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Reverse osmosis pretreatment: Quality control to extend membrane life span

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PROFESSIONAL MASTER'S DEGREE

Healthcare Management and Quality

Reverse osmosis pretreatment: Quality control to extend membrane life span

Ramez Mohammad Zayyat

DEDICATION

To my better half

ACKNOWLEDGMENT

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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.

ABSTRACT

With the rapid increase in earth population and human activity comes the increase in water consumption, which intensified water shortages all over the globe; therefore water is rapidly being perceived as a limited resource of high economic value. Brackish water and Seawater Desalination advancements in both thermal and membrane technologies rendered desalination as an important source of drinking water. The uses and application of reverse osmosis technologies has intensified rapidly throughout the globe with the construction of large reverse osmosis plants in arid regions such as Saudi Arabia and the rest of the gulf region. Seawater reverse osmosis is a highly effective desalination process; however the main drawback that has been facing this process is fouling of reverse osmosis membranes including: inorganic, organic, colloidal, and biological fouling. Additionally dealing with reverse osmosis reject is not an easy task; the brine can cause adverse environmental and economic consequences. Lebanon has a somewhat weak infrastructure, with water network wasting of 50 percent, this lead many Lebanese facilities including hospitals to seek alternatives. The most convenient and widely accepted method of water purification became the reverse osmosis. The present study aims at designing a reverse osmosis system with pre and post treatment to provide water with potable quality to a hospital. Additionally, a Laboratory scale reverse osmosis was used to test fouling and scaling information using a sea water reverse osmosis 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. The results of the study showed that fouling and scaling were both highly decreased using softened water of the aforementioned procedure. Membrane autopsies showed a drop of scaling and fouling 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 which completely eliminated bacterial fouling.

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LIST OF ABBREVIATIONS

ACS	American Chemical Society
ADD	Average Day Demand
APHA	American Public Health Association
AWWA	American Water Works Association
B	Boron
Ba	Barium
BDL	Below Detection Limit
BW	Brackish Water
BWB	Brackish Water Brine
BWRO	Brackish water Reverse Osmosis
Ca	Calcium
CEOP	Cake-Enhanced Osmotic Pressure
CESP	Chemically-Enhanced Seeded Precipitation
CP	Concentration Polarization
CRSL	Central Research Science Laboratory
DBP	Disinfection Byproducts
ED	Electrodialysis
EDI	Electrodeionization
EDL	Electrical Double Layer
EDR	Electrodialysis Reversal
EPS	Extracellular Polymeric Substances
ESCWA	Economic and Social Commission for Western Asia

GAC	Granular Activated Carbon
Gpm	Gallons per minute
ICD	Intermediate Chemical Demineralization
IMS	Integrated Membrane Systems
LSI	Langelier Saturation Index
MD	Membrane Distillation
MDC	Membrane Distillation Crystallization
MDD	Maximum Day Demand
MF	Microfiltration
MFI	Modified Fouling Index
Mg	Magnesium
MSF	Multistage Flash
NF	Nanofiltration
NOM	Natural Organic Matter
NTU	Nephelometric Turbidity Units
PEUF	Polymer Enhanced Ultrafiltration
PF	Peaking Factor
RO	Reverse Osmosis
SDI	Silt Density Index
SEM	Scanning Electron Microscope
SI	Saturation Index
Si	Silica
Sr	Strontium
SWRO	Seawater Reverse Osmosis
TDS	Total Disolve Solids

TNTC	Too Numerous To Count
UF	Ultrafilatration
UV	Ultraviolet
VMD	Vaccum Membrane Distillation
ZLD	Zero Liquid-Discharge

CHAPTER 1

INTRODUCTION

1.1 WATER SCARCITY

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 [1]. 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 [2]. 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 [3]. 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 [4].

1.2 BACKGROUND

Desalination is the process of removing salts from water to produce fresh water with total dissolved solids (TDS) less than 1000 mg/L, and is used for both seawater and brackish water. Different countries have different drinking water standards for contaminants; this is also applicable to TDS. Most desalination facilities are designed to achieve a permeate TDS value of 500 mg/L or less [5]. 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 [6].

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 [1]. 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 [4]. 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. 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 [7], and which in turn, is divided into two categories conventional and membrane pretreatment.

1.3 PROBLEM STATEMENT

Reverse osmosis membranes used in water desalination are capable of producing highly purified water by removing all the salts and some other contaminants from different water sources [8-12]. During the past several decades, tremendous strides were made in the research related to development of Reverse Osmosis (RO) membranes, which has resulted in the production of new membranes capable of withstanding wide pH ranges, higher temperatures and pressures, increased flux and reduced solute concentration in the permeate. But unfortunately, with all these new findings, membrane fouling and scaling remain the two major operational and maintenance issues faced by membrane water treatment plant operators. The short-term effects of fouling and scaling are; reduction of treated water productivity, deterioration water quality combined with increase in energy consumption. The long term effect being membrane replacement [13, 14].

Membrane fouling stands as one of the major issues in controlling sustainable operation of both BRWO and SWRO systems as fouling normally leads to deterioration of the basic membrane functions such as salt passage through the membrane, reduction in permeate flux, pressure drop across the membrane due to membrane pore plugging as well as higher operation costs due to higher energy demand, increase of cleaning frequency, and reduced lifetime of the membrane elements [1]. Membrane fouling is normally associated with particulate matter and colloids, organic and inorganic compounds, and biological growth. Colloidal particles are typically composed of clay, organics (where humic substances constitute the major portion in seawater [15]and metal inorganics, while biological fouling is related to the presence of bacteria, fungus and algae where the microbial cells accumulate and attach to the surface of the membrane thus promoting biofilm growth [7]. Membrane autopsies carried out by various researchers have revealed membranes to have deposits of calcium/magnesium phosphonate, calcium alumino silicate, and iron, biological and organic matter [13, 16].

In the Lebanese healthcare sector the most significant costs associated with reverse osmosis plants, aside from the capital cost, are the costs of electricity, membrane replacement, and labor. This study aims at studying different strategies employed to reduce that cost and designing a more cost efficient system for a hospital with well water intake. Hospitals utilize RO membranes to provide fresh water for a variety of usages including:

- Potable Water (provided to stakeholders)
- Service water pumped through the system
- Semi-Distilled water for usage in laundry and related machinery
- Water for formula room

It can be noticed from the usages of RO permeate water in hospitals that the need for a proper evaluation of the water is necessary at all times, the presence of Calcium leads to scaling of pipes machinery and laundry equipment, the presence of bacterium leads to sentinel events. Therefore, the maintenance and proper usage of RO desalination system is vital for any hospital.

1.4 OBJECTIVES

The main aim of this research was to study the effect of operating parameters (transmembrane pressure, crossflow velocity) and solute concentrations (clayand $CaCO_3$) on scaling of a Reverse Osmosis membrane, and clay-$CaCO_3$ interaction on membrane performance as such an RO membrane at the American university of Beirut, using two different types of influent water were operated. Later on membrane autopsy took place to check for fouling and scaling considerations on each membrane. The feed water will be directly withdrawn from a well with brackish characteristics, the second variation of the feed will include the same water exposed to precipitation softening as carried out by Ayoub, et al. [17]. Afterwards permeate and reject characteristics will be analyzed to create a mass balance and account for scaling parameters. PC software including ROSA and Toray DS2 to simulate water passage through the RO membrane were employed to improve the outcome, additionally data acquired was analyzed using statistical modeling such as ANOVA and regressions to check for patterns, correlations and significant effect of different scalents, and anti scalents. Finally the design of a state of the art RO for the hospital was demonstrated with economic feasibility using different methods to avoid membrane scaling in such a facility.

1.5 THESIS OUTLINE

This dissertation is composed of 5 chapters. Chapter 1 introduces the present work. Chapter 2 includes the accumulated knowledge of the author on the topic, every single aspect was expressed in details from current studies ranging throughout the years and including top journals with high impact factors. The concept of RO pretreatment will be introduced along with chemical reactions involved. In addition, research efforts by international researchers/experts in this field will be critically reviewed and summarized. Chapter 3 expressed the methodology by which the experiments, design, and analysis took place, including a detailed report of the standard methods applied and their limitations.

Chapter 4 includes the RO design for the hospital at hand, in addition to the laboratory scale RO system scaling and fouling autopsy result. The Data collected will be used in comparing the efficiencies of the systems under varying operating conditions and determining the efficacy of the system. Finally the future prospective and research opportunities are explained in chapter 5.

CHAPTER 2

LITERATURE REVIEW

2.1 INTRODUCTION

Desalination is a process which provides alternative sources of water, and such a process is becoming the most widely accepted around the globe, never the less limitations to the process are highly affecting the extent of its spread. 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 [6, 18]. 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. There are other desalination technologies as forward osmosis (FO), membrane distillation (MD), capacitance deionization (CDI), and gas hydrates (GH), freezing, humidification dehumidification (HDH) and solar stills many of which are undergoing a phase of research and development (R&D), however non compare to the advantages of using the RO membrane system [19]. Global desalination capacity by continent and by process are shown in Figure 2-1 and Figure 2-2 respectively witch illustrates the dominance of RO and thermal treatment over other technologies [19, 20].

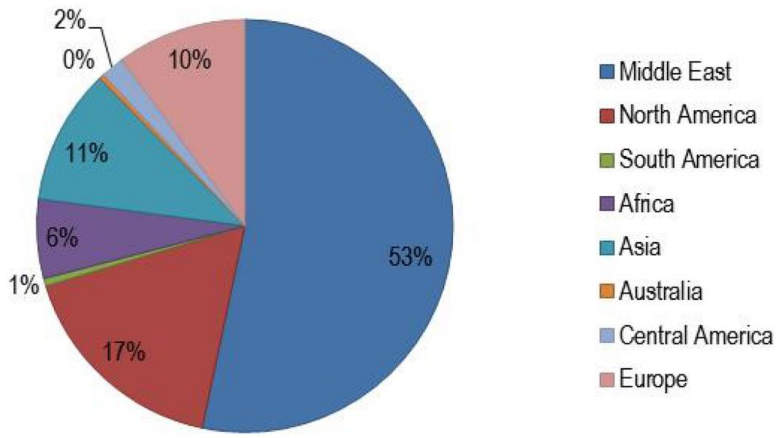

Figure 2-1: Global desalination capacity by continent.

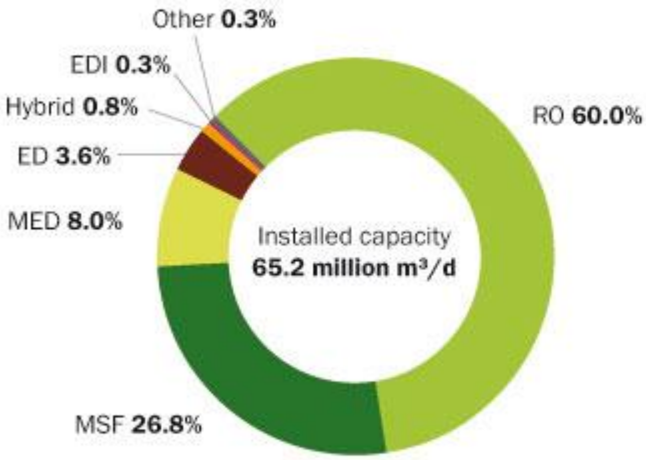

Figure 2-2: Global desalination capacity by process.

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 [21]. 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 [22]. Hospitals are highly affected by fouling, mainly because the water quality is of most importance [23, 24]. 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[6]. When it comes to membrane technologies, both SWRO and BWRO alike have faced constant challenges throughout their development, namely the disposal of the rejected brine/ concentrate, the carbon footprint of desalination plants, membrane sensitivity, and fouling [25]. As membrane fouling and thermal scaling occur, the need for pretreatment in RO and thermal desalination becomes unavoidable. Pretreatment is separated into conventional and membrane pretreatment [26].

2.2 UNDERSTADING THE RO

The definition of RO is the means by which one demineralize or deionize water by pushing it under pressure through a semi-permeable Reverse Osmosis Membrane, while thermal desalination is a processes generally use heat to evaporate water, leaving dissolved constituents behind. When it comes to water desalination, reverse osmosis is a membrane technology that is most widely applied, additionally RO is recently being used in tertiary wastewater treatment. This technology has the advantages of membrane processes such as modular construction and small footprint, which allow the combination with other treatment processes[25]. The difference between osmosis and reverse osmosis is illustrated in Figure 2-3 .

