments were carried out on seawater spiked with (Fe, Si and wastewater). The increase in concentrations of bacteria, Si, and Fe was achieved using wastewater, sodium silicate, and ferrous sulfate respectively. The effect of spiking with Fe on the color of the samples is shown in Figure 3.8.

Figure 3.8 Effect of Fe spiking on color of the samples

3.5 Testing procedure

2 L seawater samples were placed in jars with subsequent addition of the proper alkalizing agent, as determined from respective tests, until the desired pH was achieved. The samples underwent rapid mixing (100 rpm) for 1 min followed by reducing the paddles velocities down to 30 rpm for a period of 20 min to allow for floc formation, and further followed by a settling period of 60 min (Clark and Stephenson, 1999).

pH and temperature were monitored at all times during the experiment. pH fluctuations due to CO_2 dissolution was noted. CO_2 can dissolve into water leading to the formation of carbonic acid hence lowering the pH:

$$CO_2 + H_2O \leftrightarrow H_2CO_3$$

Upon determining the proper alkalizing agent, six sets of experiments were conducted under four preset pH values 10.5, 11, 11.5 and 12, and a fixed temperature of 25 ^oC, this enabled the determination of the optimal pH value for parametric removals at 25 ^oC. Removals were also assessed at temperatures of 10, 20, and 30^oC and at pH values of 10.5, 11, and 11.5 for each temperature.

When carrying out tests at 10 and 30 ^oC, and since the test duration was relatively long (about 80 minutes), it deemed necessary to maintain these temperatures with the least variation. For this purpose a polystyrene foam jacket was used to insulate the jars (Figure 3.9).

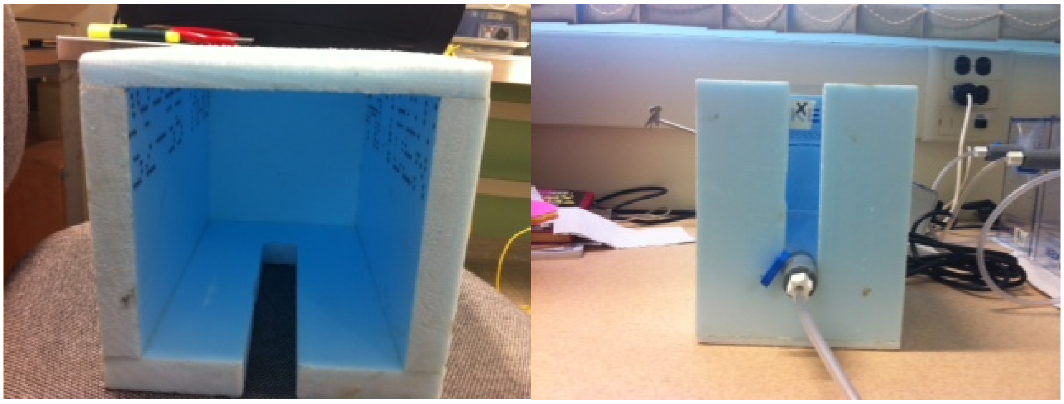


Figure 3.9 Polystyrene jacket covering the jar

The water withdrawn after the jar testing procedure was analyzed for the following parameters: TDS, TSS, VSS, TOC, Ca, Mg, total and fecal coliforms, turbidity, iron, sodium ions, pH, temperature, and boron B. Removal averages and standard deviations were determined, compared to those of the initial seawater, and removal percentages were obtained. Settling rates of the sludge mass with respect to pH and temperature were recorded, and later the sludge mass was determined for each set of experiments.

The overall procedure and decision chart followed during the experiment is illustrated in Figure 3.10.

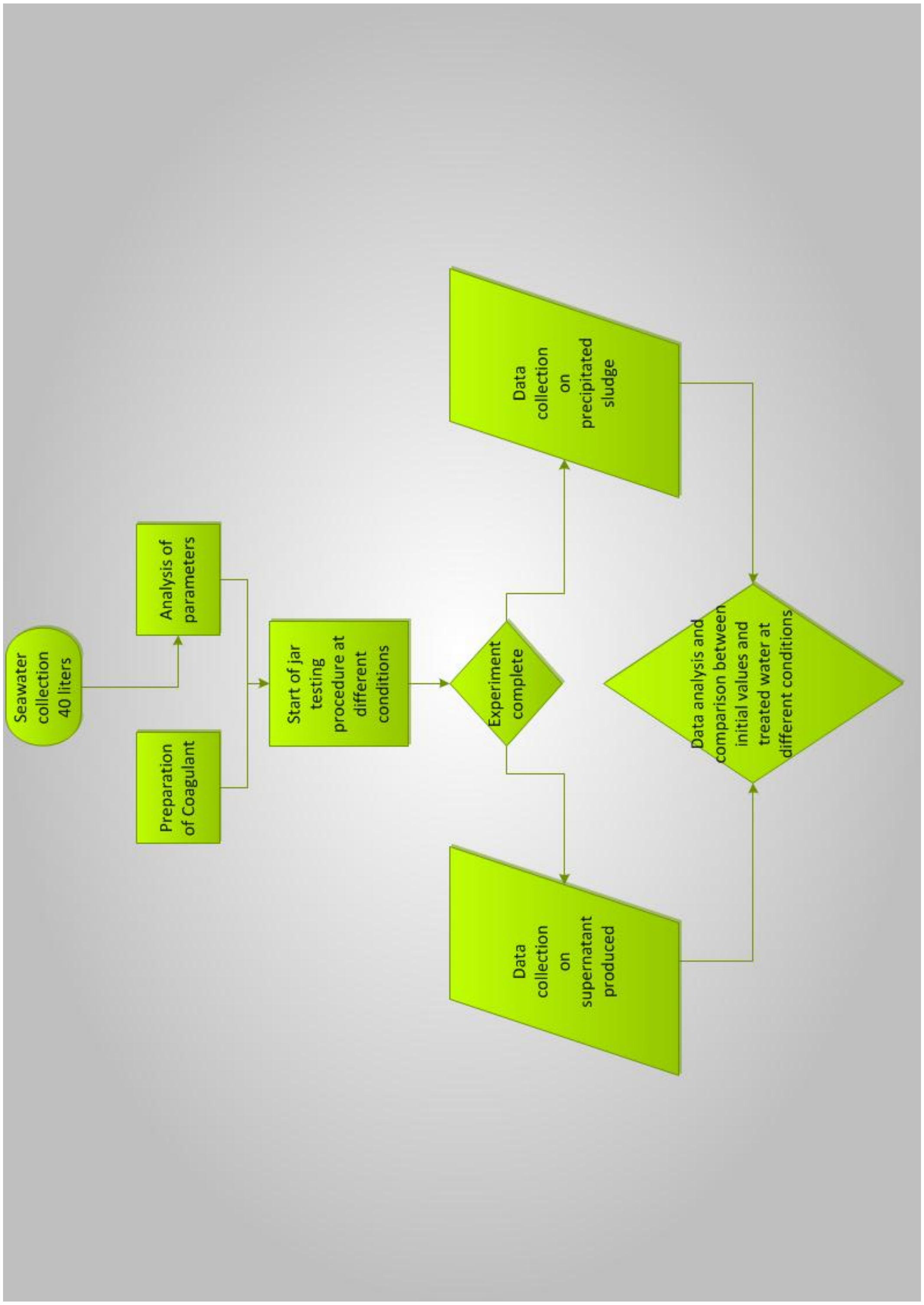


Figure 3. 10 The overall procedure and decision chart

3.6 Analytical procedure

The influent and effluent quality parameters tested were: pH, temperature, turbidity, TSS, VSS, TDS, TOC, Si, B, Fe, total hardness, Ca hardness, sodium, total coliforms, and fecal coliforms. Parameters were determined according to Standard methods (APHA, 1995), and HAAC methods. Statistical methods used in this study were 1 way ANOVA, 2 way ANOVA, F testing, hypothesis testing, and regression analysis using minitab 16. In additon interaction plots were used when applicable to elaborate the effects of pH and temperature on removal of certain parameters.

Table 3. 8 Testing parameters with their respective type of analysis and standard methods used

Parameter	Type of analysis	APHA reference method or HAACH method
pH	Potentiometry	5400-H+ B
Temperature	Thermometric	2550
Turbidity	Nephelometric	2130 B
TOC	Combustion catalytic oxidation/NDIR	5310
TDS	Gravimetric	2540 C
TSS	Gravimetric	2540 D
VSS	Gravimetric	2540 E
Sodium	AAS (atomic adsorption spectrophotometry) Flame emission	3500-Na D
Calcium hardness	EDTA titration	3500-Ca D
Total hardness	EDTA titration	2340-C
Boron	Spectrophotometric	4500-B.C/ HACH 8015
Iron	AAS (atomic adsorption	3500-Fe+ B

	spectrophotometry) Flame emission	
Silica	Colorimetric	HAACH Method 8185
Fecal coliforms	Membrane Filtration	9222D
Total coliforms	Membrane Filtration	9222B

CHAPTER 4

RESULTS AND DISCUSSION

As noted in earlier sections, seawater desalination technologies are rapidly advancing, and used to efficiently provide fresh water. Nevertheless, some obstacles hinder the widspread use of deaslination technologies, most prevalent of which is membrane fouling due to a number of feed water constituents. The increase in energy consumption and operating costs, in additon to membrane detorioration, lower permeate quality, and higher water rejections render the SWRO system inefficent. Therefore SWRO desalination invariably requires the application of a proper pretreatment procedure with the aim of lowering the propensity for membrane fouling (Morenski, 1992).

The search for more efficant pretreatment procedures is an ongoing challenge in desalination R&D centers, with the aim of decreasing fouling propensity via the removal of causitive agents present in the feed water while keeping the cost of pretreatment acceptable. This section will elaborate on the use of a simple one step procedure and its effect on removal of seawater constituents known to cause membrane fouling in additon to the removal of boron to comply with WHO standards. The experimental work is directed at determining an optimized conventional method for pretreatment of SWRO. The method used herein is adapted from coagulation-flocculation while using $Mg(OH)_2$ and $CaCO_3$ as coagulents. The abundance of Mg in seawater renders this approach feasible especially that it has been previously reported that the formation of $Mg(OH)_2$ proved its efficacy in removing most, if not all, of the fouling onstituents. Work in this section will deal with an experimental study that will determine the efficacy of this process while at the same time evaluating the impact of pH, Temperature, and effect of different concentration of these pollutants on the treatment process and finally determining the optimal operating conditions that will provide the most effective treatment.

4.1 Seawater characterization

Characteristics of collected seawater was presented in Table 3.1, in comparison to composition of seawater presented in Table 1.1 the collected seawater may be considered as a representative of that of the eastern Mediterranean. This type of seawater is expected to cause:

1. Inorganic and crystalline fouling governed by the presence of Mg (1535.8 ± 55 mg/L), and Ca (521± 9.2 mg/L), and Si (1.5 mg/L)
2. Organic fouling due to VSS (52.6 ± 5 mg/L) and TOC (5.1 ± 0.44 mg/L)
3. Colloidal fouling due to TSS (206 ± 13 mg/L)

The presence of these impurities renders the need for treatment prior to SWRO a necessity.

Pretreatment permeate quality standards prior to SWRO operations were not assessed so far. Pretreated water characteristics are dependent on the used SWRO membrane specifications for instance waters with high microorganisms content require disinfection in which chlorine is a major disinfectant used, which in turn induces adverse effects on the membrane. Thus residual chlorine removal is mandatory. In the event that some residual chlorine in the feed water is to be maintained then chlorine tolerant membranes could be used (Pontié et al., 2005).

4.2 Jar testing results

A coagulation-flocculation apparatus was used to performing the experimental study where different volumes of alkalizing agents needed to achieve the pH required for the formation of $Mg(OH)_2$, being the coagulant responsible for the removal of the targeted contaminants, were added to the sampled sewater. Experiments were carried out under different operating conditions (pH and temperature variations) to arrive at the optimal process. Spiking with certain contaminants that are normally found in relatively small concentrations in seawater such as silica, iron, and bacteria was carried out in order to evaluate the impact of these contaminants, when present in larger concentrations, on the treatment process and visa versa.

4.2.1 The effect of pH

The effects of pH variation on removal of seawater constituents affecting membrane fouling were apparent. For that purpose, four pH values (10.5, 11, 11.5, and 12) were chosen to assess the removal of contaminants at a sample temperature of 20 °C (room temperature 24 °C). The mean removal results and standard deviations are presented in Table 4.1.