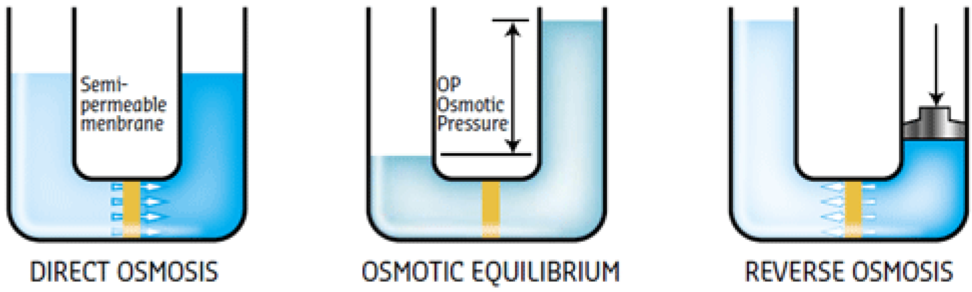

Figure 2-3: Reverse Osmosis vs. Osmosis.

The RO uses a combined amount of semi-permeable membranes that allow to separate a solution into two streams: permeate, containing the purified water that passes through the membrane, and concentrate, the portion that contains salts and retained compounds and therefore needs a suitable and environmentally friendly management option [27]. The desalinated water that was treated is called permeate (or product) water, while on the other hand the water carrying the salts is called the reject (or concentrate) stream [21, 25]. The functioning mode of such a system involves using a high pressure pump to increase the pressure on the salt side of the RO and force the water across the semi-permeable RO membrane, salts rejection rates range between 90 to 99 percent which is concentrated in the reject stream of the system, as such the higher the concentrations of salts and contaminants in the feed water, the more pressure is required to overcome the osmotic pressure[28]. An important notion of RO membrane systems is the cross filtration, as opposed to standard filtration where the contaminants are collected within the filter media, the solution passes through the filter or crosses the filter. The filtered water moves in a separate stream than the contaminated or saturated water, a very clear advantage of such a pathway is the cleanup of membrane surface whereby cross flow filtration allows water to sweep away contaminant build up and also allow enough turbulence to keep the membrane surface clean. According to empirical data RO has the ability to remove 99%+ of the dissolved salts (ions), particles, colloids, organics, bacteria and pyrogens from the feed water, the major factor of the rejection rates of contaminates is the respective size and charge of each contaminant[29]. Any contaminant that has a molecular weight greater than 200 is likely rejected by a properly running RO system (for comparison a water molecule has a MW of 18). Likewise, the greater the ionic charge of the contaminant, the more likely it will be unable to pass through the RO membrane. Removal capacity of RO alongside other filtration processes are illustrated in Figure 2-4. Additionally a model of typical hollow fiber RO membrane is shown in Figure 2-5.

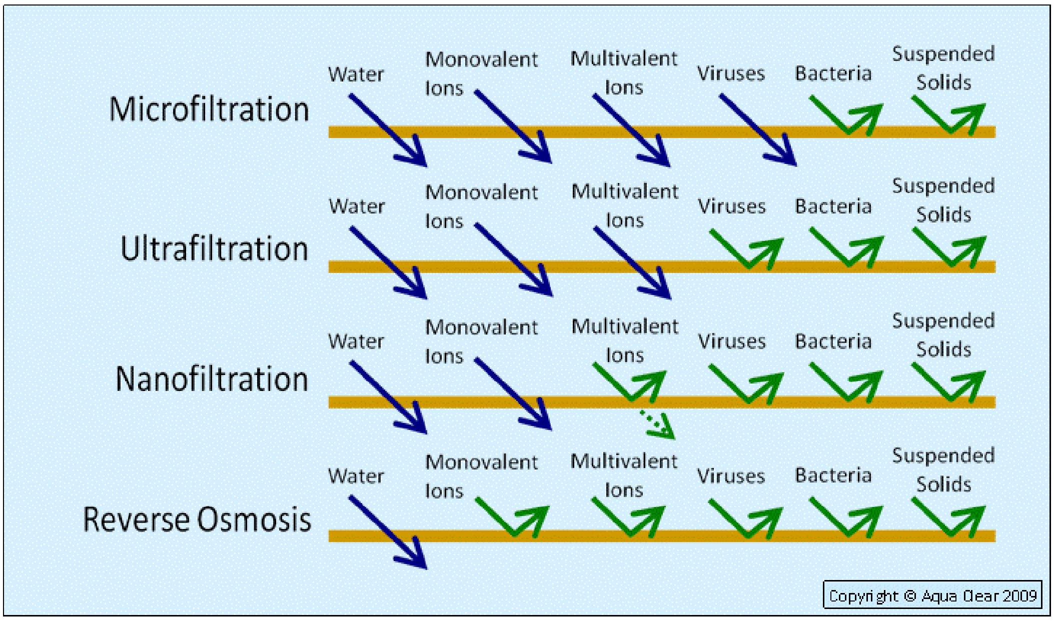

Figure 2-4: Removal capacity of RO NF MF and UF.

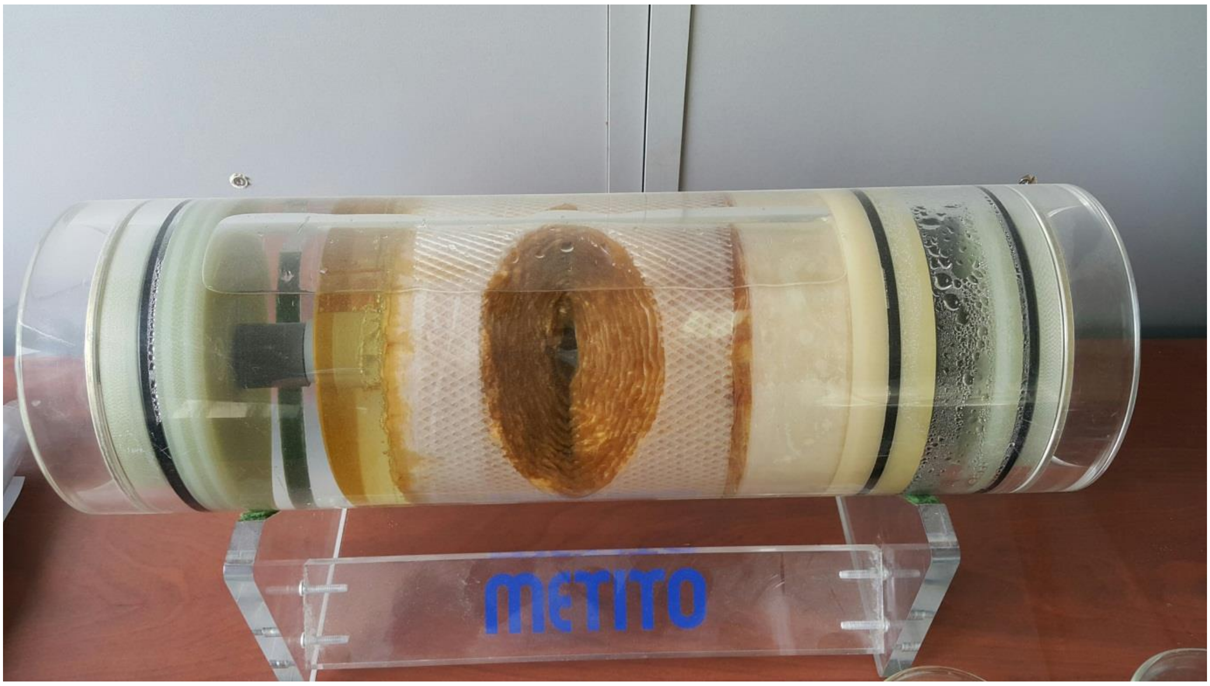

Figure 2-5: RO membrane model.

2.3 MEMBRANE FOULING

The major limitation for RO membrane performance is membrane fouling. Four types of fouling can occur, including inorganic (scaling), particulate, organic and biological. It has been shown that fouling has adverse effects on membrane operation such as an increase in pressure drop, decrease in salt rejection and flux decline [7, 30, 31]. 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 [32]. 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 [33]. 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[34]. Si, Al, Fe, Ca and Mg were found as the major inorganic foulants deposited on the RO membranes[35]. Humic and non-humic NOM is the cause of organic fouling [36, 37]. 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[37]. 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 [38]. Membrane fouling is conventionally measured using two indexes the silt density index (SDI) and the modified fouling index (MFI) [39]. As such the types of fouling in this review will be divided into 4 major categories as proposed by Vrouwenvelder et al. [40-42]:

- Crystalline/ inorganic material: Crystalline Si, Mg, Ca, etc.
- Organic material: humic substances and oils
- Colloidal/ particulate: Clay, humic substances, Si, debris
- Biological: microorganisms forming biofilms on the membrane

According to Chong, et al. [43] the osmotic-resistance filtration model best describes the fouling effect on flux with the following equations:

$$J_0 = \frac{\Delta P - M_0 \Delta \Pi_b}{\mu R_m} \quad (1)$$

$$J_f = \frac{\Delta P - M_f \Delta \Pi_b}{\mu (R_m + R_f)} \quad (2)$$

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 ΔΠb is the osmotic pressure difference between the bulk feed water and the permeate, μ is the feed water viscosity, Rm is membrane hydraulic resistance, and Rf is additional hydraulic resistance caused by the cake layer, M0 and Mf are the concentration polarization (CP) modulus for the clean membrane and that for the fouled membrane[38, 42, 43]. General membrane fouling processes caused by different types of foulants are shown in Figure 2-6 [44].

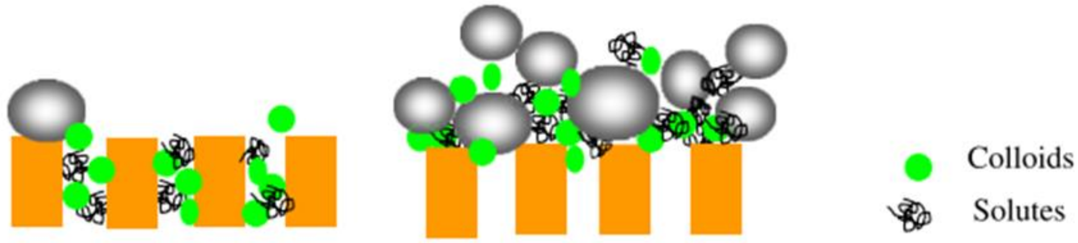

Figure 2-6: Membrane fouling process pore blocking and cake layer.

2.3.1 Inorganic Fouling

The abundance of Mg and Ca compounds in seawater and brackish water composition makes inorganic fouling an expected encounter in SWRO and BWRO respectively. Research conducted by Ognier, et al. [45] 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[46]. 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 [47]. The contribution of inorganic foulants to the overall fouling process was found to be more significant than that of biopolymers due to the fact that inorganic scaling is not easily eliminated by chemical cleansing of the RO membrane[34, 44].

Inorganic fouling can occur in two ways both of which are considered to be precipitative: biological precipitation and chemical precipitation [44]. Meng, et al. [44] 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[34]. 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^-[44]. 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) [48]. 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[44]. Both Inorganic fouling and the formation of bio-cake layer mechanisms are presented in Figure 2-7.

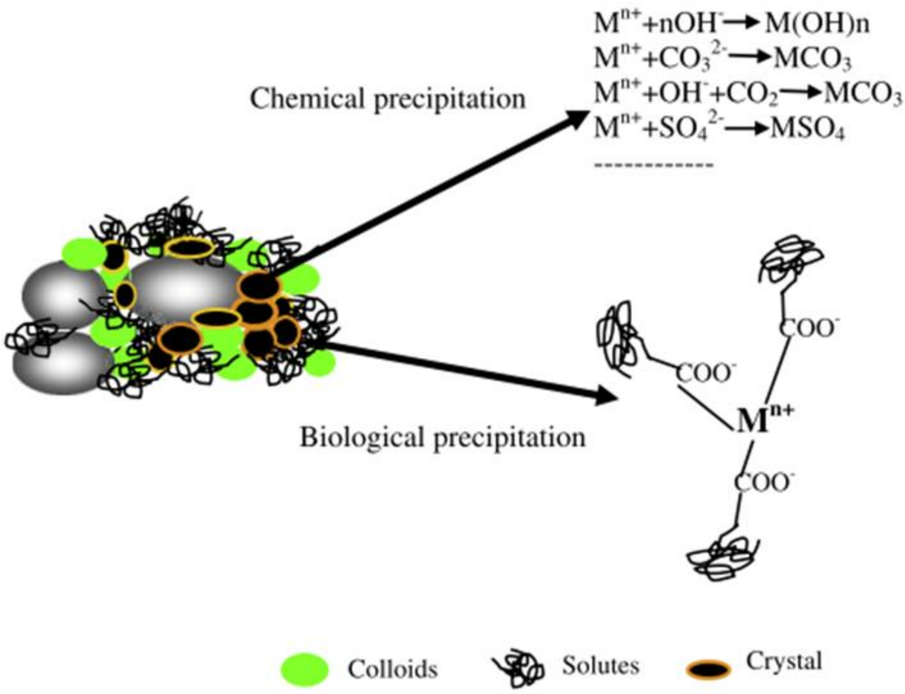

Figure 2-7: Schematic illustration of the formation of inorganic fouling.

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 [49, 50]. 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[17, 49, 50]. 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. 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[50]. 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 [17, 49, 50].

The mechanisms of precipitation of inorganics 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 Mg2+ ions will result in the following reaction [49]:

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

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[51]:

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

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

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

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

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. 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 Ca2+ which might efficiently remove inorganics [51].

2.3.2 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) [52]. Kim, et al. [53] stated that “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.

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 [17].On the other hand chemical dosing will not completely restore the flux in case of irreversible fouling due to the presence of colloidal organic matter and the increase in concentration polarization . 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, an illustration of the two types is presented in Figure 2-6. Organic fouling by NOM is affected by ionic strength (solution chemistry), pH, membrane surface, permeate flux and operating pressure [54]. General effects on NOM fouling in membrane treatment is illustrated in Figure 2-8.

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 [55]. 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. Flux drops were not nearly as extensive in the presence of monovalent ions such as Na^{+}[55].

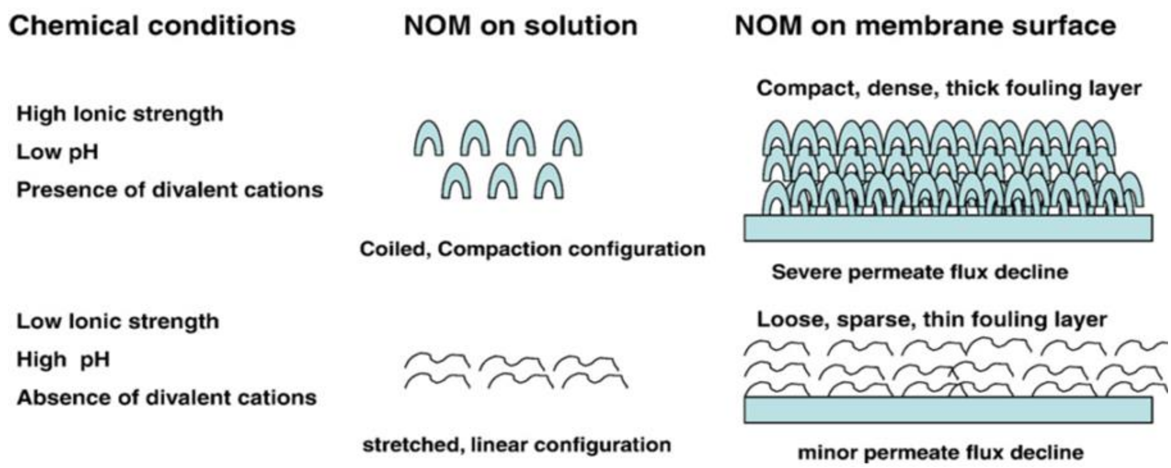

Figure 2-8: Schematic description of the effect of solution chemistry on the conformation of NOM macromolecules in the solution and on the membrane surface, and the resulting effect on membrane permeate flux.

It was also reported that membrane organic fouling potential and its effects on flux loss is strongly dependent on Ca2+ concentration. Greenlee, et al. [21] offered an explanation to the Ca2+ 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 [54]: "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 [21, 39, 55]. Al-Amoudi [54] summarized the methods used in NOM treatment by the following:

- Changing operating conditions (in terms of flux, pressure, etc.)
- Modifying the membrane (surface, type)
- Antifoulants addition to the feed water

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

2.3.3 Colloidal Fouling

Despite developments in research on RO fouling the mechanisms involved in colloidal fouling are still not entirely clear [56].Due to the size of colloids, which range between 1-1000 nm, such particles are capable of severely fouling RO membranes[57]. 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 [58], while organic colloids include polysaccharides, proteins, and natural organic matter [59]. Also present are microorganism cells and cell debris which are classified as bio-colloids [59].

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 [56, 59]. 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.

Valavala, et al. [60] stated that : "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). 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 [60].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 [59]. Colloidal cake formation can be affected by many factors, and according to Tang, et al. [59] factors can be summarized in three groups shown in Figure 2-9.

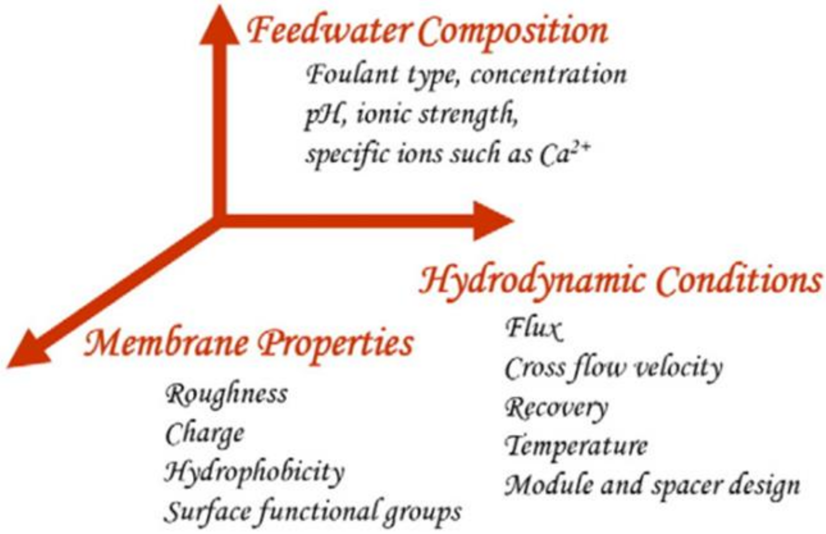

Figure 2-9: Factors affecting colloidal fouling on membrane.

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 [61]. The second factor is the membrane itself, the properties of membranes differ according to manufacturers' preferences, surface roughness, charge properties, and hydrophobicity [62]. In addition, studies reported by Jeong, et al. [63] 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 [56, 59]. A higher cross flow will limit membrane fouling potential due to colloidal particles by reducing the boundary layer thickness and concentration polarization. Temperature variation can also significantly affect colloidal fouling [59]. A scheme of colloidal fouling on the RO membrane surface is shown in Figure 2-10.

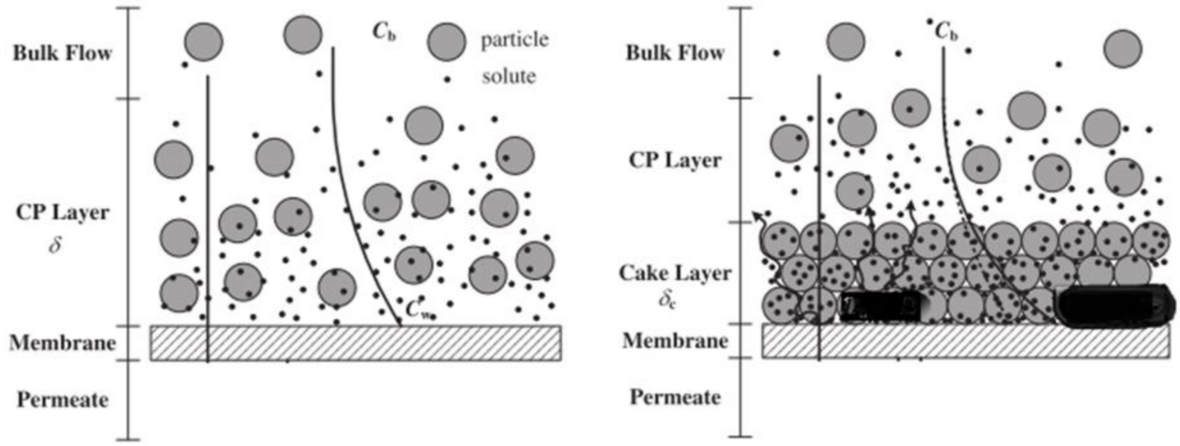

Figure 2-10: Concentration polarization and CEOP (a) before membrane is fouled and (b) after membrane is fouled.

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 [38, 62, 64].The control and removal of colloidal silicates and colloidal sulfate through chemical addition (disinfectants and anticoagulants) proved to be effective. The removal of colloidal silica and colloidal organic matter will be discussed in their respective sections. Some treatment methods employed in removing colloids are:

- Disinfection (to eliminate Bio colloids)
- Membrane cleaning
- Coagulation-flocculation with aluminum sulphate and ferric chloride

The coagulation-flocculation reactions as reported by Kim, et al. [65]:

$$Al_2\ (SO4)_3 + 3\ Ca\ (HCO_3)_2 \leftrightarrow 2\ Al(OH)_3\ (\downarrow) + 3\ CaSO_4 + 6\ CO_2$$

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

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

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

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

2.3.4 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 [53]. 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[31]. Biofouling has already infected 70% of the seawater RO membrane installations [7]. It was found that such fouling occurs even after water intake pretreatment and the addition of Cl disinfectant [31].

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 [31]. Biofilm's physical and physiological properties are reliant on the EPS and the nature of bacterial cells respectively, events through biofilm formation occur as explained by Matin, et al. [7] are presented in Figure 2-11.

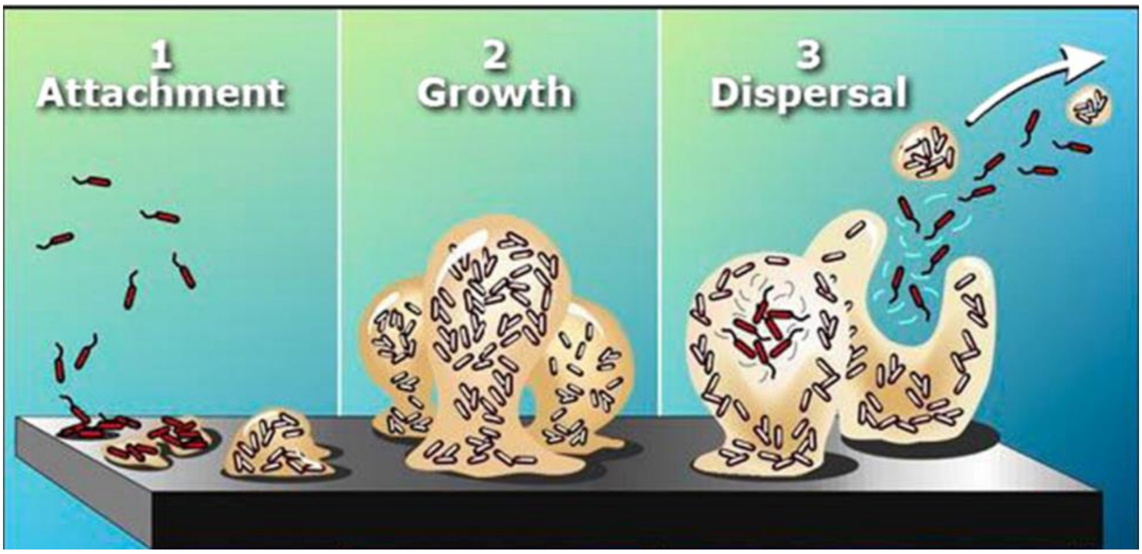

Figure 2-11: of Sequence events leading to the formation of a Biofilm.

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[36, 66]. 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.

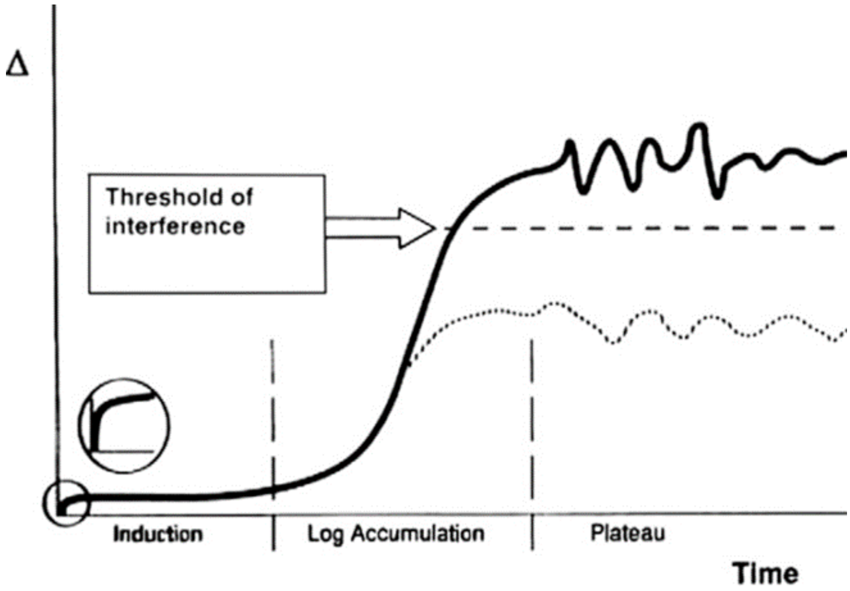

Figure 2-12: Time-dependent development of biofilm accumulation: Δ, biofilm growth parameter (thickness, weight, etc.); inset, primary colonization; threshold of interference, arbitrary extent of biofilm development above which the biofilm interferes with the performance of a membrane system.