Table 4.1 Treated seawater constituents at different pH values and T=20 °C**

Parameter	**Unit**	**Raw Seawater**	**pH 10.5**	**pH 11**	**pH 11.5**	**pH 12**
pH	pH units	8.02 ± 0.1	10.5 ± 0.008	11.2±0.12	11.56±0.15	12.08±0.021
Temperature	Degrees C	N/A****	19.5±0.16	19.8±0.1	20.1±0.2	19.67±0.05
pH_f^*		N/A	10.42±0.012	11.05±0.009	11.43±0.07	11.97±0.04
Ca	mg/L	512 ± 9.2	118.64±6	BDL***	BDL	BDL
Ca removal	%	N/A	77.2±1.2	≈ 100	≈100	≈100
Mg	mg/L	1535.8 ± 55	238±13.7	6.5±2.3	9.8±1.9	13.394±4.2
Mg removal	%	N/A	84.5±0.9	99.6±0.16	99.37±0.12	99.13±0.27
Boron	mg/L	5.1 ± 0.3	1.4±0.18	2±0.14	2.5±0.08	3.2±0.14
Boron removal	%	N/A	72.5±3.6	60.78±2.77	51±1.6	37.25±2.8
SiO_2	mg/L	3	0.1±0.001	BDL	BDL	BDL
Si	mg/L	1.5	BDL	BDL	BDL	BDL

*pH_f represents the pH recorded at the end of the jar test procedure, and is compared to pH to check for pH variation due to CO_2 escape or entry.
* *The numbers of observations were 6 for each pH value.
***BDL: below detection limit. (Ca detection limit: 0.5 mg/L, Si detection limit: 0.3 mg/L)
****N/A: Not applicable

To provide a comparative graphic of the effect of pH on contaminant removal, the percent removal values for Ca and Mg are demonstrated in Figure 4.1, while the percent removal of boron is shown in Figure 4.2.

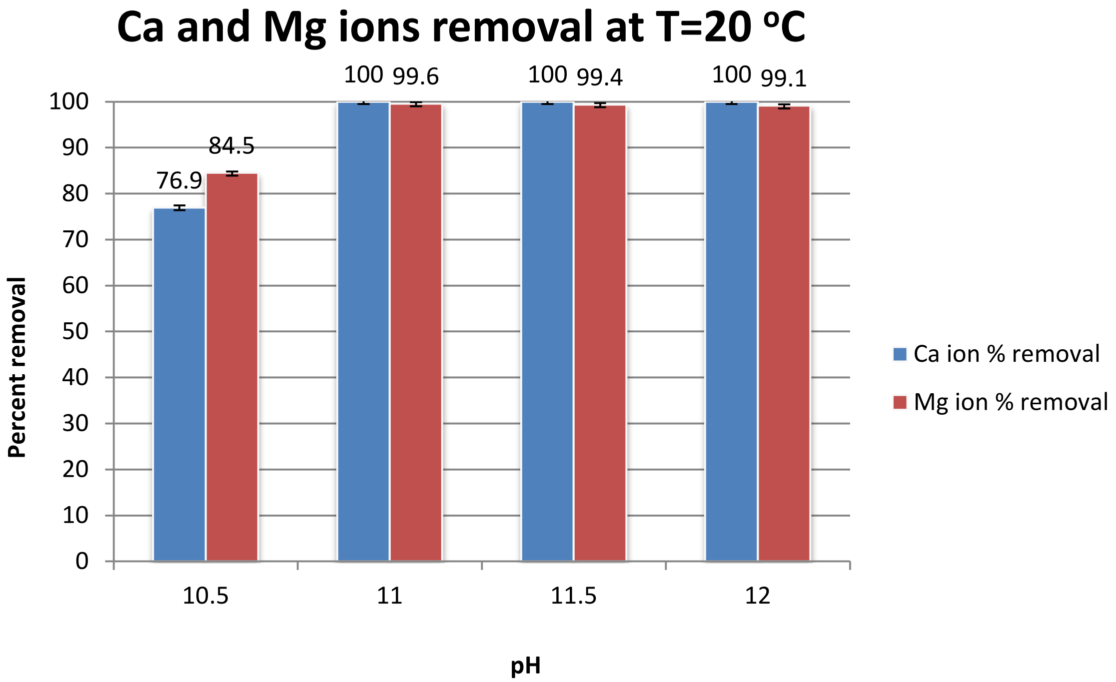


Figure 4.1 Removal percentages and error bars of Ca and Mg at different pH values and T= 20 °C

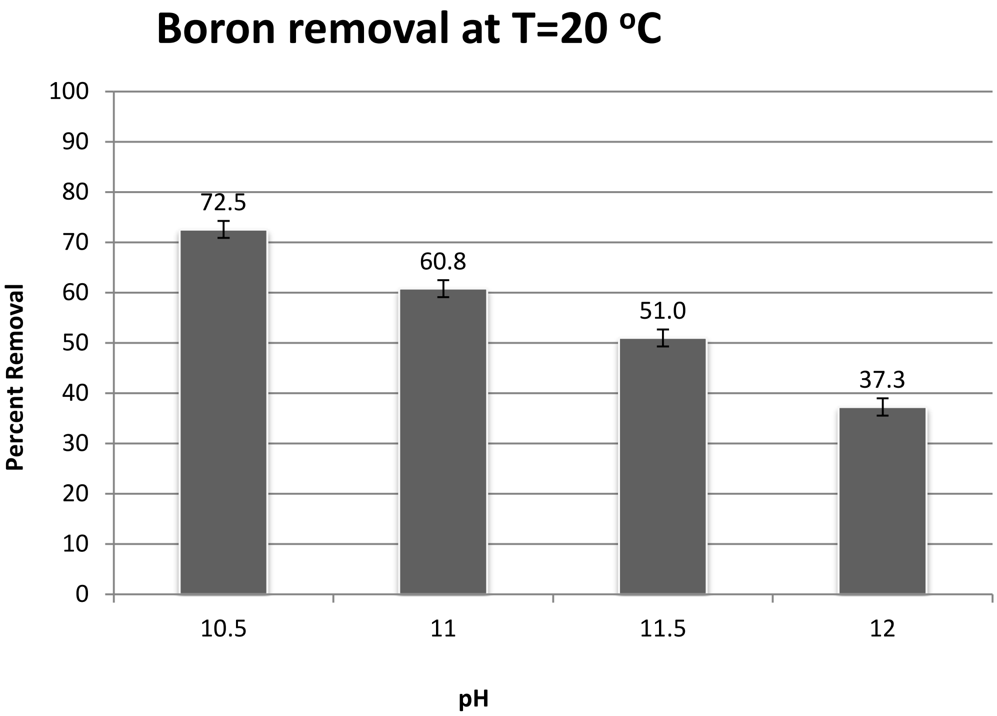


Figure 4.2 Removal percentages and error bars of Boron at different pH values and T= 20 °C

In order to relate and assess the significance of pH on the removal of Ca, Mg, and B, a Polynomial Regression Analysis was performed.

Regression analysis of %removal of Ca T=20 ^{o}C versus pH:

$$\%removal\ of\ Ca\ at\ 20\ ^{o}C\ =\ -5661\ +\ 1025\ pH\ -\ 45.54\ pH^2$$

With S = 0.673595, R^2 = 99.7%, and R^2(adj) = 99.6%

Furthermore the variance analysis of Ca removal was prepared and presented in Table 4.2.

Table 4.2 Analysis of Variance Ca removal at T=20^{o}C.

Source	DF	SS	MS	F	P
Regression	2	1728.39	864.196	1904.65	0.000
Error	12	5.44	0.454		
Total	14	1733.84			

The respective values of F and P in Table 4.2 confirm that the pH variation effects the removal of Ca at 100 percent significance, thus concluding that the percent removal of Ca is a function of the pH value. Results of a similar analysis carried for Mg removals are presented by the following equation and Table 4.3.

Regression analysis of %removal of Mg T=20^{o}C versus pH:

$$\%removal\ of\ Mg\ at\ T\ 20^{o}C = -3761\ +\ 687.1\ pH\ -\ 30.56\ pH^2$$

With S = 0.527469, R^2 = 99.6%, and R^2(adj) = 99.5%

Table 4.3 Analysis of Variance Mg removal at T=20^oC

Source	DF	SS	MS	F	P
Regression	2	745.998	372.999	1340.64	0
Error	12	3.339	0.278		
Total	14	749.336			

The respective values of F and P in Table 4.3 also show that the pH variation effects the removal of Mg at 100 percent significance, thus concluding that the percent removal of Mg is a function of pH value.

As for boron removal, a similar analysis indicates the following:

Regression analysis of % Removal of Boron T=20^oC versus pH:

$$\%\ Removal\ of\ Boron\ T\ 20^oC\ =\ 772.5\ -\ 107.8\,pH\ +\ 3.922\,pH^2$$

With S = 2.77297, R^2 = 93.1%, and R^2(adj) = 91.6%

Table 4.4 Analysis of Variance B removal at T=20^oC

Source	DF	SS	MS	F	P
Regression	2	932.97	466.487	60.67	0.000
Error	9	69.20	7.689		
Total	11	1002.18			

The respective values of F and P in Table 4.4 prove that pH variation affects the removal of B at 100 percent significance, indicating further that the percent removal of B is a function of the pH value.

The results shown in this section support the effectiveness of alkalization with a combined chemical mixture of NaOH and Na_2CO_3. This shows that the production of $Mg(OH)_2$ impacts the removal of Ca, Mg, and Boron. It is deduced that the pH value of 10.5 is optimal for boron removal, and as the pH increases the % removal of boron decreased therefore pH and % removal are inversely related in the pH range of 10.5 to 12 at 20 ^{o}C.

On the contrary, Ca and Mg were removed at higher efficiencies with increase in pH values from 10.5 to 12. Their removal efficiencies, as observed from Figure 4.1, increase with pH increases from 10.5 to 11, and plateaus at pH 11 through 12, which leads to the deduction that pH 11 is the optimal pH for removal of Ca and Mg with the least added alkalizing agent, therefore the breakpoint of coagulant addition is at pH 11. However, more experiments are needed to assess the effect of pH on other seawater constituents, and the effect of temperature and the interaction of pH and temperature. Such experiments were performed and results are presented in latter sections of this report.

4.2.2 The effect of temperature

The impact of temperature on the operating efficiency of the pretreatment system was evaluated by conducting a series of experiments relating contaminant removal to temperature (10, 20, 25, 30 ^oC) at different pH values (10.5, 11, 11.5). Results of the experiments depicting the % removal of the tested parameters at different temperatures (10, 25, 30 ^oC) and pH values (10.5, 11, 11.5) are presented in Tables 4.5, 4.6, 4.7. Also graphs showing the % removals of Ca, Mg, and B at fixed temperatures and variable pH values are presented in Figures 4.3 – 4.8.

Table 4.5 Treated seawater constituents at different pH values and T=10 ^oC**

Parameter	**Unit**	**Raw Seawater**	**pH 10.5**	**pH 11**	**pH 11.5**
pH	pH units	8.02 ± 0.1	10.52±0.05	11.21±0.009	11.57±0.08
pH_f *	pH units	N/A****	10.47±0.004	11.04±0.1	11.49±0.12
Temperature	Degrees C	N/A	9.8±0.01	9.5±0.08	10.2±0.1
Ca	mg/L	512 ± 9.2	149.3±2.5	BDL	BDL
Ca removal	%	N/A	71.34±0.49	≈100	≈100
Mg	mg/L	1535.8 ± 55	243.49±4.98	21.1±1.1	4.1±0.67
Mg removal	%	N/A	84.14±0.32	98.6±0.07	99.7±0.04
Boron	mg/L	5.1 ± 0.3	2.2±0.14	3.45±0.21	4.2±0.28
Boron removal	%	N/A	56.86±2.78	32.35±4.1	17.16±5.3
SiO2	mg/L	3	BDL	BDL	BDL
Si	mg/L	1.5	BDL	BDL	BDL

*pHf represents the pH recorded at the end of the jar test procedure, and is compared to pH to check for pH variation due to CO2 escape or entry.
* *The numbers of observations were 5 for each pH value.
***BDL: below detection limit. (Ca detection limit: 0.5 mg/L, Si detection limit: 0.3 mg/L)
****N/A: Not applicable

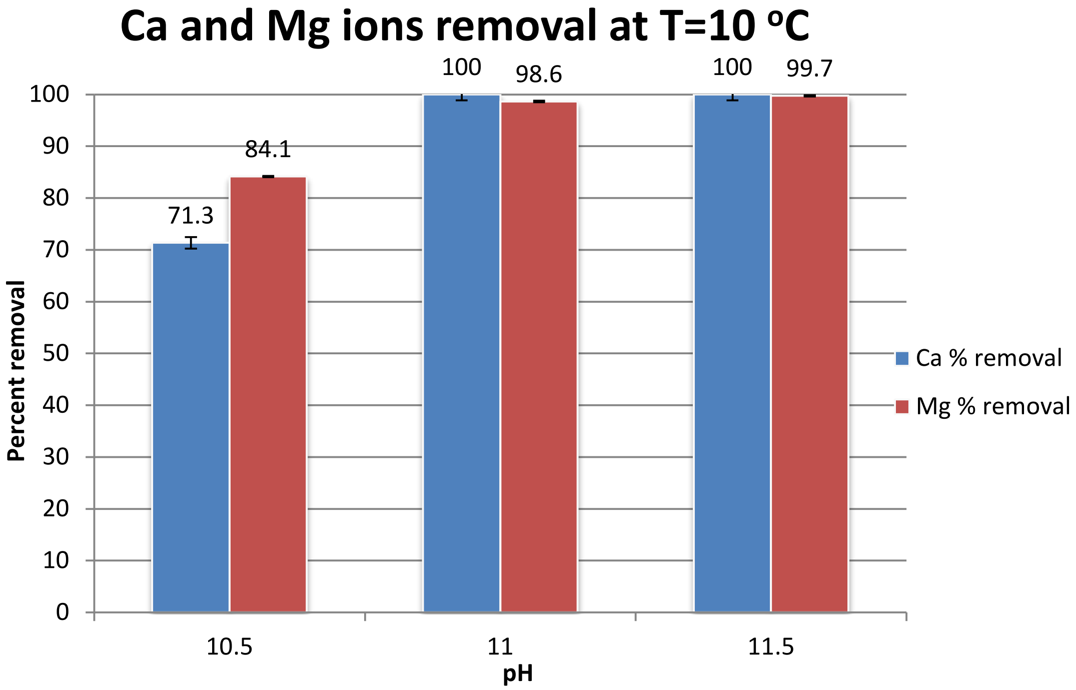


Figure 4.3 Removal percentages and error bars of Ca and Mg at different pH values and T= 10 °C

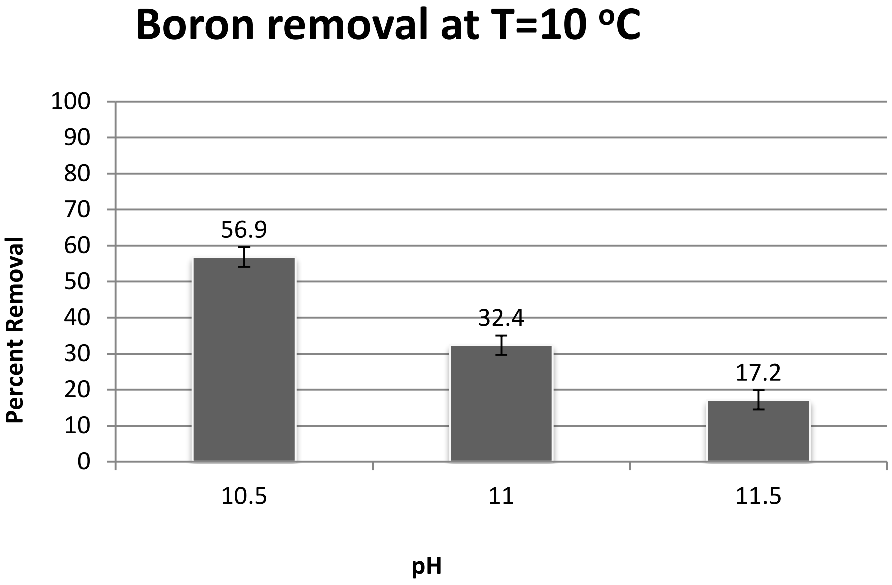


Figure 4.4 Removal percentages and error bars of B at different pH values and T= 10 °C

Table 4.6 Treated seawater constituents at different pH values and T=25 °C*

Parameter	Unit	Raw Seawater	pH 10.5	pH 11	pH 11.5
pH	pH units	8.02 ± 0.1	10.54 ± 0.1	11.21±0.02	11.52±0.15
pHf		N/A	10.48±0.045	11.01±0.25	11.5±0.1
Temperature	Degrees C	N/A	24.35±0.2	25.1±0.1	25.0±0.04
Ca	mg/L	512 ± 9.2	123.24±3.84	BDL**	BDL
Ca removal	%	N/A	76.34±0.74	≈ 100	≈100
Mg	mg/L	1535.8 ± 55	246.65±3.9	6.68±1.6	3.95±1.9
Mg removal	%	N/A	83.9±1.49	99.56±0.1	99.7±0.04
Boron	mg/L	5.1 ± 0.3	1.7±0.22	2.1±0.08	2.52±0.47
Boron removal	%	N/A***	66.7±4.2	58.8±1.6	50.5±9.3
SiO2	mg/L	3	BDL	BDL	BDL
Si	mg/L	1.5	BDL	BDL	BDL

*The number of observation were 4 for each value
**BDL: below detection limit. (Ca detection limit: 0.5 mg/L, Si detection limit: 0.3 mg/L)
***N/A: Not applicable

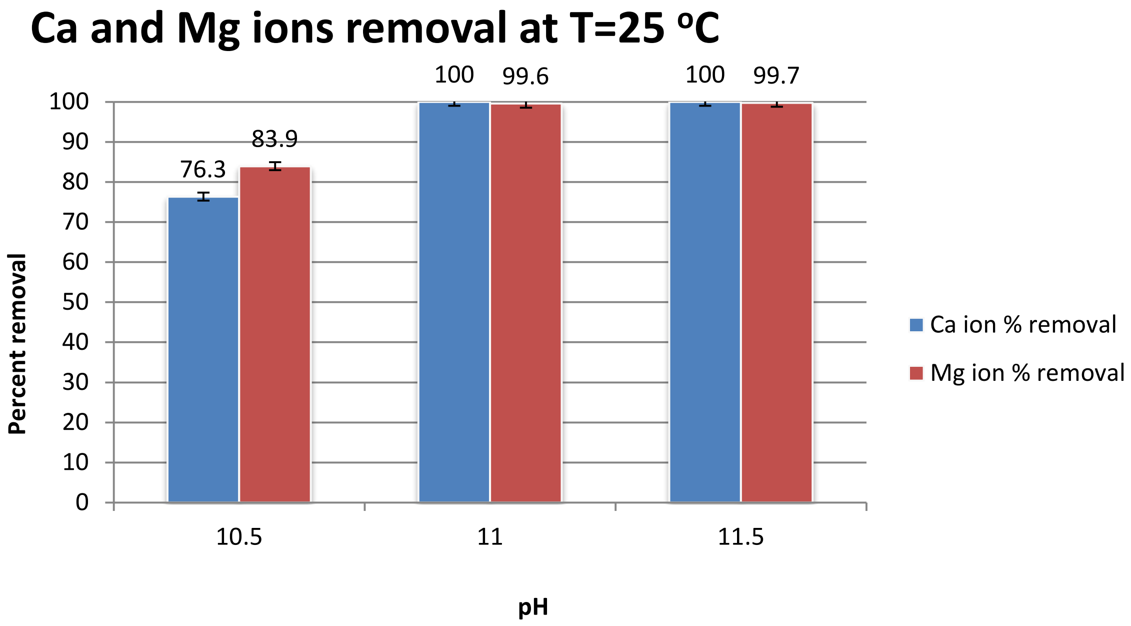


Figure 4.5 Removal percentages and error bars of Ca and Mg at different pH values and T= 25 °C

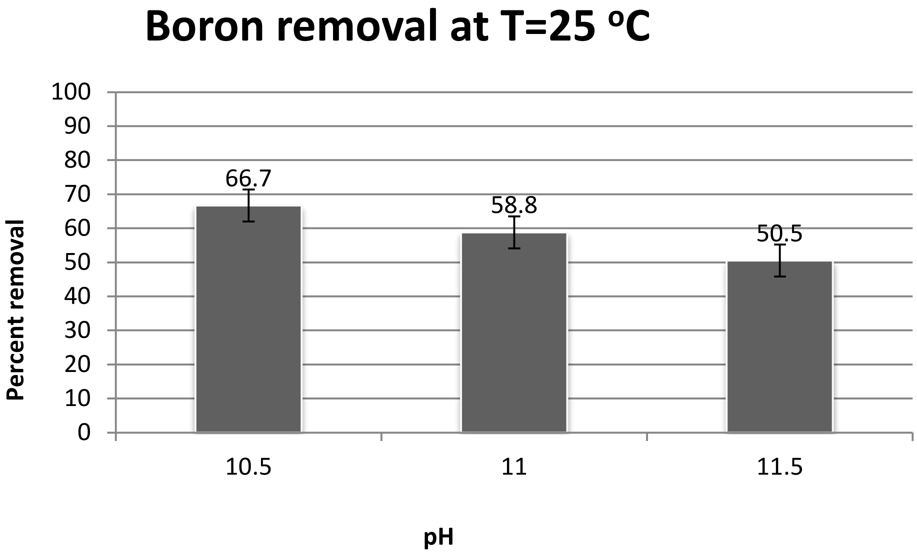


Figure 4.6 Removal percentages and error bars B at different pH values and T= 25 °C

Table 4.7 Treated seawater constituents at different pH values and T=30 °C*

Parameter	Unit	Raw Seawater	pH 10.5	pH 11	pH 11.5
Ph	pH units	8.02 ± 0.1	10.52 ± 0.18	11.22±0.2	11.61±0.17
pHf	pH units	N/A***	10.44±0.01	11.01±0.07	11.52±0.22
Temperature	Degrees C	N/A	30.1±0.04	29.52±0.14	3.04±0.01
Ca	mg/L	512 ± 9.2	95.2±1.8	BDL**	BDL
Ca removal	%	N/A	81.92±0.33	≈ 100	≈100
Mg	mg/L	1535.8 ± 55	260.6±1.5	6.2±0.8	4.19±0.5
Mg removal	%	N/A	83±0.09	99.6±0.05	99.72±0.03
Boron	mg/L	5.1 ± 0.3	1.53±0.13	1.95±0.13	3±0.0816
Boron removal	%	N/A	70.1±2.5	61.7±2.5	42.2±1.6
SiO2	mg/L	3	BDL	BDL	BDL
Si	mg/L	1.5	BDL	BDL	BDL

*Number of observations was 4 for each pH value

**BDL: below detection limit. (Ca detection limit: 0.5 mg/L, Si detection limit: 0.3 mg/L)

***N/A: Not applicable

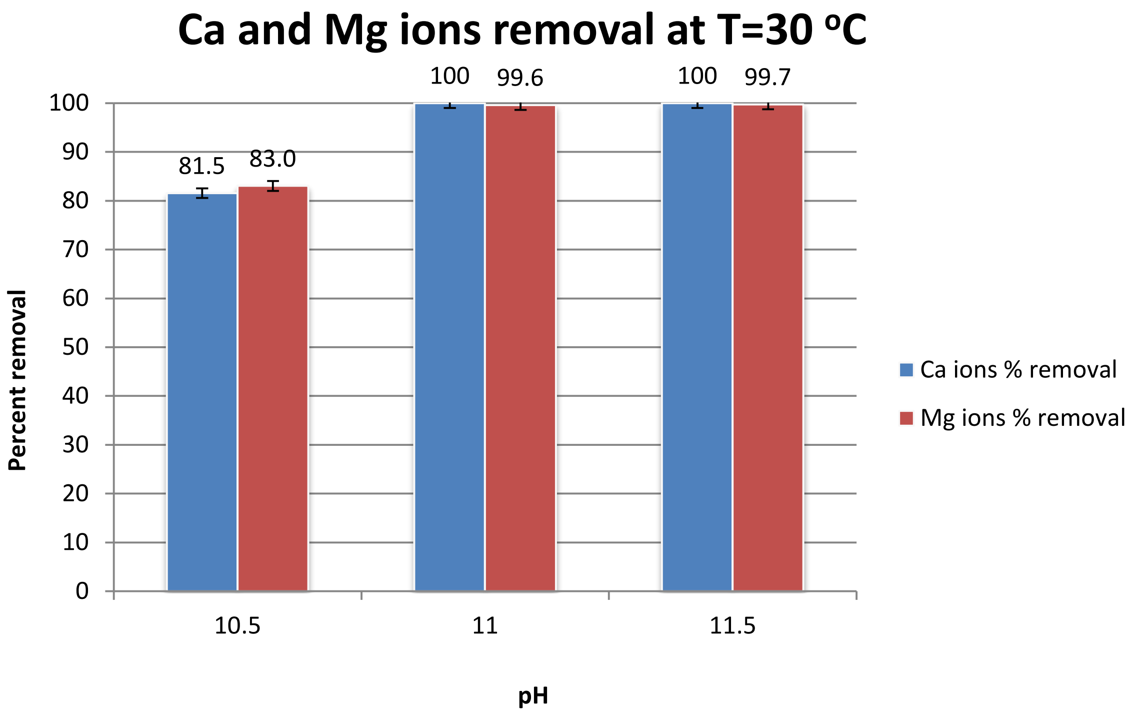


Figure 4. 7 Removal percentages and error bars of Ca and Mg at different pH values and T= 30 °C