According to Matin, et al. [7] “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”

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 4×106 L/day capacity where high electrical pumping costs are needed to maintain operating pressures and constant product output [7]. Biofouling of the RO membrane can be separated into two mechanisms, bacterial cells which 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 EPS contributes to the decrease in flux by increasing hydraulic resistance to permeate flow.

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 [36]. Membrane pretreatment can obtain a lower SDI thus it can be more effective than conventional pretreatment in inhibiting biofouling [42]. The most common method of treatment when it comes to biofouling is the continuous dosage of chemicals which are able to deactivate microorganisms [32, 67]. 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 [7]. Chemical used in disinfection processes include free chlorine (i.e. $HOCl$, OCl^-), chloramines (NH_2Cl), and chlorine dioxide (ClO_2).

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[46]. 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) [46]. 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. Another major disadvantage of ozone usage is the generation of bromine compounds that are carcinogenic and cause membrane surface deterioration [30].

Photochemical inactivation via UV radiation has recently seen a rebirth in usage, it is independent of pH and does not produce disinfection byproducts it should also be noted that both, high and low pH values, result in the inactivation of bacterial and viral content in water [68]. In conclusion all treatment methods adopted for biofouling prevention exhibit advantages and disadvantages.

2.4 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 [69]. Reverse osmosis membranes are very sensitive to foulants such as Si, Colloids, organic matter, bacteria, Ca, and Mg [70, 71], 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 [69]. Pretreatment includes a variety of methods (conventional/membrane) incorporated to alter the components of seawater thus improving the RO overall process [60]. Overall simplified scheme of current pretreatment methods is illustrated in Figure 2-13.

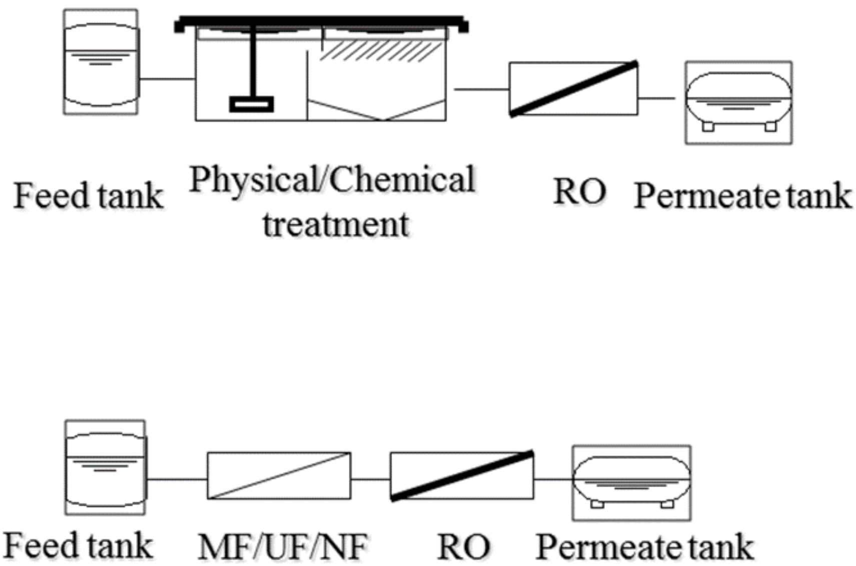

Figure 2-13: Conventional pretreatment and membrane pretreatment.

2.4.1 Conventional pretreatment

Conventional pretreatment typically consists of acid addition, coagulant addition, disinfection, media filtration, and cartridge filtration, and activated carbon adsorption [21]. The first chemical additions, including acid, coagulant, and flocculent, prepare the feed water for granular media filtration[72]. 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 (H2SO4)[70]. According to Ma, et al. [69] the steps of conventional pretreatment are:

“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 [60]. Conventional pretreatment is costly, space-consuming, and the filtrate quality and quantity are usually not steady [29].

2.4.2 Membrane pretreatment

Irreversible RO membrane fouling was reported in many SWRO and BWRO desalination plants even in the presence of conventional pretreatment, due to the passage of colloids and suspended particles through such treatment systems[73], 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[60]. 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[21, 74].

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 Greenlee, et al. [21]:

- Chemistry of the water intake, whereby the quality of the MF/UF product water was found to be independent of feed quality
- Capacity of the system and the space available
- Amount of cleaning or maintenance required for the pretreatment system
- Reliability, capital and operating costs of the NF or RO system reaching an SDI<2

- Turbidity of the pretreated water can be lowered to less than 0.05 NTU

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 and turbidity was recorded to be around 0.1 NTU [73]. 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 [21]. 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[74]. The fact that membrane pretreatment technologies are exposed to fouling just as intensely as the RO membrane itself, coagulation with FeCl3 or Al3SO4 has been successfully used in line with MF, UF, and NF membranes[60].

2.5 RJECT AND BRINE DISPOSAL AND TREATMENT

The properties of the brine are a function of the feed water quality, the desalination process of choice, the recovery rate, and the added chemicals during the process [75]. Disposal and treatment of RO rejects/concentrate from desalination plants is a function of plant location, for example coastal desalination plants directly discharge to seawater, while in inland plants the most widely accepted method is to reduce the concentrate volume prior to disposal [56]. Volume reduction can be easily achieved via evaporation techniques, the main premise of such techniques is to obtain and easily manageable solid waste portion with a decontaminated liquid portion that can be reused [76]. Another aspect is to reduce contaminant load of the reject which occupies a significant amount of allocated funding towards RO optimization R & D. Stanford, et al. [77] elaborated on the beneficial use of brine byproducts and proved the technical feasibility of isolating salts of the required morphology and purity, therefore proving that recovering commercial byproducts from RO concentrates would be the optimum treatment option, as it solves the environmental problem of concentrate disposal, as well as the economic profitability of reverse osmosis is improved at the same time.

Malaeb and Ayoub [25] Conducted an extensive literature review and summarized the **t**raditional treatments available for reject disposal such as evaporation and crystallization other technologies that have emerged in recent years to reduce the volume of the concentrate before disposal, the WWTP section focused on reducing the organic pollutant load through the application of innovative advanced oxidation technologies as shown in

Table 2-1.

Table 2-1: Evaluation of viability of treatment technologies applied to RO concentrates.

RO concentrates source	Technology	Technological maturity	Operation drawbacks and economic considerations
Desalination plants	Solar evaporation (Evaporation ponds)	Industrial application	Large land areas
			Low productivity
			Moderate investment and maintenance cost
	WAIV *wind aided intensified evaporation*	Pilot plant scale	Industrial feasibility not proved
			Moderate investment cost
	Membrane distillation	Laboratory level	Difficult operational control
			Scaling and fouling
			Moderate energy consumption
	Forward osmosis	Laboratory level	Use of drawn solution
			Moderate energy consumption
	Liquid–liquid extraction	Laboratory level	Several treatment stages
			Extractants consumption
Wastewater treatment plants	Ozonation	Laboratory level	High chemical dosage
			High investment cost
	Fenton processes	Laboratory level	High chemical dosage
			Moderate investment cost
	Photocatalysis and photooxidation	Laboratory level	High chemical dosage
			Moderate energy consumption
	Sonolysis	Laboratory level	High energy consumption
	Electrochemical oxidation	Laboratory level	High energy consumption
			Moderate investment cost
	Adsorption	Laboratory level	Regeneration of exhausted resins (High chemicals consumption)
Desalination and wastewater treatment plants	Electrodialysis	Pilot plant scale	Maintaining energy efficiency with high saline concentrates
			Precipitation on the membrane
			High capital and operation cost
	Crystallization	Laboratory level	Stricted operational conditions
	SAL-PROC	*Patented process*	*Applicability to RO concentrates not completely proved*
Other industrial sources	EFC	Pilot plant scale	Complex control of operation
			Moderate energy consumption

2.5.1 Brine Disposal

Managing brine can from RO plants can prove to be a difficult task, both economic and environmental aspects of the process need to be addressed. For example; evaporation ponds, can be reasonably priced but require land availability and pose a significant risk of flooding and leakage of salts and adverse chemicals into the soil or groundwater[78, 79]. In some regions, irrigation using the brine can be implemented, however the adverse effect on plant growth and salt levels in the soil has proven to be a serious issue [80]. Estuaries or lakes discharge may disturb the stability in the aquatic ecosystem, thus impairing the livelihood of certain sensitive species, since it may have up to ten-fold the concentration as the raw water, containing toxic chemicals, with an even higher density [78, 81]. Other discharge methods include land disposal in unlined surface depressions, addition of the reject flow to a wastewater stream, further concentration into solid form, and injection below water aquifers [28, 80]. And additional problem to discharge of brine arises when the fact that high temperature brine disposal gets into the picture, BWRO plants seldom discharge brine at high temperatures, so thermal pollution to the receiving habitat is not a serious concern[82]. Yet, brackish water reject tends to be more difficult and perhaps more costly to manage, particularly if the RO plant is located away from the coast or from any wastewater network that would otherwise facilitate the selection of disposal technique[10, 83]. As well, costs of brine disposal are subject to regulatory enforcement, and they are affected by the quality and quantity of the concentrate [28, 80, 84, 85]. According to the ESCWA, concentrate disposal expenses can account for up to 33% of total costs in a desalination plant, especially so for inland BWRO plants due to the limited availability of disposal options [17, 25].

2.5.2 Brine Treatment

It is important to add that in some cases, the brine undergoes treatment, depending on local environmental guidelines and on the disposal option selected. These include, but are not limited to, disinfection, aeration, degasification, and other processes [25]. The ideal target would be to minimize liquid effluent and recover useful or valuable products from the brine, transforming the waste into commodity [75, 76, 79]. Precipitation or lime and soda ash softening has also been tested for treating RO concentrate by effect of pH increase, in order to aid in the removal of certain scaling precursors like calcium, magnesium, and barium [10, 84, 85]. Moreover, carbon dioxide air stripping was explored as a method to enhance calcium precipitation by pH increase for BWRO concentrates with high carbonate concentrations. According to Malaeb and Ayoub [25] “Membrane distillation has been studied as alternative for the processing of highly concentrated aqueous solutions. Vacuum Membrane Distillation (VMD) is an evaporative technology that uses a membrane to support the liquid–vapor interface”. Additionally Urtiaga, et al. [86] studies the main advantages of membrane distillation over conventional distillation processes are that the operating temperature is in the range of 60–80°C and that the membranes provide a high contact area per unit of equipment volume, allowing very compact installations and reduced footprint. Mericq, et al. [87] Assessed such systems at higher yield (40000 m^3/d) and concluded that recovery has increased by a significant fraction of 40% to 89% of water after coupling the RO with VMD.

Another advanced treatment option for RO brine is the coupling with Membrane distillation-crystallization MDC (only applicable with seawater RO brine with TDS >50,000 ppm) [88]. MDC process allows crystallization via super salt saturation which is turn allows its crystallization [89]. The MDC employs hollow fiber membranes to reach a high contact state which allows the process to achieve reliable evaporation fluxes at moderate temperatures (40–50 °C) with energy consumption of about 15–20 kW h/m^3 half the energy requirement of the conventional treatment process which is about 30 KW h/m^3 [90].

2.5.3 Zero Liquid Discharge Systems

Some efforts include selling recovered salts and byproducts, irrigating salt-tolerant crops, cultivating marine species like brine shrimps, and applying the zero liquid-discharge concept (ZLD) [19, 75, 79]. ZLD can be achieved once the recovery reaches 100% approximately, where all the salts are retrieved and good-quality water is produced [21]. Some attempts toward ZLD include intermediate chemical demineralization (ICD) processes like using seawater RO along with further chemical addition to induce precipitation for BWRO concentrate, where Gabelich, et al. [10], [91] accomplished higher removal levels of calcium, strontium, barium and silica. As well, electrodialysis (ED) and electrodialysis reversal (EDR) can give higher recovery than RO when used in several stages [28, 80, 84, 85]. Also, since the presence of antiscalants and major scale-causing species, such as silica and barium sulfate, hinders the effectiveness of the mentioned processes, researchers have examined treatments like ozonation for their removal [74, 83, 92]. Experiments have been conducted using membrane distillation (MD), a cross between membrane and thermal processes, to effectively concentrate a groundwater RO reject [25, 93]. The salt recovery scheme for a sample ZLD is illustrated in Figure 2-14 [84, 85].

2.6 CONCLUSION

RO technologies are continuously advancing throughout the years, R& D efforts towards optimizing RO systems and its related fields are widely practiced throughout the globe. Such actions rendered RO as the optimal system for both sea and brackish water desalination. Even though the RO system possesses some disadvantages such as membrane fouling and scaling, solutions to limit such issue are always available. Pretreatment of water intake is a must in almost all systems, this includes conventional pretreatment which has been employed for more than three decades. Alternatives to such systems are the membrane pretreatment which is more adequate and aids in conserving the RO membrane and eventually a better quality of product water. However the cost of such systems might vary tremendously, some of which are much higher than that of a conventional pretreatment. Brine disposal and management is a new trend in the RO industry due to raised awareness towards ecological and environmental matters, new systems with ZLD aided in transforming the RO technology into a green technology.