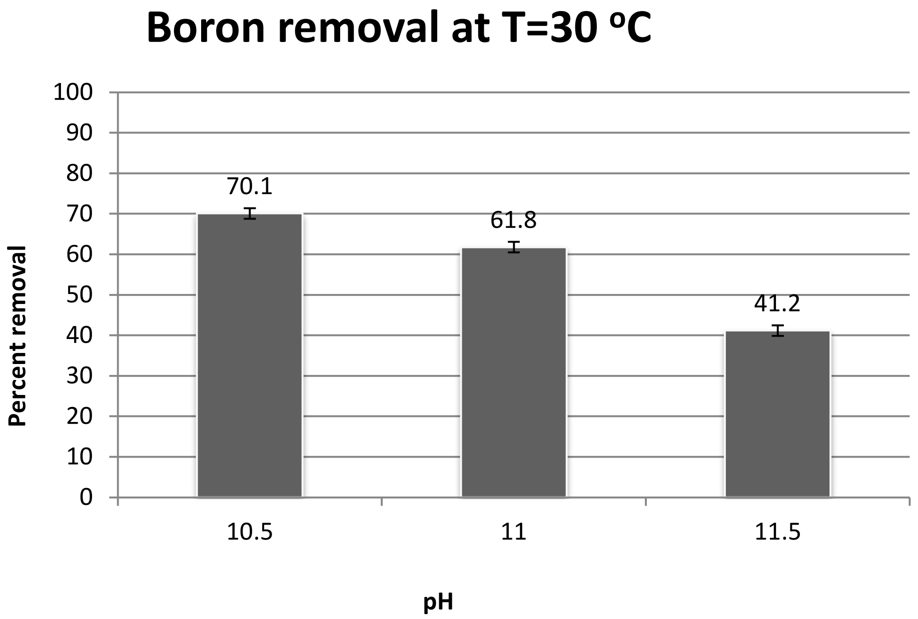


Figure 4.8 Removal percentages and error bars of B at different pH values and T= 30 °C

Regression analysis was performed to obtain regression equations for each condition with the results shown in Tables 4.8, 4.9, and 4.10. Statistical analyses lead to the conclusion that temperature has an apparent effect on the % removal of Ca, Mg, and B, however not of the same magnitude for all parameters. The removal of boron was the most affected parameter by temperature variations, while the effect on the removal of Ca and Mg was not as significant. Regression lines showing the approximate Ca removals at different temperatures are presented in Figure 4.9

Table 4.8 Regression analysis of Ca % removal

Temperature ^{o}C	**S**	**R^2 %**	**R^2 (adj) %**	**Regression equation: % removal of Ca**
10	0.275	100	100	- 7152 + 1290 pH - 57.33 pH^2
20	0.67	99.7	99.6	- 5661 + 1025 pH - 45.54 pH^2
25	0.425	99.9	99.9	- 5885 + 1065 pH - 47.31 pH^2
30	0.195	100	100	- 4474 + 813.5 pH - 36.16 pH^2

Table 4.9 Regression analysis of Mg % removal

Temperature ^{o}C	**S**	**R^2 %**	**R^2 (adj) %**	**Regression equation: % removal of Mg**
10	0.193	99.9	99.9	- 3308 + 603.8 pH - 26.74 pH^2
20	0.527	99.6	99.5	- 3761 + 687.1 pH - 30.56 pH^2
25	0.867	99.0	98.8	- 3812 + 695.4 pH - 30.89 pH^2
30	0.066	100	100	- 4061 + 739.8 pH - 32.87 pH^2

Table 4.10 Regression analysis of B % removal

Temperature ^{o}C	**S**	**R^2 %**	**R^2 (adj) %**	**Regression equation: % removal of B**
10	4.22	95.2	94.2	2723 - 449.5 pH + 18.63 pH^2
20	2.78	93.1	91.6	772.5 - 107.8 pH + 3.922 pH^2
25	3.5	75.6	70.2	854 - 131.6 pH + 5.392 pH^2
30	2.24	97.5	97	- 2586 + 510.3 pH - 24.51 pH^2

Consistent relationships were deduced from the data obtained for pH variations with the four tested temperatures. As for boron removal, the optimal pH at which maximum recorded removals for all temperatures was 10.5. A definite trend denoted that boron removal decreased with increase in pH, however the lowest recorded values occurred at 10◦C with the highest at 20◦C. At 25 and 30◦C the values were close to but lower that those attained at 20◦C.

A constant trend of very high removal efficiencies was recorded at all temperatures for Ca and Mg at pH values of 11.0 and 11.5. At pH 10.5, inferior removals were depicted at all temperatures. However improved removals of Ca were noted with increase in temperature at pH 10.5 with removal figures of 71.3%, 76.9%, and 81.5 for temperatures of 10, 20, and 30◦C, respectively, suggesting about a 5% increase in removal per 10 ^{o}C increase in temperature. As pointed in section 4.2.1 the results shown above reconfirm that pH 11- 11.5 is the optimal value for removal of Ca and Mg thus reflecting an optimized alkalizing dose needed for a successful coagulation-flocculation process.

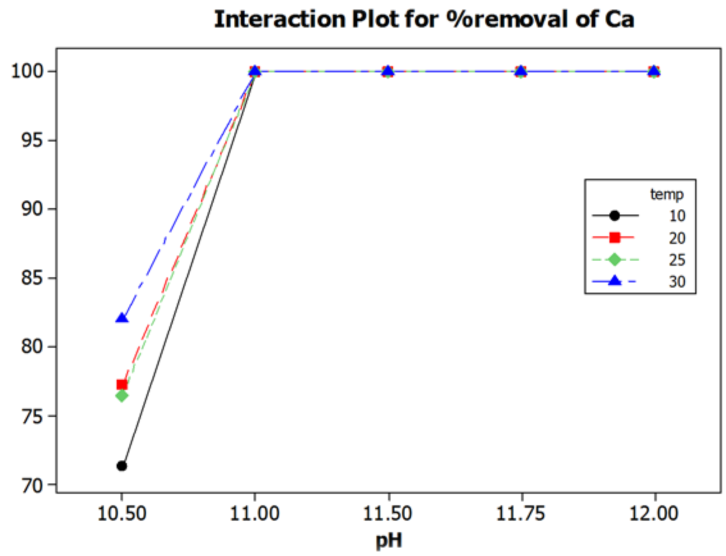


Figure 4.9 Percent removal of Ca at different T vs. pH

4.2.3 Combined effect of pH and temperature

In order to establish the significance of the combined effects of temperature and pH variations on the process, a regression analysis was performed while combining the collected data. Intervals of removal at 95 percent confidence for boron illustrate the removal range at specific pH and temperature values (Figure 4.10). The plot establishes that the combined effect of pH and temperature is significant. In order to obtain an effects plot, a statistical analysis was performed using 2-way ANOVA.

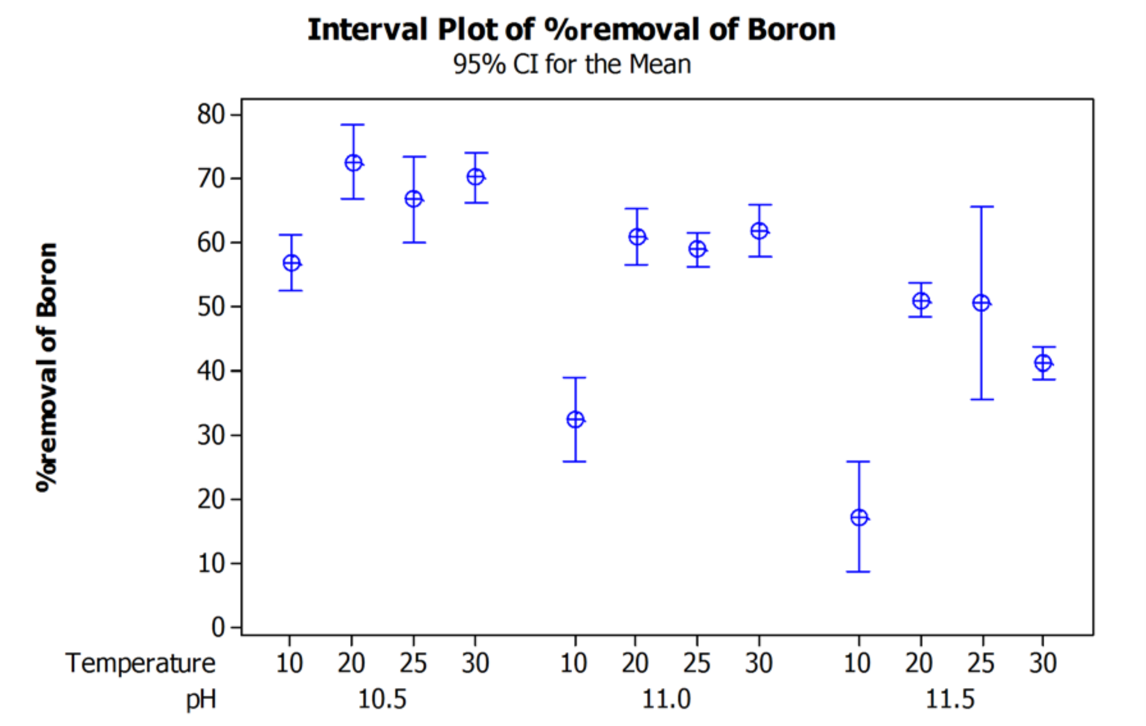


Figure 4.10 Interval plot for % removal of B at 95 percent CI

Table 4.11 Two-way ANOVA: %removal of Boron versus Temperature and pH

Source	DF	SS	MS	F	P
Temperature	3	5189.9	1729.97	103.67	0.000
pH	2	5657.9	2828.96	169.53	0.000
Interaction	6	782.6	130.43	7.82	0.000
Error	36	600.7	16.69		
Total	47	12231.1			

S = 4.085 R^2 = 95.09% R^2(adj) = 93.59%

From the p values it may be concluded that the effect of temperature, pH, as well as the effect of their interaction is highly significant at any α. An interaction plot comparing the effects of pH and temperature is presented in Figure 4.11 to support the hypothesis.

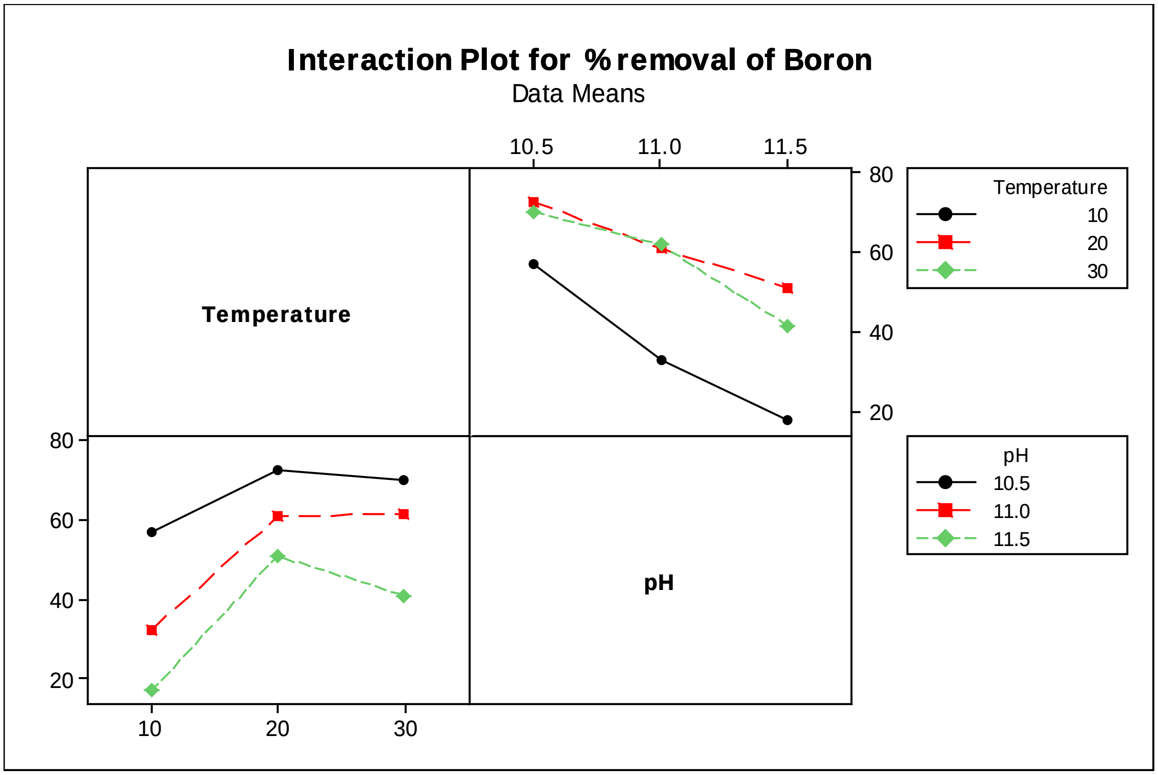


Figure 4.11 Interaction plot comparing the effects of pH and temperature

Due to the fact that temperature variation was not significant (at 90 percent CI) for Ca and Mg % removals, a regression analysis was performed. Multiple regressions were performed; however the most suitable regression type was cubic regression. Results are shown in Table 4.12

Table 4.12 Cubic regression analysis for Ca, Mg, and B

parameter	S	R^2 %	R^2 (adj)%	regression equation
Br	5.7	93.30	87.70	%removal of Boron = 110 + 20.6 T - 10 pH - 0.887 T^2 - 0.7 pH^2 + 0.0123 T^3
Ca	1.77	97.20	96.90	%removal of Ca = - 43722 + 11422 pH + 2.44 temp - 992 pH ^2 - 0.125 T^2 + 28.7 pH ^3 + 0.00205 T^3
Mg	0.57	99.30	99.30	%removal of Mg = - 28381 + 0.003 T + 7423 pH + 0.0022 T^2 - 644 pH^2 - 0.000069 T^3 + 18.6 pH^3

It should be noted that using cubic regressions might cause an overfitted regression equation. For that reason a few points of the data were omitted from the regressoin analysis and were used as test points to check the fit of the model. Results were equalized and the regression equations shown in table 4.12 were assumed accurate based on the data used.

4.2.4 Effect of spiked samples on parametric removal efficiency

Seawater from many parts of the world and specifically from the Eastern Mediterranean Sea could be contaminated with constituents other than the ones presented in

Table 3.1. Discharge of wastewater into the sea introduces in the water a variety of contaminants in the form of microorganisms including bacteria and viruses. Iron is also found in relatively higher concentrations. Moreover the combined presence of Mg and Si in seawater induces the formation of a MgSi compound which tends to attract borate at high pH and thus enhances boron removal. For this reaction to take place, a Mg:Si ratio of lower than 5:1 should exist (Parks and Edwards, 2007).

4.2.4.1 The addition of sodium silicate

In the presence of Si, boron removal was evaluated by the application of one-way ANOVA at the optimal temperature and pH ($T=20^oC$ and $pH=10.5$) as determined from boron removal efficiencies in sections 4.2.1-4.2.3 and at a room temperature of 24 ^oC. The effect of Si concentration on Mg and Ca removals was negligible. Results for 1 way unstacked ANOVA are presented in Table 4.13.

Table 4.13 One-way ANOVA: based on spiking with 3 mg/L, 5 mg/L, 10 mg/L, 15 mg/L, 20 mg/L Si

Source	DF	SS	MS	F	P
Factor	4	258.0	64.5	5.89	0.009
Error	11	120.5	11.0		
Total	15	378.5			

S = 3.309 R^2 = 68.17% R^2 (adj) = 56.59%

From Table 4.13 F tabulated = 5.89 and P=0.009 therefore the ANOVA provided enough evidence that at 99% confidence interval, and α=0.01 to support the claim that there is a significant difference imposed by Si spiking on the removal efficiency of Boron. The effect of Si spiking is illustrated in Figure 4.12. The addition of Si to seawater samples increased the efficiency of removal of boron up to 86% in comparison to 72% removal when Si was not spiked. Table 4.14 presents the data means of % removal with respect to Si spiking concentrations, indicating that the higher the Si concentration the more efficient is the boron removal. The study reported by Parks and Edwards (2007) explains this increase in percent removal of B and its relation to Si concentration from which it is concluded that reaching a higher Si:Mg ratio is essential in removing boron at optimal pH of 10.5 and 20 ^{o}C temperature

Table 4.14 Si concentration effect on boron mean percent removal

Si concentration	**Number of observation**	**Mean % removal**	**StDev**	**Average temperature**	**Average pH**
3 mg/L	4	72.55	3.58	20±0.02	10.49±0.001
5 mg/L	3	79.74	2.26	19.5±0.1	10.49±0.08
10 mg/L	3	80.27	1.79	19.7±0.11	10.51±.0.012
15 mg/L	3	80.595	0.351	19±0.015	10.48±0.011
20 mg/L	3	85.196	0.995	19.5±0.008	10.49±0.009

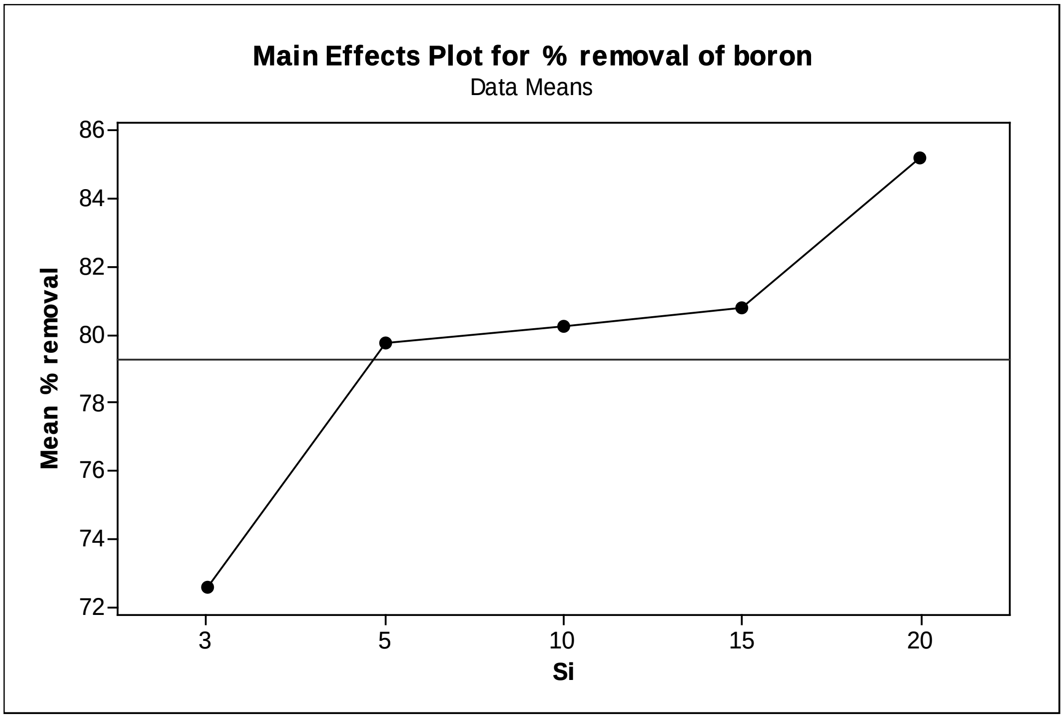


Figure 4.12 Effect of Si spiking on boron removal

4.2.4.2 The addition of Fe

Iron is present in water in two forms, ferrous and ferric. Ferric iron is basically ferrous iron which has been oxidized; this form of iron is easily removed via filtration. On the other hand ferrous iron is more water soluble and cannot be easily removed. Ferrous iron in the form of ferrous sulfate ($FeSO_4$) was used to spike the samples prior to jar testing in order to assess the efficiency of removal of dissolved iron of concentration ≥ 3.5 mg/L as acquired seawater has an iron concentration of 0.29 mg/L which is too low to be considered an effective pollutant. The effect of iron spiking on the color of the samples is presented in

Figure 3.8. The temperatures of the spiked samples were selected based on prior experiments, and their recorded efficiencies of removal of Ca and Mg both being the leading cause of inorganic fouling in SWRO. From Section 4.2.2 it was concluded that the optimal temperature for the process is 20°C. Therefore, the removal of dissolved Fe will be assessed at pH 10.5, 11, and 11.5 and at sample temperature of 20°C.

To evaluate the effect of Fe addition on the process 7 experiments were performed at each pH value in addition to 3 control jars. The purpose of the control jars is to check for settling of oxidized iron (ferric form) throughout the duration of the experiment. The initial concentrations of Fe were recorded based on the control jars at the end of the experiments and percent removals were calculated at room temperature 23.4°C results are presented in Table 4.15. A percent removal bar chart showing the efficiency of iron removal at the assessed pH values is presented in Figure 4.13

Table 4.15 Iron concentrations and % removal at pH 10.5, 11, and 12

	Initial (control jars)	**pH 10.5**	**pH 11**	**pH 11.5**
Number of observations	7	7	7	7
Temperature	19.2±0.01	20.14±0.05	19.8±0.12	20.05±0.2
pH	8.13± 0.04	10.48± 0.001	11.2 ± 0.11	11.57± 0.05
Iron mg/L	3.6±0.85	0.029±0.003	0.03±0.0025	0.049±0.0026
% Removal of Iron	N/A*	99.2±0.08	99.16±0.07	98.6±0.072

*N/A: Not applicable

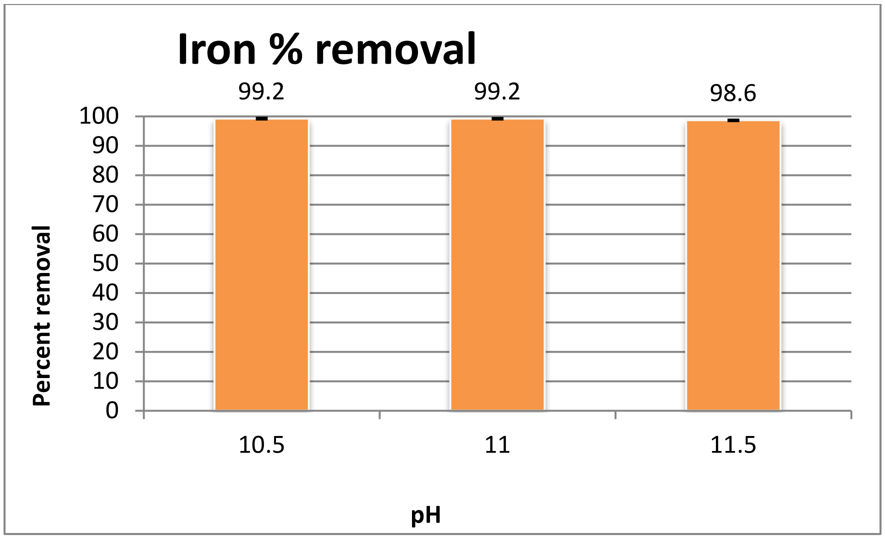


Figure 4. 13 % removal of Iron at pH 10.5, 11, and 12

From Figure 4.13 it can be deduced that iron removal is related to the formation and adsorption of $CaCO_3$ and $Mg(OH)_2$ flocs starting at pH 10.5, with negligible effect resulting from pH variations.

4.2.4.3 The addition of wastewater

A multitude of microorganisms and specifically bacteria could be found in seawater as a result of wastewater discharge into the marine environment. The fact that bacteria could lead to bio-fouling of membranes, they need to be inactivated prior to coming in contact with the membrane. Accordingly the appropriate disinfection process should be included in the pretreatment of the feed water. Besides the use of conventional disinfection processes including chlorination, ozonation and UV application, which have proved also to have certain drawbacks as related to membrane safety, low and high pH values, having been shown to be effective in inactivating bacteria (Zebger et al., 2003), and can be used as a bacterial control process. This process is basically already built in the proposed basic pre-treatment process as raising the pH to high values is mandatory for the proper operation of the overall pretreatment activity.

To assess the effectiveness of bacterial inactivation at high pH values, a series of experiment were conducted whereby seawater samples were spiked with 1% municipal wastewater in order to increase the bacterial population in the samples which will assist in properly evaluating the impact of bacterial inactivation.

Municipal wastewater normally contains organic and inorganic contaminants as well, for that reason the samples were analyzed after spiking and prior to conducting the experiments. The effect of wastewater addition on seawater constituents (Table 3.1) was minimal and within the provided standard deviations for Mg, Ca, Na, B, Si, and turbidity. Iron concentrations were recorded as 1.2 ± 0.1 mg/L, whereas total and fecal coliforms, which have been used as indictor organisms, were too numerous to count. Both iron and coliforms removal where assessed at room temperature of 24.1 ^{o}C. Figure 4.14 presents plate counts for the total and fecal coliforms.

Table 4.16 Total and fecal coliforms removal

	Initial (spiked sample)	**pH 10.5**	**pH 11**	**pH 11.5**
Temperature	20.1± 0.5	19.43± 0.01	21± 0.5	19.8± 0.04

Number of observations	4	4	4	4
Total coliforms cfu	Too numerous to count	0	0	0
Fecal coliforms cfu	Too numerous to count	0	0	0
Iron mg/L	1.2± 0.1	0.028± 0.0015	0.022± 0.004	0.031± 0.01

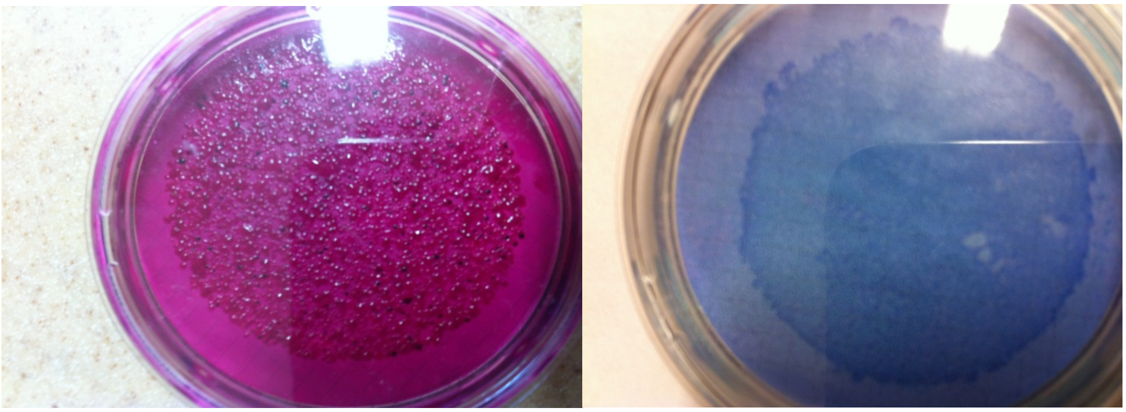


Figure 4.14 too numerous to count total (a) and fecal coliforms (b)

After the removal of all the fecal and total coliforms in the seawater samples by inactivation and precipitation, the removal of Ca, Mg, Br, and Si was assessed and the results fell within the standard deviations of the previously recorded removal efficiencies at the temperature of 20°C. Table 4.16 shows that total and fecal coliforms are entirely inactivated with this jar testing procedure at the covered pH levels.