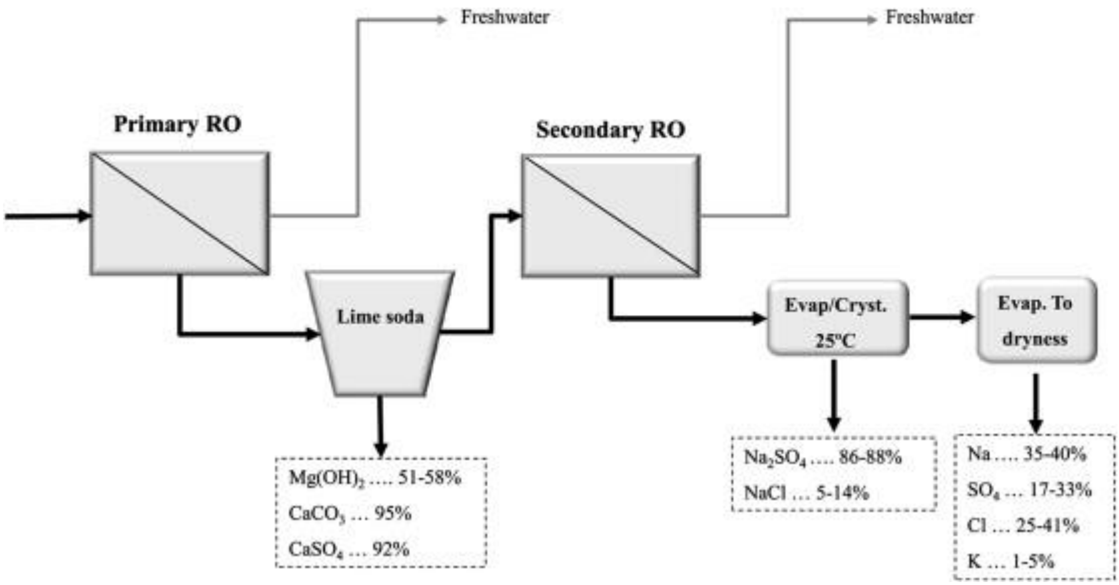

Figure 2-14: ZLD Salt recovery scheme used by Mohammad Esmaeili.

CHAPTER 3

RESEARCH DESIGN AND METHODOLOGY

3.1 INTRODUCTION

The proposed research entailed the collection of brackish water, which was obtained from a groundwater well with slightly high salinity (TDS) in Tyre, South Lebanon. This particular well water was selected based on prior laboratory analysis showing that its chemical constituents are comparable with those of other typical brackish waters reported in the literature.

3.2 WATER INTAKE

The proposed research entailed the collection of brackish water, which was obtained from a groundwater well with slightly high salinity (TDS) in Beirut, Lebanon. This particular well water was selected based on prior laboratory analysis showing that its chemical constituents are comparable with those of other typical brackish waters reported in the literature. Three 500 L tanks were used to collect and transfer the brackish water from the sampling location to the American University of Beirut. The water was stored in the 500 L tanks over a period of 5 months from October 2016 until the end of the experiment on the beginning of March 2016. All storage tanks were cleaned and rinsed twice with the sample water itself before filling and storage. The second type of feed was that of alkalized pretreatment using NaOH:Na2CO3 1:1 as explained by Ayoub, et al. [17].

Figure 3-1: 500 Liter tanks employed for water storage.

3.3 EXPERIMENTAL SETUP

A household RO membrane setup was obtained due to the courtesy of Mr. Mohammad Zayyat shown in Figure 3-2 a 500 liter Tank was connected to the RO with a head of 2 meters. A pressure tank was installed to regulate pressure accordingly.

Figure 3-2: Household RO system.

The two types of feed water were passed through the RO system at hand, after 1000 liters of feed 1 the membrane was changed and 500 to 600 liters of feed 2 was passed.

Membranes were collected and placed on the proper autopsy setup holder as shown in Figure 3-3.

Figure 3-3: Membrane and Autopsy Preparations.

3.4 PRODUCT AND REJECT

BWRO and BWRO product water were collected after the process of a Laboratory scale RO system. The water was stored in 20 liter gallons at 23-25 degrees Celsius for the span of the experiment. The BWRO membrane was placed at American University of Beirut, Faculty of Engineering, chemical engineering Lab FS1 at around 50% recovery rate.

3.5 TESTING AND ANALYTICAL PROCEDURES

Within the objectives of the research at hand, both types of the sample water were analyzed frequently based on the standard methods by APHA, AWWA and ACS for the following parameters: pH, temperature, conductivity, TDS, TSS, VSS, calcium, magnesium, silica, iron, boron, strontium, barium, sodium ions, and fecal and total coliform. The experimental study was carried out at the Environmental Engineering Research Center at AUB, over a year’s time, with a total of 6 months of uninterrupted laboratory work. These experimental conditions were chosen to be consistent with findings from the literature and previous work done in this field of study and are presented in Appendix A.

Software used for analyzing data was Minitab, Excel and phreeqc. Phreeqc was used to determine the actual variation between the theoretical settling material and those who fouled the RO membrane. Additionally ROSA and TORAY DS2 were used to check the hospital RO design system. A comparative analysis was performed in comparison to program simulation data and that obtained in laboratory testing.

3.6 MEMBRANE AUTOPSY

As demonstrated in Figure 3-4 the membrane was placed on a membrane holder and the adhesive layer was carefully removed. Contact with hands was avoided at all times due to contamination risk.

Figure 3-4: Membrane autopsy setup.

The membrane was separated into two parts, membrane layers and spacers. Spacers are not of huge significance as they do not hold any deposits; the purpose of the spaces is to

The fouling is principally a result of dissolved organic material, or fine suspended solids that have made it past the pre-filter system. As such samples collected shown in Figure 3-5 will be analyzed for total organic Carbon, Total Carbon, Total inorganic Carbon using Shimadzu TOC analyzer TOC-V CSH with Solid sample module SSM 5000A. The next step was to collect foulant off of the membrane sheet, and analyze it for chemical composition using SEM.

Figure 3-5: Membrane surface foulant removal.

3.7 MEMBRANE SURFACE ANALYSIS BY SEM

The SEM (scanning electron microscope) enables an investigator to create and examine an image of the morphological features of a material. The SEM creates a seemingly three-dimensional image of material by bombarding it with a focused electron beam. It is used to characterize particle size, shape, texture, and topography. In this research it was employed to determine the chemical (elemental) composition by measuring the energy of characteristic X-rays emitted when the material is bombarded by the SEM electron beam. Scanning electron microscope-energy dispersive spectroscope capability offers timely, comprehensive, accurate data analysis and evaluation. The SEM from TESCAN, VEGA 3 LMU with OXFORD EDX detector (INCA XMAW20) present at CRSL AUB is show in Figure 3-6. Samples obtained from the RO membranes were attached to a High Purity Conductive Carbon Tabs, 12mm double coated from PELCO Tabs™ Figure 3-7. The samples were later placed into the SEM for analysis. Elemental analysis was performed using INCA software provided by Oxford-Instruments.

Figure 3-6: SEM at CRSL AUB.

Figure 3-7: Double coated carbon tabs with adhesive layers.

3.8 CONCLUSION

The autopsy carried out will provide a good understanding of how composites of foulants damage the RO membrane, coupled with phreeqc the study will show the proximity of simulation software to real life conditions. This will aid in limiting and understanding such fouling in the near future. The design of water treatment system to a given hospital will also aid in proving the point that fouling is a major issue and must be addressed in any system available.

CHAPTER 4

RESULTS AND DISCUSSION

4.1 DESIGNING A WATER SUPPLY SYSTEM FOR A HOSPITAL

Prior to designing the actual system the water demand of such a facility need to be calculated, additionally strategic choices should be made depending on the resources available. Major considerations for such a facility are listed below:

1. Water network status
2. Water intake (seasonal and yearly data must be present)
3. Continuous funding (maintenance and operation)
4. Staff training and availability(proper management is key)
5. Design parameters

4.1.1 Water Network Status

The hospital at hand has a relatively good water distribution system, nevertheless it should be noted that the system is linked to the entire facility, as such the RO water will be used for the entire operations available at the hospital which includes but not limited to: Toilets, floor cleaning, AC systems, medical operations, patient rooms, laundry, and external services.

It can be argued that many operations does not require high quality water permeate that will be produced via the designed RO unit while other operations such as Kidney dialysis require water of higher purity reaching MilliQ water grade levels. In simple terms changing the entire system network or separating the network to compensate for such water demand is too costly and present little economic feasibility. As such for the current study this option will be discarded.

4.1.2 Water intake

In order to properly design an RO system, the water intake constituents should be analyzed, as such both the water parameters and system design information are presented in Table 4-1 and Table 4-2 respectively.

Table 4-1: Brackish water analysis.

Parameter	Unit	Brackish water		
		Number of Observations	Mean	Standard Deviation
pH	pH units	11	7.54	0.1
Temperature	ºC	11	25.3	1.7
Conductivity	mS	2	10.62	0.1
Total Dissolved Solids	mg/L	2	5305	49.5
Total Suspended Solids	mg/L	4	34	15.5
Volatile Suspended Solids	mg/L	4	33.33	20.8
Alkalinity (hydroxide)	mg/L as $CaCO_3$	7	0	0
Alkalinity (carbonate)	mg/L as $CaCO_3$	7	0	0
Alkalinity (bicarbonate)	mg/L as $CaCO_3$	7	113.2	25.9
Alkalinity (Total)	mg/L as $CaCO_3$	7	113.2	25.9
Ca Hardness	mg/L as $CaCO_3$	18	920.6	115.02
Mg Hardness	mg/L as $CaCO_3$	18	1625.6	168.8
Total Hardness	mg/L as $CaCO_3$	18	2524.4	148.9
Chlorides	mg/L	14	3812.9	80.4
Silica	mg/L as Si	17	4.2	1.3
	mg/L as SiO_2	17	9.02	2.5
Fe	mg/L	4	0.04	0.004
Boron	as B (mg/L)	6	1.92	0.4
	as H_3BO_3 (mg/L)	6	10.93	2.5
Strontium	mg/L Sr	7	5.56	1.5
Barium	mg/L Ba	4	BDL	BDL
Sodium	mg/L Na	5	1695.96	216.5
Potassium	mg/L K	2	18.49	4.2
Fecal Coliforms	CFU in 100 mL After 24 hrs	3	4	NA
Total Coliforms	CFU in 100 mL After 24 hrs	3	150	NA
Biochemical oxygen demand	mg/L O2	**4**	**59**	**5**
Chemical oxygen demand	mg/L O2	4	180	10
Total Organic Carbon	mg/L C	**4**	**25**	**2**
Nitrate	mg/L $NO3^{2-}$	8	10	2
Nitrite	mg/L NO2-	**8**	**0.2**	**0.005**
Ammonia	mg/L NH3+	8	0.1	0.014
Ortho phosphates	mg/L PO_4^{2-}	**8**	**2**	**0.1**
Sulfide	mg/L S^{2-}	8	2.2	0.1
Sulfates	mg/L SO_42-	**8**	**19**	**3**
Calcium	mg/L Ca	**4**	**362**	**20**
Magnesium	mg/L Mg	4	395	15
Manganese	mg/L Mn	4	2	0.04
Aluminum	mg/L Al	**4**	**0.5**	**0.1**
Turbidity	NTU	**5**	**80**	**4**
Silt Density index	SDI	5	3	NA

*BDL Below Detection Limit **NA not applicable

Table 4-2: System design information.

BWRO	
Flow (Cubic meters/day)	121.2
Flow (Cubic meters/hr)	5
Expected Recovery	85-90 %
Water Temperature range	21-28
Design Temperature	25
System placement	Indoors
Pretreatment (type)	Conventional
Water Source	Well water
Water type	Brackish
Bacterial Control	Yes
Chemical Additions	Antiscalent, Acidification, chlorine
Dechlorination	Yes, GAC
Water Application	Potable water
Water feed type	Continuous

The membrane system is a complete plant with an inlet for feed water and outlets for permeate and concentrate. The most important aspect while designing an RO system is characterized by permeate flow and quality. The goal of the designer of an RO system for a certain required permeate flow is to minimize feed pressure and membrane costs while maximizing permeate quality and recovery.

4.1.3 Flow considerations

The design of RO systems normally use continuous flow into consideration, however it is possible to design the system based on batch process. For this study the hospital operates the RO on continuous bases.

As such the water demand for such a facility needs to be calculated. It should be noted that the realistic demand for any entity is not easily obtained; flow meters need to be installed over a period of time on an existing system to achieve such an accurate result. Therefore total theoretical demand for a water supply system is the next step to be determined in this study. Such a demand can easily be calculated by adding known maximum demand for all fixtures in the system. As explained in the previous section, the flow will be calculated based on continuous operation and water usage, while in real life the nature of water usage is intermittent which insures that demand will never exceed the designed water supply.