4.3 Sludge considerations

To assess the effectiveness of any pretreatment system especially coagulation-flocculation, the resulting sludge mass and contents should be taken into consideration. The excess of OH^- and CO_3^{2-} anions provided by both NaOH and Na_2CO_3 respectively, induced the creation of $Mg(OH)_2$ and $CaCO_3$ floc. These flocs, white in color, precipitate to form a sludge layer. Figure 4.15 shows the sludge layers formed in the different jars as a result of the floc settling process.

Figure 4.15 Sludge layers after settling

4.3.1 The effect of pH and temperature on sludge settling

Both pH and temperature had an effect on sludge settling rates. Therefore 3 tests covering sludge settling for each pH (10.5, 11, and 11.5) were taken at temperatures 10, 20, and 30 °C and their averages were recorded; in addition 3 tests at pH 12 and 20 °C were conducted and results recorded. Settling was recorded in terms of depth vs. time and regression equations for each pH value at distinctive temperatures were established. Settling (hindered) and compaction results are illustrated in Figures 4.16 through 4.25, while Table 4.17 presents the sludge depth recorded after 200 minutes of settling at different temperatures and pH values.

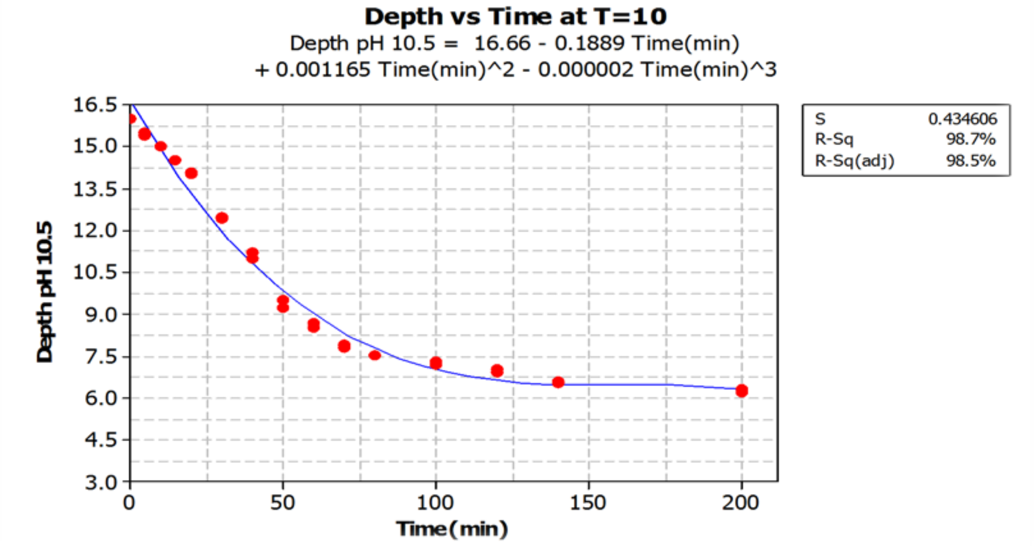


Figure 4.16 Sludge settling (cm) depth vs. time (min) at T= 10 °C and pH 10.5

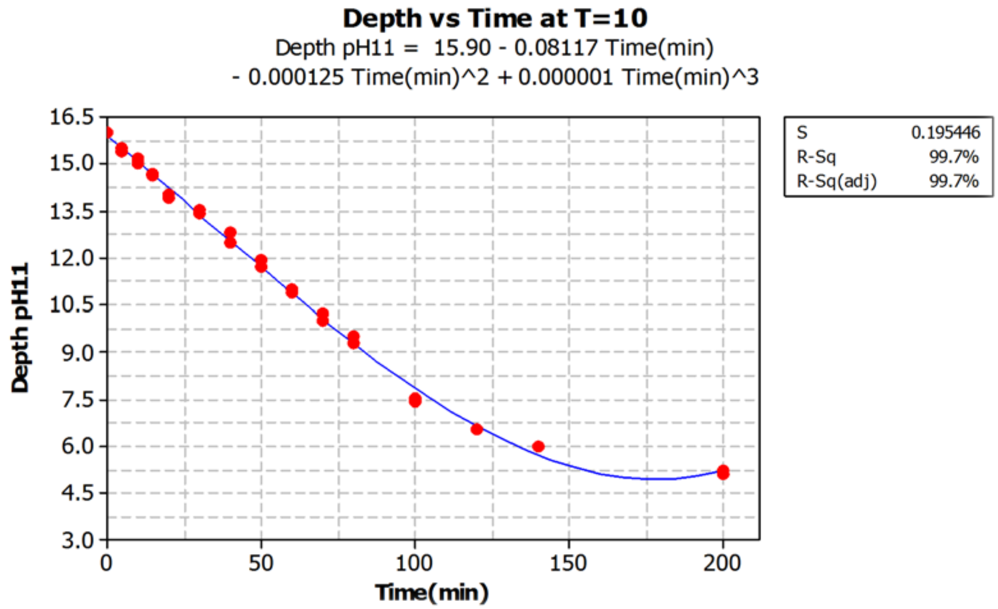


Figure 4.17 Sludge settling (cm) depth vs. time (min)at T= 10 ^{o}C and pH 11

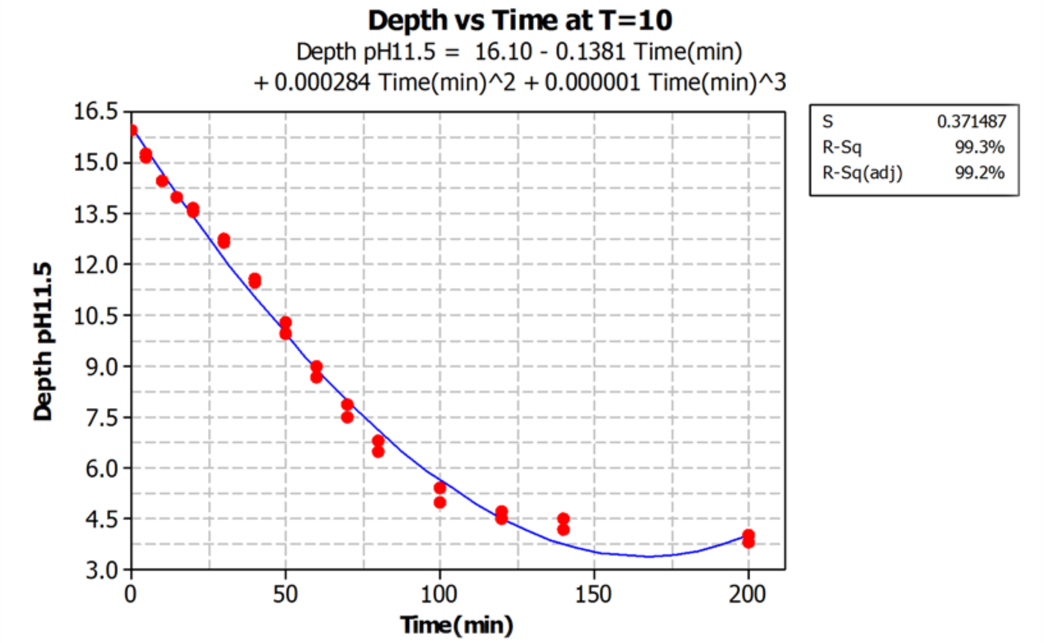


Figure 4.18 Sludge settling (cm) depth vs. time (min) at T= 10 ^{o}C and pH 11.5

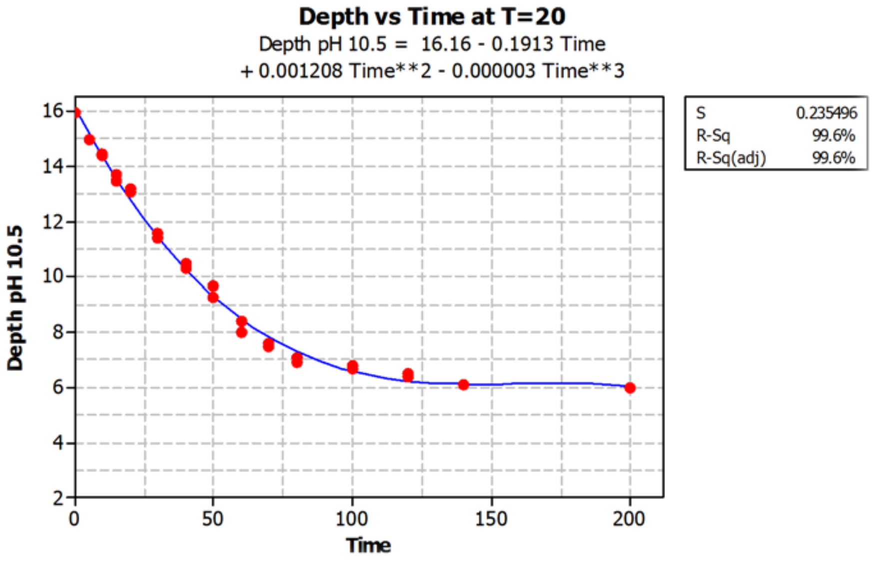


Figure 4.19 Sludge settling (cm) depth vs. time (min) at T= 20 ^{o}C and pH 10.5

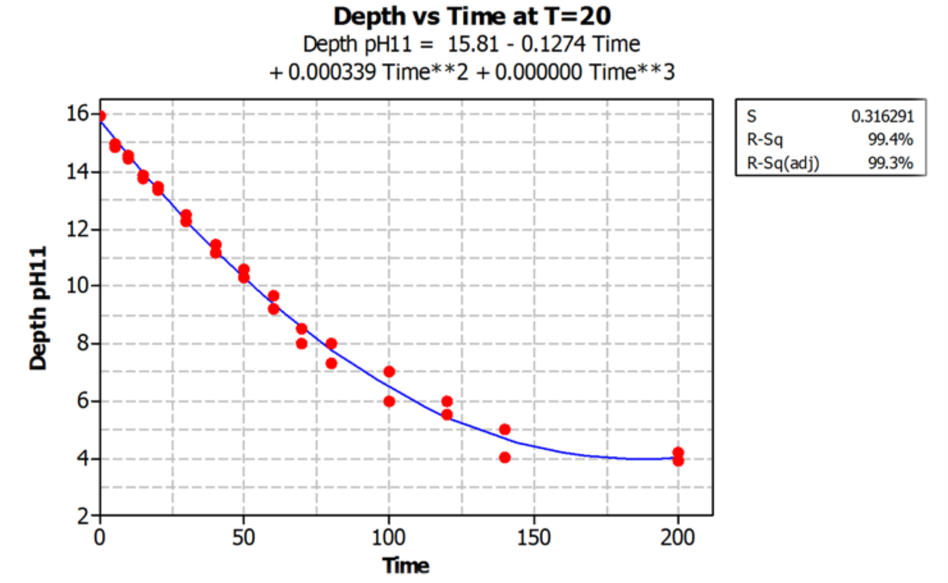


Figure 4.20 Sludge settling (cm) depth vs. time (min) at T= 20 ^{o}C and pH 11

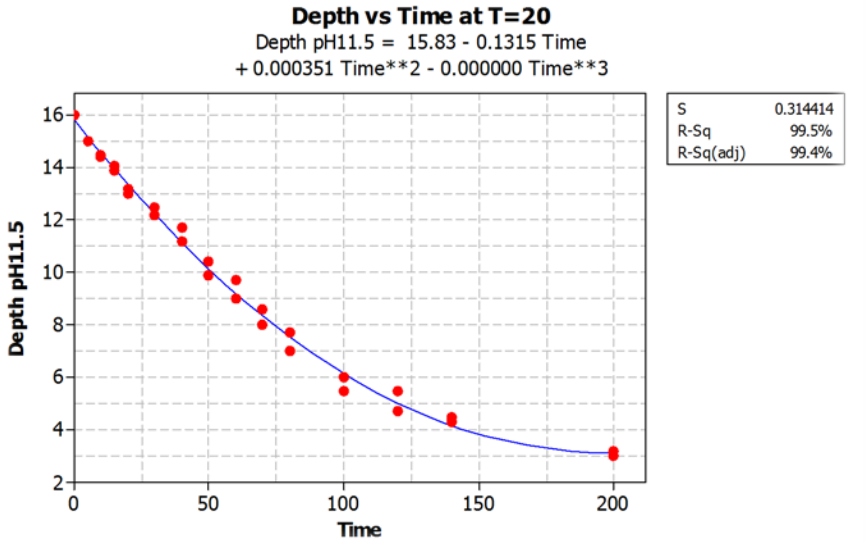


Figure 4.21 Sludge settling (cm) depth vs. time (min) at T= 20 ^{o}C and pH 11.5

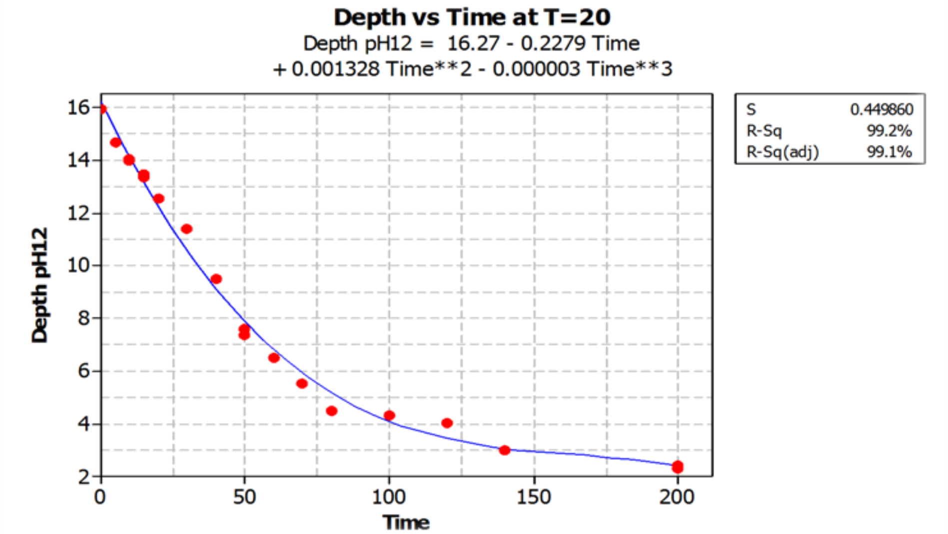


Figure 4.22 Sludge settling (cm) depth vs. time (min) at T= 20 °C and pH 12

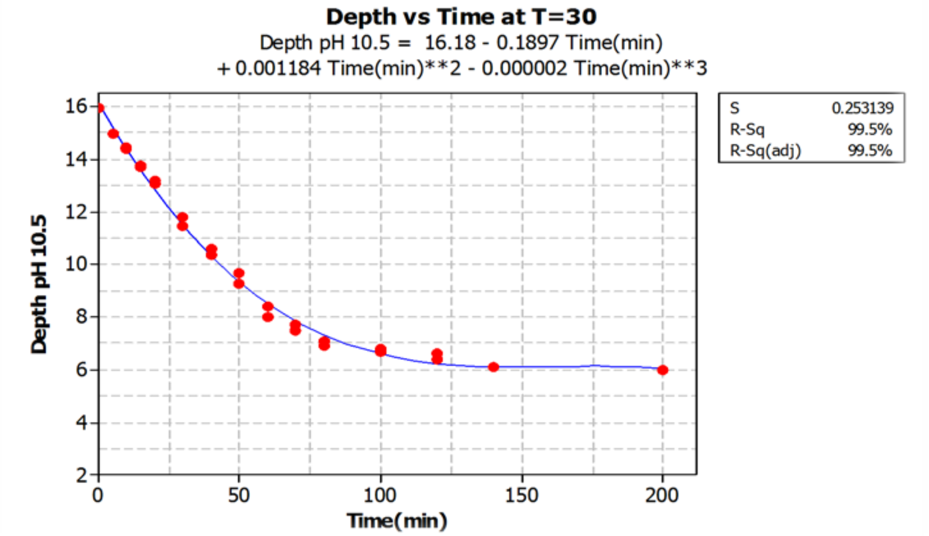


Figure 4.23 Sludge settling (cm) depth vs. time (min) at T= 30 °C and pH 10.5

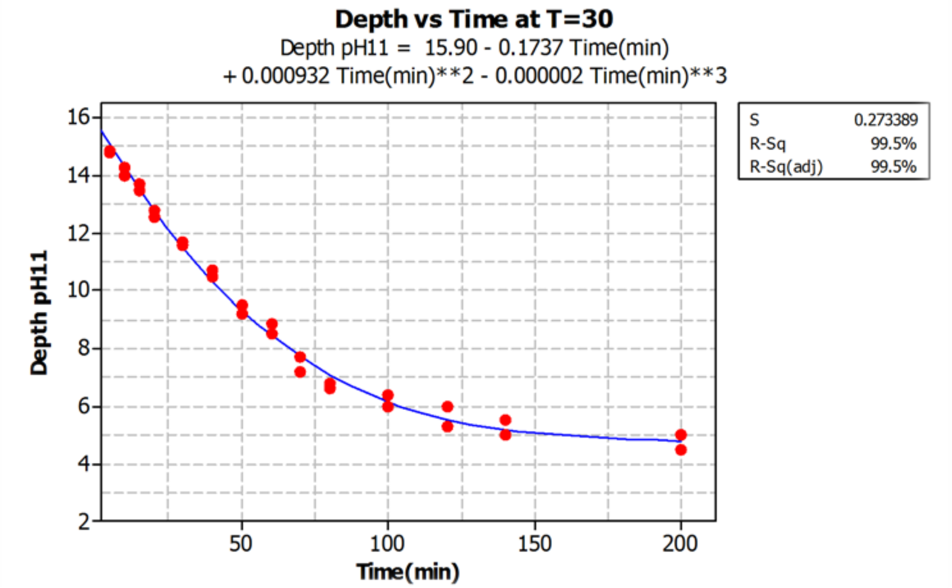


Figure 4.24 Sludge settling (cm) depth vs. time (min) at T= 30 °C and pH 11

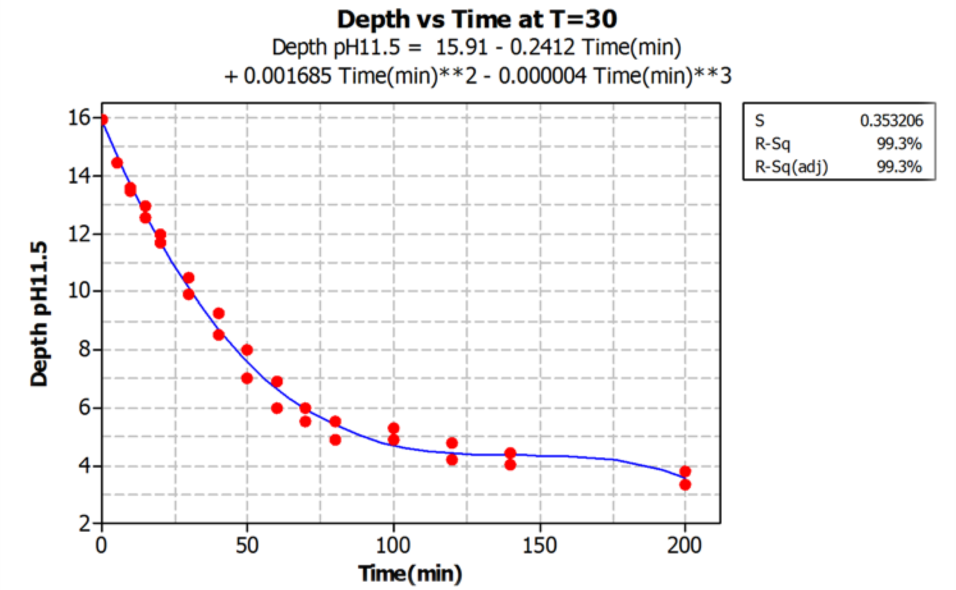


Figure 4.25 Sludge settling (cm) depth vs. time (min) at T= 30 °C and pH 11.5

Table 4. 17 Final depth of sludge with respect to pH and temperature

Ph	Temperature ^{o}C	Mean final depth of sludge (cm) at 200 min settling
10.5	10	6
	20	6
	30	6
11	10	5
	20	3.9
	30	4.75
11.5	10	4
	20	3
	30	3.4
12	20	2.3

To determine the significance level of pH on sludge depth, a two-way ANOVA for the data presented in Table 4.17 was performed and the results recorded as depicted in Table 4.18.

Table 4.18 2 way ANOVA results for the effect of pH and temperature on sludge depth

Source	DF	SS	MS	F	P
pH	2	9.6939	4.84694	45.32	0.002
Temperature	2	0.7439	0.37194	3.48	0.133
Error	4	0.4278	0.10694		
Total	8	10.8656			

With S = 0.3270 R^2 = 96.06% R^2(adj) = 92.13%

Table 4.18 shows that the significance of pH on sludge depth is very high. The ANOVA provided ample evidence that at 99 confidence interval and α=0.01 to support the claim that there is a significant difference imposed by pH variation on sludge depth. On the other hand the effect of temperature is not found to be significant and this can only be proven by choosing a higher α value.

A regression equation showing sludge depth as a function of pH and temperature was deduced by applying polynomial regression for the mean data presented in Table 4.17

$$final\ depth\ of\ sludge\ (cm)(at\ t = 200mins) \\ = 123 - 18.7\,pH - 0.237\,T + 0.733\,pH^2 + 0.00558\,T^2$$

Where T is the temperature and based on S = 0.327024, R^2 = 96.1%, and R^2(adj) = 92.1%.

The interaction relation of pH and temperature is depicted in the main effects plot presented in Figure 4.26, which further reconfirms the low impact of temperature on depth of sludge in comparison to that of the rise in pH.

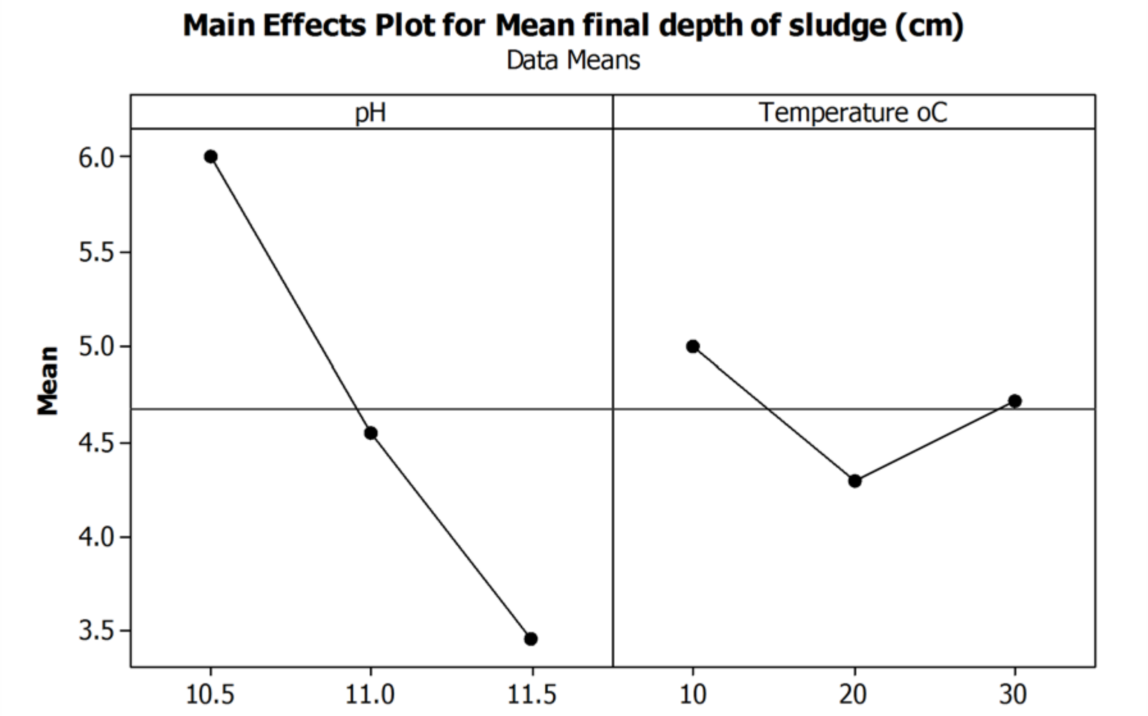


Figure 4. 26 Main effects plot of pH and temperature on final depth of sludge

After determining the compaction rate of the sludge at different pH and temperature values, it was deemed crucial to obtain the mass of sludge produced by the system. The temperature of 20^{o}C was chosen as the optimal temperature to assess the sludge mass produced and the effect of the added coagulant.

Before settling, the flocs are present in the form of suspended solids and thus their concentration can be determined by the standard TSS test procedure. Samples of aliqouts were withdrawn from the jars after coagulation-flocculation and prior to settling at pH values of 10.5, 11, and 11.5 and tested for the TSS. The resulting concentrations were then converted to solids mass present in the two-liter jar and recorded as shown in Table 4.19.