Water system source, treatment, and equalizing storage must be designed to meet the MDD for the water system. Prior to calculating the MDD, ADD should be calculated as a total sum of separate consumptions at the hospital as elaborated in Table 4-3.

Table 4-3: Average Day and Maximum Day Demand Calculation.

	Per unit consumpion (L/day)	Number of Units	Water Consumption
Hospital beds	290	200	58000
Staff	50	450	22500
Auxiliary departments	3500	1	3500
Laundry	10000	1	10000
ER	3000	1	3000
outpatient Clinics	200	20	4000
		Total Consumption (L/day)	101000
		Average day demand (m^3/day)	101
		Peaking factor	1.2
		Maximum day demand (m^3/day)	121.2

4.1.4 Calculating number of elements and pressure vessels

RO elements represent the membranes present in the system; Governing factors in element type selection are feed water salinity, feed water fouling tendency, required rejection and energy requirements. Different elements have different sizes and surface areas which determine the optimal functionality and application. Guidelines followed in this study are FILMTEC™ which state element size for systems greater than 10 gpm (2.3 m^3/hr) is 8-inch in diameter and 40-inch long.

Next step is to select the flux and the SDI, which will be obtained from empirical data published in the membrane system design section from FILMTEC™. Thus the flux value used will be 22 liters per cubic meter hour (L/m^2h), and the SDI will be set to < 3.

Using the MDD as permeate flow, divide the design permeate flow rate Qp by the design flux f and by the membrane surface area of the selected element SE (ft^2 or m^2). The Surface area of every type of membrane is also provided by the company as to obtain the number of elements NE as shown in

$$N_E = \frac{Q_p}{f.S_E}$$

$$N_E = \frac{120\ m^3/d \times\ 41.7(L/hr)/(m^3/d)}{22\ L/mhr \times 37.2m2} = 6.1 \cong 7$$

4.1.5 Number of Vessels, Stages and Staging Ratio

In order to obtain the number of pressure vessels divide the number of elements NE by the number of elements per pressure vessel, NEpV. For large systems, 6-element vessels are standard.

$$Nv = \frac{N_E}{N_{EpV}}$$

$$Nv = \frac{N_E}{N_{EpV}} = \frac{7}{6} = 1.17 \cong 2$$

As such the total vessels so far should be 2 containing 4 and 3 respectively, another design alteration in this case can be using 2 vessels with each containing 4 elements to decrease pressure on each individual element.

After calculating the number of vessels in the system, the next step is to determine the number of stages, which defines how many pressure vessels in series the feed will pass through. A single stage contains a number of pressure vessels arranged in parallel, a schematic of a multi stage system is shown in Figure 4-1.

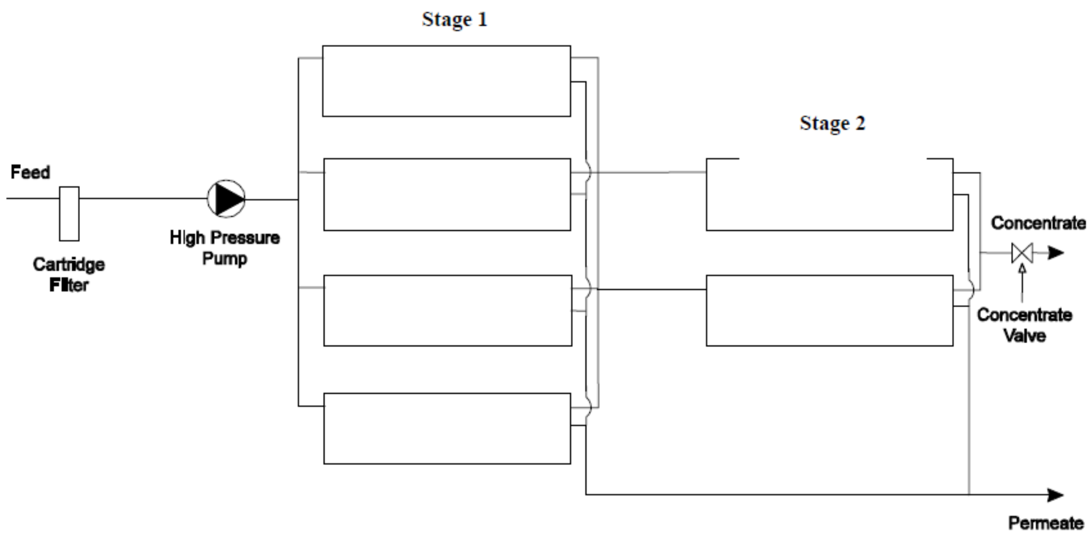

Figure 4-1: Multi stage RO system.

Additionally the number of stages is proportional to the planned water recovery which is highly dependent on feed water quality and the number of elements calculated in the previous section. The higher the system recovery and the lower the feed water quality, the longer the system will be with more elements in series.

Typically, the number of serial element positions is linked with the system recovery and the number of stages as illustrated in Table 4-4 for brackish water systems and Table 4-5 for seawater systems.

Table 4-4: Number of stages for BWRO.

System Recovery	Number of Serial elements positon	Number of stages
40-60	6	1
70-80	8-12	2
85-90	18	3

Table 4-5: Number of stages for SWRO.

System Recovery	Number of Serial elements positon	Number of stages 6 element vessels	Number of Stages 7 element vessels
35-40	6	1	1
45	7-12	2	1
50	8-12	2	2
55-60	12-14	2	2

After analyzing the water quality in Table 4-1 BWRO is mostly effective at a TDS range 500 mg/L up to 8000 mg/L which is the accepted range for our water quality. Thus the number of stages for our system will be 2 stages with 8-12 serial elements in order to achieve a recovery percentage of at least 75.

The final step is to calculate the staging ratio which represents the relation of the number of pressure vessels in each stage.

$$R = \frac{Nvi}{Nvi + 1}$$

According to Filmtec in two-stage seawater systems with 6-element vessels, the typical staging ratio is 3:2. For this study ideal staging of the system will be calculated to account for each stage operating at the same fraction of the system recovery, provided that all pressure vessels contain the same number of elements which was accounted for in the current design in the previous section. The staging ratio R of a system with n stages and a system recovery Y (as fraction) can then be calculated:

$$R = \left[\frac{1}{1 - Y}\right]^{\frac{1}{n}}$$

$$R = \left[\frac{1}{1 - 0.5}\right]^{\frac{1}{2}} = 1.4142$$

Total number of vessels calculated at 2 from before will be applied to calculate the first stage number of vessels:

$$1.4142 = \frac{2}{Nvi + 1}$$

$$Nvi = 1.17$$

Which will be rounded to the largest number, as such 2 vessels with 4 elements each in stage 1. For stage 2 the number of vessels calculated was 1 according to the equation below:

$$Nv2 = \frac{Nv1}{R} = \frac{1.17}{1.4142} = 0.83$$

Therefor in theory the system will have 2 stages with 2:1 ratio of vessels and 3 elements in each vessel of stage one and 2 elements in stage 2 summing up to 8 elements which meets the requirements of BWRO design in Table 4-4. However in order to improve membrane life span and lower cost for 121.2 cubic meter flow, a third stage can be added dividing the total number of elements on 3 stages leaves us with the ratio of 4:3:1.

4.1.6 Balancing and comparing results with Toray DS2

The membrane simulation returned 62 percent recovery for the given water intake, basically due to the lack of pretreatment which leaves a high SDI. As such the membrane rejection efficiency is decreased, never the less to keep the system running and intact percent recovery can be lowered in addition to reject recirculation as shown in Figure 4-2 and Tables (see Table 4-6 to Table 4-8).

Toray returned the following data for the RO water intake reject and product, which makes it easy for the designer to estimate energy consumption and create a proper operation and maintenance report tailored for this specific design based on fouling data and membrane deterioration provided by the software. The addition of Phreeqc data in later section can also be employed for the same purpose.

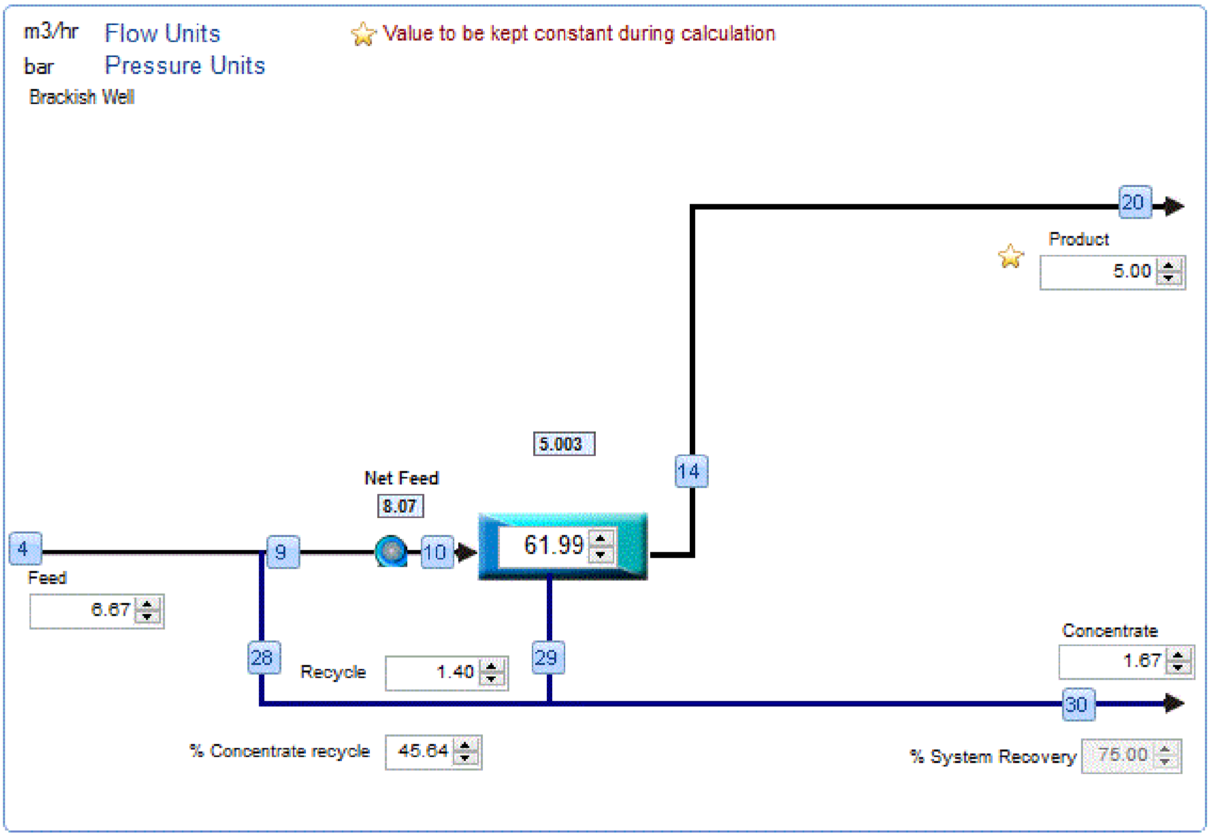

Figure 4-2: Flow diagram for Designed RO system.

Table 4-6: Toray DS2 Status for Run at 62 percent recovery.

Parameter	Unit	Pass 1
Raw water TDS	mg/l	7,570
Feed EC @25C / @15.00C	uS	12,884.3 / 10,041.8
Feed Pressure	bar	26.65
Temperature	deg C	25
Total DP	bar	0.388
Brine Pressure	bar	26.26
Fouling Max	4 yrs	0.8
SP % Increase (Max)	4 yrs	33.10%
Recovery	%	62.00%
Feed Flow	m^3/hr	8.07
Recycle Flow	m^3/hr	1.4
Product Flow	m^3/hr	5.002
Average Flux	$l/m^2/hr$	26.92
Concentrate Flow	m^3/hr	1.668
Product TDS	mg/l	60.97
Concentrate TDS	mg/l	19,813
Primary HP Pump kW	kilowatt	7.51
Power Consumption	kWh/m^3	1.501

Table 4-7: Simulation Software Ionic concentrations.

Ions	Unit	Concentrate	Product
Ca	mg/l	502	0.542
Mg	mg/l	692.8	0.748
Na	mg/l	5,688	20.41
K	mg/l	208.8	1.144
Ba	mg/l	0.279	0.0003
Sr	mg/l	7.015	0.0076
NH_4	mg/l	0.0393	0.0002
Fe	mg/l	0	0
HCO_3	mg/l	981.4	4.069
CO_3	mg/l	7.168	0.002
CO_2	mg/l	20.52	19.122
Cl	mg/l	10,189	31.9
SO_4	mg/l	1,488	1.922
NO_3	mg/l	15.07	0.0949
F	mg/l	1.178	0.0073
Br	mg/l	0	0
PO_4	mg/l	0.0399	0
SiO_2	mg/l	33.22	0.124
B(Boron)	mg/l	0	0
TDS	mg/l	19,813	60.97
Feed EC @25C / @15.00C	uS	31,123 / 24,390	123.8 / 95.3
pH	pH	7.797	5.512
Osmotic Press (DS1 / Pitzer)	Bar	13.894 / 13.18	0.047 / 0.06
LSI / SDSI		1.44 / 0.75	0.956822107
$CaSO_4$ / $SrSO_4$ %	%	23.0% / 10.4%	0.0% / 0.0%
$BaSO_4$ / SiO_2 %	%	970.7% / 31.0%	
Pitzer % Solubility	Calcite/Dolomite	1,052% / 85,797%	
Pitzer % Solubility	CaSO4/$SrSO_4$	26% / 17%	

Table 4-8: Toray DS2 results by stage.