Table 4. 19 Sludge mass produced in 2 L sample at different pH values and T=20^{o}C

pH value	Number of observations	Sludge mass in 2 liters (mg)	Standard deviation
10.51±0.08	3	15067	61.1
11.15±0.1	3	15840	212
11.56±0.014	3	15293	983

Although the relative difference in the mass for the 3 pH values is low, it is noted from Table 4.19 that the highest sludge mass occurred at pH 11.15±0.1 which leads to a possible deduction that the optimal pH for overall removal is about 11.

4.3 Optimal process selection

In order to determine the amount of 2:1 NaOH: Na_2CO_3 to be used to obtain the optimal pH value, further testing was needed. TOC, TSS, VSS, and TDS values were necessary to evaluate organic as well as colloidal fouling potential of effluent. The fouling types included:

1. Organic fouling: VSS and TOC
2. Colloidal fouling: TSS

On the other hand TDS is dominated by the presence of sodium salts, in addition to other constituents that may or may not cause RO membrane fouling. Tables 4.20-4.23 show the percentage removals for mentioned pollutants.

Table 4.20 TOC values and % removal

Sample	Number of observations	TOC mg/L	Standard deviation	% removal
initial seawater	4	5.285	0.1063	N/A*
pH 10.5	4	3.03	0.0245	≈ 43
pH 11	4	2.205	0.1936	≈ 58.4
pH 11.5	4	2.402	0.432	≈ 55

*N/A: Not applicable

Table 4.21 TSS values and % removal

Sample	Number of observations	TSS mg/L	Standard deviation	% removal
initial seawater	4	217.750	10.010	N/A*
pH 10.5	4	41.250	4.270	≈ 81
pH 11	4	41.500	7.330	≈ 81
pH 11.5	4	52.080	5.300	≈ 76

*N/A: Not applicable

Table 4.22 VSS values and % removal

Sample	Number of observations	VSS mg/L	Standard deviation	% removal
initial seawater	4	49.547	1.980	N/A*
pH 10.5	4	7.667	1.277	≈ 85
pH 11	4	5.885	0.879	≈ 88
pH 11.5	4	3.567	0.780	≈ 93

*N/A: Not applicable

T**able 4.23** TDS values

Sample	Number of observations	TDS mg/L	Standard deviation
initial seawater	3	37701	718
pH 10.5	3	39890	185
pH 11	3	40580	430

pH 11.5	3	41207	950

TOC and VSS values show a high removal percentage of organic matter, thus the system has the ability to limit organic fouling.

4.3.1 Scaling considerations

Supernatant after coagulation-flocculation and settling was characterized for the seawater constituents shown in Table 3.1 to compare the results of different additions of alkalizing agents to that of seawater. Results of the tests are recorded in Table 4.24.

Table 4.24 Characteristics of obtained effluents and that of initial seawater

Parameter	**Unit**	**Initial seawater**	**Effluent at pH 10.5**	**Effluent at pH 11**	**Effluent at pH 11.5**
pH	pH units	8.02 ± 1.1	10.5 ± 0.008	11.2±0.12	11.56±0.15
TDS	mg/L	37701±718	39890±185	40580±430	41207±950
TSS	mg/L	217.750 ± 10	41.25±4.3	41.5±7.3	52.08±5.3
VSS	mg/L	49.547± 1.98	7.667±1.28	5.885±0.88	3.567±0.78
TOC	mg/L	5.285 ±0.106	3.03±0.025	2.205±0.194	2.402±0.432
Mg	mg/L	1535.8 ± 55	238±13.7	6.5±2.3	9.8±1.9
Ca	mg/L	521 ± 9.2	118.64±6	BDL	BDL
Boron	mg/L	5.1 ± 0.3	1.4±0.18	2±0.14	2.5±0.08
Turbidity	NTU	3.2 ± 0.1	0.54±0.04	0.43±0.02	0.66±0.12
Iron	mg/L	0.29 ± 0.03	0.029±0.003	0.03±0.0025	0.049±0.0026
Silica (as Si)	mg/L	1.5 ± 0.05	BDL	BDL	BDL
Silica (as SiO2)	mg/L	3.0± 0.02	0.1±0.001	BDL	BDL
Total Coliforms	CFU	0	0	0	0
Fecal Coliforms	CFU	0	0	0	0

Al-Shammiri et al. (2005) developed a simple program for the estimation of scaling potential in RO systems in terms of the most abundant inorganic foulants. Using this model the estimation of scaling potential of the following parameters is possible:

1. Calcium sulfate, barium sulfate and strontium sulfate scaling
2. Calcium carbonate, and magnesium related scaling
3. Calcium fluoride and silica scaling

In SWRO following conventinal pretreatment, membrane scaling is inevitable since Ca, Mg and Si are not completely removed (Pontié et al., 2005), therfore the three types of scaling shown above have a very high probability of occuring. Membrane pretreatment effectively protects the SWRO membrane from such scaling, however the scaling occures at the pretreatment membrane itself, especially NF (Tang et al., 2011), causing irreparable damage. Wherase the efficient removal of Ca, Mg, Si, as well as bicarbonates recorded in Table 4.24 will effectively eliminate such scaling.

4.3.2 Mass balance

Mass balances will be performed on the inorganic chemicals that are involved in the reaction, which is controlled by Na, Ca, Mg, and concentration of carbonates.

Percent mass calculations

5N NaOH has a 200,000 mg/L concentration

% by mass Na of NaOH is 57.7%

$$Concentration\ of\ Na = \frac{200{,}000 \,{}^{mg}/_{L}}{100} \times 57.7 = 115{,}400 \,{}^{mg\ Na}/_{L\ NaOH}$$

10% Na_2CO_3 has 100,000mg/L concentration

% by mass Na of Na_2CO_3 is 37.7%

$$Concentration\ of\ Na = \frac{100{,}000 \,{}^{mg}/_{L}}{100} \times 37.7 = 37{,}700\ mgNa\ /\ (L\ Na_2CO_3)$$

Table 4.25 Total Na concentration added to sample seawater

pH	NaOH volume (ml)	Na from NaOH mg/L	Na_2CO_3 volume (ml)	Na from Na_2CO_3 mg/L	Total Na concentration added mg/L
10.5	40	4616	20	754	5370
11	50	5770	25	943	6713
11.5	53.3	6151	26.7	1007	7158

To perform a proper mass balance for the system we calculate the added mg/L from constituents affecting TDS vs. the ones removed. Assumptions made in the mass balance calculations are:

1. Na concentrations in table 4.25 are considered as the added concentration
2. Ca and Mg removals recorded in table
3. Bicarbonates complete removal, bicarbonate concentrations in seawater were calculated as an average of 4 readings to be 202±5.2 mg/L

Table 4.26 Mass balance at pH 10.5, 11, and 11.5

pH	Added Na mg/L	Removed Ca mg/L	Removed Mg mg/L	Removed bicarbonates mg/L	Net concentration mg/L
10.5	5370	403	1300	203	3464
11	6713	521	1535	203	4454
11.5	7158	521	1535	203	4899

Table 4.27 Comparison of mass balance and TDS value

pH	Net concentration added mg/L	TDS increase recorded (compared to initial seawater TDS) mg/L	Difference mg/L
10.5	3464	2189	1275
11	4454	2879	1575
11.5	4899	3506	1393

As table 4.27 shows, the difference of 1275 mg/L to 1575 mg/L can be considered as a result of both the standard error of the data and the instrumental errors of the utilized measurement technique.

CHAPTER 5

CONCLUSION AND RECOMMENDATIONS

5.1 Conclusion

The presented pretreatment process proposes the alkalization of seawater obtained from the shores of the Mediterranean Sea, Beirut. The alkalization reaction involves the addition of 2:1 $NaOH:Na_2CO_3$, thus providing CO_3^{2-} and OH^- ions which react with seawater constituents, inducing precipitation reactions. Results and analysis lead to the following conclusions:

- pH variation proved to have a significant effect on the removals of Mg and Ca, whereas temperature variations were found to be less significant. Temperature under which the system was found to be most effective was 20^oC , efficiencies of removal at a temperature of 20^oC were as follows:
- Ca removal at pH 10.5 was recorded to be 77.2%, whereas at pH of 11, 11.5, and 12 Ca removals were ≈ 100 percent, i.e. the effluent's concentration of Ca was below the detection limit of the used EDTA titration procedure.
- Mg removals at pH 10.5, 11, 11.5, and 12 were found to be 84.5%, 99.6%, 99.37%, and 99.13% respectively.

- Optimal removals of boron were recorded at temperature and pH of 20 °C and 10.5 respectively, where an average of 72.5% removal was recorded. At pH 11, 11.5, and 12 boron removal percentages were found to be 60.78%, 51%, and 37.25% respectively. This leads to the conclusion that boron removal is optimal at pH 10.5, and decreases as pH value increases.
- The addition of Si from sodium silicate improved the percent removal of Boron significantly. At optimal pH 10.5 and temperature 20°C spiking of Si 3, 5, 10, 15, and 20 mg/L resulted in boron removals of 72.55%, 79.74%, 80.27%, 80.6%, and 85.2% respectively.
- Spiking with dissolved iron, to emulate water with iron contamination of around 5 mg/L resulted in high efficiencies of removals of iron. At pH 10.5, 11, and 11.5 the removal of iron was recorded as 99.2%, 99.1%, and 98.6% respectively.
- Spiking with wastewater contaminated the samples with a high value of total and fecal units of bacteria. Complete removal of bacterial content was achieved via inactivation and precipitation at pH values of 10.5, 11, and 11.5.
- TOC removals at pH 10.5, 11, and 11.5 were found to be 43%, 58.4%, and 55% respectively. VSS removals at pH 10.5, 11, and 11.5 were found to be 85%, 88%, and 93% respectively.
- TSS removals at pH 10.5, 11, and 11.5 were recorded as 81%, 81%, and 76% respectively.
- Sludge mass after treatment at pH 10.5, 11, and 11.5 was recorded to be 15067 mg, 15840mg, and 15293 mg per 2 liters of seawater treated respectively. Which implies

that the treatment at pH 11 has the highest removal efficiencies in relation to sludge mass produced. Therefore the sludge mass produced from the proposed treatment is 7.9 Kg/m^3.

- TDS increase was recorded at pH of 10.5, 11, and 11.5 in comparison to that of initial seawater used, TDS values were found to be 39890, 40580, and 41207 mg/L respectively.

Optimal addition of coagulant with respect to the overall removal percent of seawater constituents was found to be 37.5 ml per liter, reaching a pH value between 11.1 and 11.3. An evaluation of the effluent water after running the experiment proved that this process possesses many technical advantages such as:

- The removal of hardness (Ca and Mg hardness), almost completely removes the corrosive effect of the water and significantly lowers the potential for inorganic fouling.
- The removal of silicates, iron, and boron limits colloidal and inorganic fouling.
- TSS, VSS, and TOC were also removed at high percentages, causing a decrease in potential organic, colloidal, and crystalline fouling.
- Inactivation of total and fecal coliforms without the use of chlorine for disinfection, thus minimizing membrane oxidation, reducing the harmful byproducts of the chlorination reaction, and eliminating irreversible and reversible bacterial fouling.
- Moderate sludge volume of chemical nature, and the possibility of extraction of salts and $Mg(OH)_2$

Such technical and economic advantages rendered this system as a fast, clean, and economic one step process.

The increase in TDS value compared to that of initial seawater leads to an increase in osmotic pressure, however the slight increase in TDS recorded (≈2500 mg/L) will not induce a large additional cost on energy input to operate the RO system.

5.2 Recommendations

Based on the results of this study the following recommendations are proposed:

- Performing more experiments under the same condition, thus increasing the number of trials and lowering standard deviations.
- Further characterization and elemental analysis for elements such as Na^+, which will enable the calculation of osmotic pressure change at different pH levels.
- Characterization of the sludge produced after each sequence, and developing methods to benefit from the constituents of the sludge, such as:
    1. The elemental extration of Mg, Ca, and silicates can lead to waste minimization and aleviate costs (Zhang et al., 1997; Nascentes et al., 2001; T. Wang et al., 2008; Xie et al., 2010; Mahmoud & Haggag, 2011; Bortolon et al., 2011).

2. Utilizing salt concentrats via the transformation of NaCl to Na_2CO_3 NH_4Cl, and $NaHCO_3$(El-Yakubu & Ibrahim, 2001) Extraction of salts by solar evaporation (Veza & Rodriguize, 2002).

- The used of scaling software such as SCALE 2000 to accurately define every possibility the effluent water has for scaling the RO membrane.
- Performing a detailed feasibility study after determining the benefit from sludge separation process, and the advantages of anti-scaling characteristics of the effluent on lowering maintenance and membrane changing costs.
- Comparing the cost of the studies system to that of conventional and membrane pretreatment.
- Assessing the efficiency of such pretreatment procedure on other types of saline waters utilized in RO treatment such as brackish water.

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