Stage/Bank Data		Stage 1	Stage 2	Stage 3
Lead Element Type		TM720D-400	TM720D-400	TM720D-400
Last Element Type		TM720D-400	TM720D-400	TM720D-400
Total Elements	8	4	3	1
Total Vessels	3	1	1	1
Elements per Vessel		2	2	1
Feed Flow	m^3/hr	8.07	5.641	3.756
Product Flow	m^3/hr	2.429	1.885	0.689
Average Flux	$l/m^2/hr$	32.68	25.36	18.537
Brine Flow	m^3/hr	5.641	3.756	3.068
Recovery %	%	30.09%	33.41%	18.34%
Feed Pressure	bar	26.65	26.43	26.3
dP Elements	bar	0.22	0.127	0.0406
Boost Pressure	bar	0	0	0
Piping Loss	bar	0	0	0
Net (Boost - dP piping)	bar	0	0	0
Brine Pressure	bar	26.43	26.3	26.26
Permeate Pressure	bar	0	0	0
Feed TDS	mg/l	7,570	10,815	16,205
Perm TDS	mg/l	33.94	69.65	132.5
Lead Element	Pass1	Stage 1	Stage 2	Stage 3
Feed Flow	m^3/hr	8.07	5.641	3.756
Product Flow	m^3/hr	1.27	1.022	0.689
Product TDS	mg/l	28.77	56.74	132.5
Flux	$l/m^2/hr$	34.19	27.51	18.537
Last Element	Pass1	Stage 1	Stage 2	Stage 3
Product Flow	m^3/hr	1.158	0.863	0.689
Product TDS	mg/l	39.62	84.93	132.5
Brine/Product Ratio	ratio	4.871	4.353	4.453
Brine Flow	m^3/hr	5.641	3.756	3.068
Net Driving Pressure	bar	17.063	12.738	10.187

4.1.7 Pretreatment

Two errors were returned by the design program, scaling and fouling might occur and highly impact membrane life span, flux, permeate and concentrate water quality, and as such a proper pretreatment system should be installed. This case study will assume the installation of a conventional pretreatment system with Acid and anti-scalent addition.

4.2 LABORATORY SCALE SYSTEM

After collecting water prior to RO treatment the BWB was assessed for similar chemical parameters of BW and values are presented in Table 4-9 [17] .The comparison between the values presented by the design software will vary tremendously from the values given in Table 4-9 because the RO used in the study is a simple household FILMTEC RO while the ones designed for the hospital are 8 inch RO membranes with industrial grade certification, additionally the percent recovery is significantly different. As the max recovery for the acquired RO is about 25 percent for water with TDS less than 6000 ppm.

Table 4-9: BWB charachteristics.

Parameter	Unit	BWB		
		Number of Observations	Mean	Standard Deviation
pH	pH units	11	7.4	0.1
Temperature	ºC	11	25.5	1.9
Conductivity	mS	2	15.3	0.3
TDS	mg/L	6	9053.3	539.9
TSS	mg/L	4	44	24
VSS	mg/L	5	20	9.6
Alkalinity (hydroxide)	mg/L as $CaCO_3$	7	0	0
Alkalinity (carbonate)	mg/L as $CaCO_3$	7	0	0
Alkalinity (bicarbonate)	mg/L as $CaCO_3$	7	117	59.1
Ca Hardness	mg/L as $CaCO_3$	18	1197	130.7
Mg Hardness	mg/L as $CaCO_3$	18	2111	182
Total Hardness	mg/L as CaCO3	18	3273	166.5
Chlorides	mg/L	14	5489	216
Silica	mg/L as Si	17	6	1.4
	mg/L as SiO_2	17	13.1	4.6
Fe	mg/L	4	0.041	0.004
Boron	as B (mg/L)	6	2.1	0.2

	as H_3BO_3 (mg/L)	6	11.9	1.4
Strontium	mg/L	7	7.5	2.2
Barium	mg/L	4	BDL	BDL
Na	mg/L	5	2842.7	349.7
K	mg/L	2	35.2	1.4
Fecal Coliforms	CFU in 100 mL After 24 hrs	3	0	0
Total Coliforms	CFU in 100 mL After 24 hrs	3	0	0

After running the RO membrane sections on SEM the results are shown in Figure 4-3 and Figure 4-4 which clearly shows the cake layer mentioned in the literature review of this study. Such high poring and cake formation will lead to rapid membrane flux drop eventually leading to full membrane deterioration.

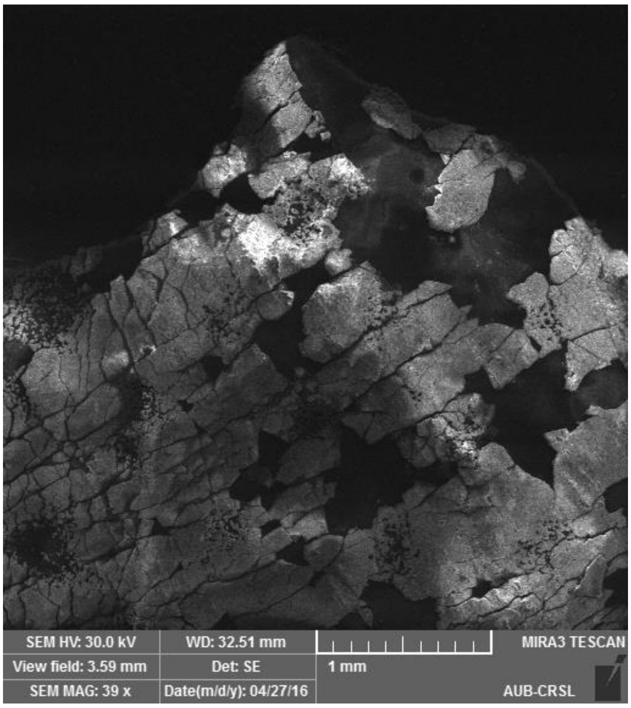

Figure 4-3: SEM imaging of foulant at 1mm.

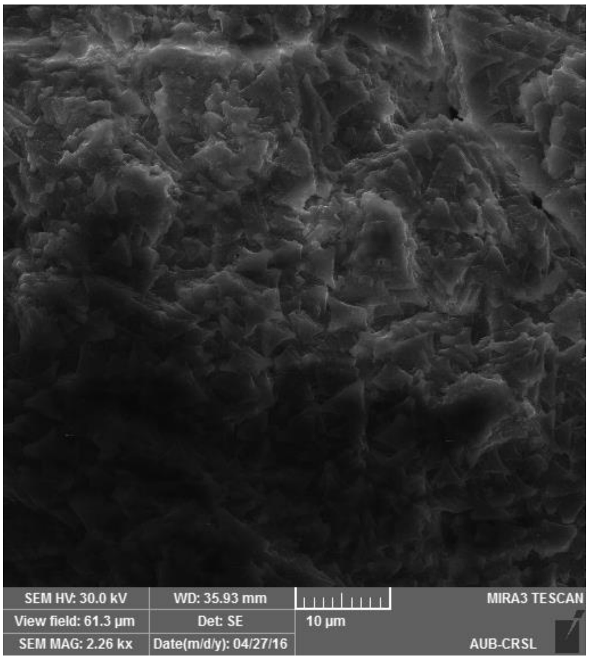

Figure 4-4: SEM imaging of foulant at 10 μm.

Table 4-10: Elemental Analysis of membrane surface.

	Moderate Fouling Region		**Intensive Fouling Region**		**Pre-treated RO region**	
Element	Weight%	Atomic%	Weight%	Atomic%	Weight%	Atomic %
C	19.71	27.91	42.24	53.57	72.33	77.69
O	59.63	63.38	42.35	40.32	27.67	22.31
Mg	0.59	0.41	0.29	0.18	0	0
S	0.39	0.20	2.86	1.36	0	0
Ca	18.08	7.67	11.59	4.41	0	0
Zn	1.60	0.42	0.67	0.16	0	0
Totals	100.00		100		100	

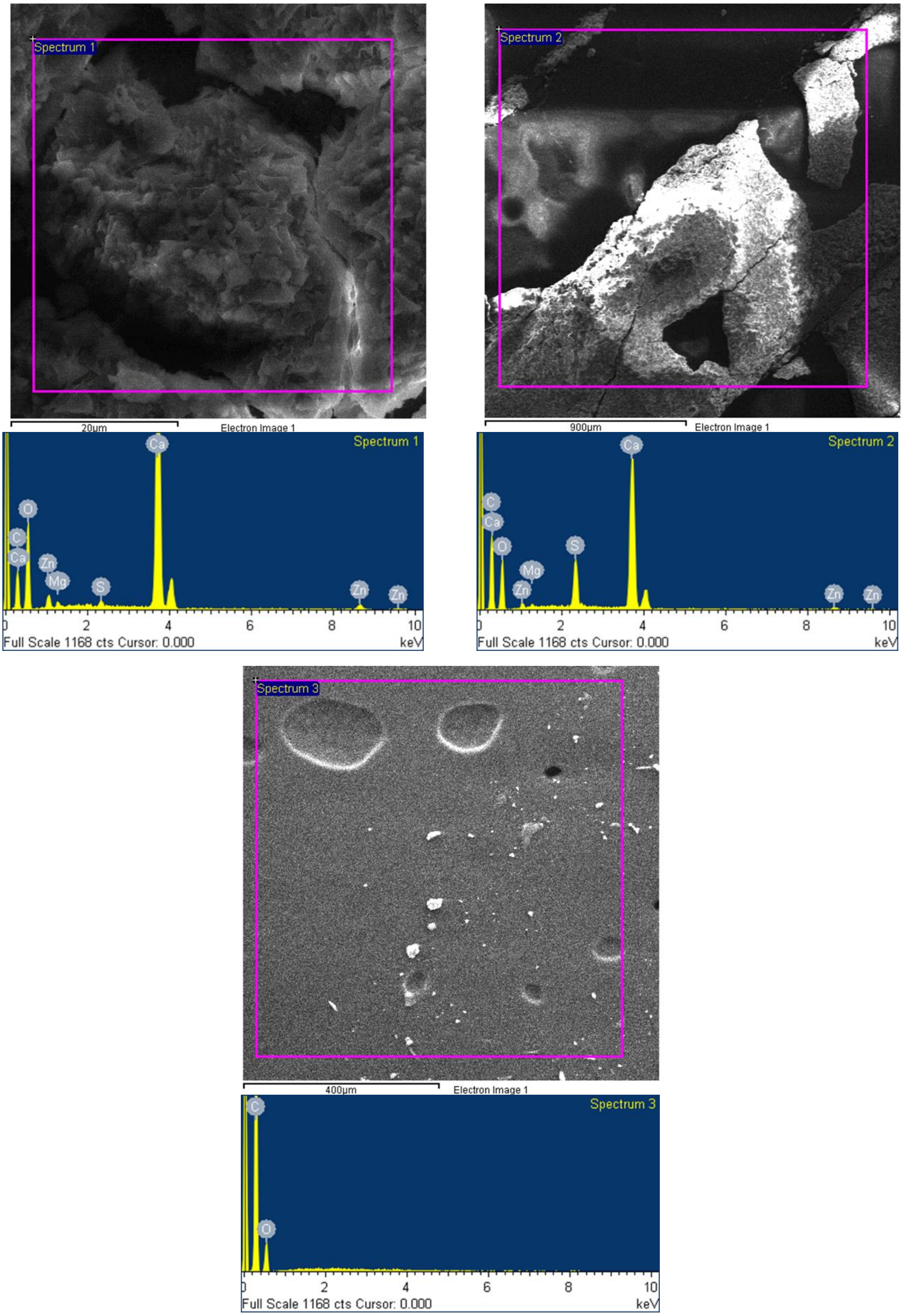

Figure 4-5: Spectrum and imaging of membrane surface. Spectrum 1 and 2 represent moderate add intensive foluing regions respectively, spectrum 3 represent the membrane exposed to pretreated water.

Major foulants can now be identified as $CaCO_3$, SO_4, and $Mg(OH)_2$ which is consistent with the coagulation data provided in the literature review. However, the complex nature of these compounds cannot be determined solely via the SEM, these compounds are present is highly clustered matrix forms and will be addressed using a geochemical calculation software.

On the other hand, spectrum 3 prove that this fouling only occurred on the level of $CaCO_3$ which is mainly due to high alkalinity knowing that the feed water pH is 11. The normalized permeate flux with respect to the initial permeate flux under various feed solution pH is expected.

4.3 USING PHREEQC

PHREEQC version 3 is a computer program written in the C and C++ programming languages that is designed to perform a wide variety of aqueous geochemical calculations. PHREEQC implements several types of aqueous models. PHREEQC has capabilities for:

- Speciation and saturation-index calculations
- batch-reaction and one-dimensional transport calculations with reversible and irreversible reactions, which include aqueous, mineral, gas, solid-solution, surface-complexation, and ion-exchange equilibria, and specified mole transfers of reactants, kinetically controlled reactions, mixing of solutions, and pressure and temperature changes
- Inverse modeling, which finds sets of mineral and gas mole transfers that account for differences in composition between waters within specified compositional uncertainty limits.

For the purpose of this study a complete model results obtained for BW via Phreeqc is presented in Appendix B, the major settling parameters are presented in Table 4-11.

The higher the log SI of a certain species the more likely it will precipitate out of solution at the given pH value.

4.4 CONCLUSION

Flux decline and membrane deterioration due to the presence of smaller particles was attributed to the high cake layer resistance due to the formation of the void-less cake layer as discussed in Chapter 2. In addition, our approaches to mitigate the colloidal fouling revealed that the hydraulic cleaning by increasing the cross-flow rates was not effective to eliminate the compact cake layer. However, adjusting the feed solution pH showed the high potential to relieve the colloidal fouling resulting from the more stabilization of particles at low solution pH. The results presented in appendix B show severe decline of Log SI indices for each and every compound matrix, as such a flux normalization is expected. This trend can be rationalized by noting that silica particles became destabilized in the alkaline condition and therefore the interactions between silica particles were weakened, resulting from the increased salt concentration at the membrane surface mainly caused by the reverse salt diffusion. As such a proper pretreatment will aid in preserving the RO and decreasing the significant operation and maintenance cost associated with the process.

Thus for the hospital RO system a proper pretreatment should include anything that removes the contaminants causing the rapid membrane deterioration, which will lead to high power usage, water quality issues, and membrane shortened lifespan.

Table 4-11: Log SI of Settling Species at pH 8.5.

Phase	Log SI	Species
Aragonite	0.5	$CaCO_3$
Calcite	0.65	$CaCO_3$
Chrysotile	3.96	$Mg_3Si_2O_5(OH)_4$
Dolomite	2.25	$CaMg(CO_3)_2$
$Fe(OH)_3$(a)	1.49	$Fe(OH)_3$
Goethite	7.38	FeOOH
$Pb(OH)_2$	0.91	$Pb(OH)_2$
Rhodochrosite	1.25	$MnCO_3$
Sepiolite	1.67	$Mg_2Si_3O_7.5OH:3H_2O$

CHAPTER 5

FINANCIAL STUDY

This financial study will consider water treatment procedure for an entire plant (not just a hospital) this will allow the author far more flexibility in the process and it will also allow for a much clearer breakeven analysis

5.1 PRETREATMENT COST

Wolf, et al. [94] reported into the cost of the two types of pre-treatment coupled with a two pass RO system. The two systems at hand are the conventional system and the membrane system, each has its unique set of disadvantages and advantages which can be directly related to cost effectivity of each system. The breakdown of costing is shown in **Error! Reference source not found.** [94].

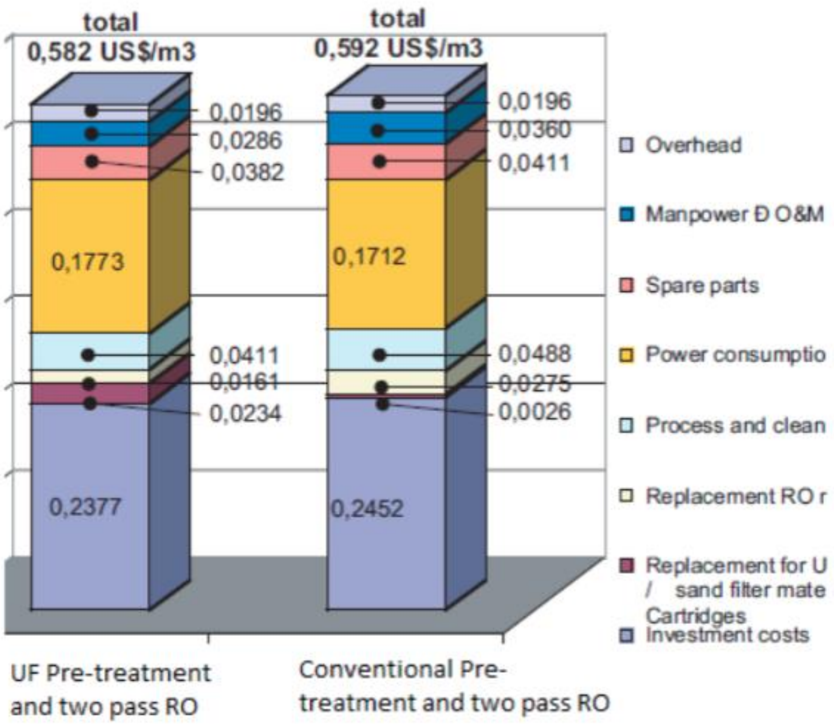

Figure 5-1: Costing of pretreatment processes.

The graph clearly shows that both investment cost and process and overall cost are less for UF membrane pre-treatment. Using the designed product flow of plant *x* is 10,000

m^3/day, the use of UF membranes as pre-treatment as opposed to conventional filtration the daily saving can be calculated as such:

$$10{,}000\frac{m^3}{d}\times 0.592\frac{\$}{m^3}-10{,}000\frac{m^3}{d}\times 0.582\frac{\$}{m^3}=100\frac{\$}{d}$$

There is no publically available data for costing. Attempts at contacting both GE Power and Water and Huber Technology UK have been made in search of costing data but at the time of this report, nothing had been received in return. Due to this, the costing for the Pre-treatment will be done using **Error! Reference source not found.**. This costing method will include the costing for the dosing pumps needed for the anti-scaler due to its cost as a pre-treatment system as a whole.

The cost of US$202 per m3/day of product water from the plant is from 2005 [94], using the scale that US$ 1.00 (2005) = US$ 1.10 (2009) (Worth)[95], this is raised to US$ 222 per m^3/day product water. With a product water output at maximum capacity of 10,000 m^3/day, the total capital cost for the pre-treatment system is US$ 2.2 million.

After calculating the capital cost, the maintenance cost should be estimated from **Error! Reference source not found.** [94]:

- Costing Values per m^3/day product water are;
- Replacement Membranes – US$ 0.0234
- Process and Clean – US$ 0.0206
- With a product water flow of 10,000 m^3/day, and the adjusted costs of yearly inflation;
- Replacement Membranes – US$ 500 /day
- Process and Clean – US$ 500 /day Totalling – US$ 1,000 /day for maintenance.

5.2 RO COSTING

Costing in RO system will be based on energy requirements and replacement membranes, in addition to maintenance of the RO plant at hand. Using ROSA software[96], the exact consumption in KW.hr can be calculated as such:

$$Total\ Energy\ Consumption\ in\ theRO\ system$$
$$= Total\ power\ consumed\ by\ each\ of thepumps\ (available\ in\ ROSA)$$
$$= 82 + 93 + 137 = 312\ K$$

Therefore, the overall product water flow leaving the system is 10,000 m^3/d. The specific energy consumption per cubic meter can be calculated as follows:

$$SE = \frac{w_{Total}}{\frac{Q \times 3600}{24 \times 3600}} = 0.748\ kWh/m^3$$

The total cost of membranes will be

$$Total\ Cost = Cost\ of\ single\ membran \times Number\ of\ membranes \times Number\ of\ replacements$$

For our project the lifespan will be set to 5 years, and in RO systems most membranes start to deteriorate by approximately the 5th year of its life thus leading to the replacement of the membranes.

The total cost of membranes according to ROSA (the study assumes the BWRO membranes are utilized at full capacity with proper replacement) is 100,000$. The cost of pressure vessels is 160,797 $, that of high pressure pumps is 290,000 $ and the cost of booster pumps is 10,000 $. Note that in order to estimate cost of each pump, the power of the pump first had to be determined, and based on the power vs cost curve and the corresponding value of the cost had to be noted. Therefore, the total overall cost will be 560,797 $.

5.3 POST TREATMENT COSTING

Post treatment in the form of SafeOX units [95] will be considered in this study. The capital costing for the post-treatment system would consist of 2 SafeOx units

2 x US$ 20,000 = U$ 40,000

The costs for the two chemicals used for the unit were Chlorine Dioxide and Calcium hypochlorite. The cost of Chlorine Dioxide is $4-$5 dollars per kg from Shandong Zhaoguan Medicine Industry Co., 2011 as assessed by Bell, et al. [95] with a dose of 2kg/hr needed for disinfection from the SafeOx unit was taken as the ClO_2 needed in wholesale chemical form.

- \$4.50 x 2 kg/h =9\$/h=216\$/d
- Hypochlorite cost is about 3\$ per kg and the plant utilizes 24 kg/d
- Total cost of Hypochlorite= 72\$/d
- As such the total cost of posttreatment=288\$/d

5.4 PROJECT REVENUE AND PROFIT

Revenue can be generated by selling potable water to surrounding municipality, especially that the project can produce 30,000 m^3/d (3 times the design capacity with 1.5 times increase in price). Water is the one variable in the financial analysis as the price the water is sold at can be altered to produce a more suitable annual ROI. The revenue generated by the potable water accounts for the price of water increasing annually due to inflation (again set at 2.9%).

In Lebanon the profit of \$2.0/m^3 seems about right, and kindly note that this number is based on the prices offered by private water companies and it is considered to be a very competitive price in the current market. Research performed by Bell, et al. [95] has also shown that based on current day prices Sydney Water will be charging home owners approximately \$3.5/m^3 for their drinking water supply as of 2030. The main conclusion that can be drawn from the financial analysis is that the design being proposed by this report can generate a reasonable return on the investment when it has to produce potable water for the majority of 5 year working life. It is the recommendation that the owners should sell water for approximately \$3.3/m^3.

CHAPTER 6

CONCLUSION AND FUTURE WORK

6.1 CONCLUSION

RO technologies are continuously advancing, optimizing RO systems and its related fields are widely practiced throughout the globe, mainly because RO is viewed as the most efficient system of water desalination. Disadvantages associated with RO include membrane fouling, scaling, Cake layer formation, clogging and bacterial growth, solutions to limit such issue are available and continuously being updated with alternatives being illustrated often. Brine disposal and management is an important issue in RO plants nowadays, and new trends of treatment and management of the brine are in continuous advancement, processes like ZLD aided in transforming the RO technology into a green technology.

In order to achieve a proper analysis of the membrane fouling layer, an autopsy of a used membrane and a new membrane was carried out, it aided in providing a good understanding of how composites of foulants damage the RO membrane, water chemistry testing supplied the author with proper data which was used in phreeqc and showed the proximity of simulation software to real life conditions. Flux decline and membrane deterioration due to the presence of smaller particles was attributed to the high cake layer resistance due to the formation of the void-less cake layer as discussed in Chapter 2. In addition, our approaches to mitigate the colloidal fouling revealed that the hydraulic cleaning by increasing the cross-flow rates was not effective to eliminate the compact cake layer. When the membrane was exposed for high pH feed (11.5) it exhibited high potential to relieve the colloidal fouling resulting from the more stabilization of particles at low solution pH and shown in the SEM imaging and INCA characterization, in turn the explanation of such a result was the fact that silica particles became destabilized in the alkaline condition and therefore the interactions between silica particles were weakened, resulting from the increased salt concentration at the membrane surface mainly caused by the reverse salt diffusion. As such a proper pretreatment will aid in preserving the RO and decreasing the significant operation and maintenance cost associated with the process.

The significant findings of this research was that known mechanisms for solution and solute transport onto RO membrane surface mainly $CaCO_3$, $Mg(OH)_2$, $Ca(OH)_2$, and SO_4 was clearly demonstrated through both geotechnical simulation and bech-scale testing. This leads to the easy identification of other significant scientific data such as solution diffusion, electrostatic interaction (repulsion), and steric (size). The conclusions of the associated experimental results support the objectives of this research and research hypotheses of the foulants responsible for deteriorating RO productivity and the need for a proper pretreatment procedure. Thus for the hospital RO system a proper pretreatment should include anything that removes the contaminants causing the rapid membrane deterioration, which will lead to high power usage, water quality issues, and membrane shortened lifespan.

6.2 FUTURE WORK

Although this short-term bench-testing study can predict fouling species of specific feeds through RO even the NF and UF due to membrane similarities, to accurately model full-scale operation, pilot-testing study is strongly recommended in order to address long-term exposure of RO to the contaminants at hand. The future research can be focused to

1. Investigate pretreatment
2. Identify long-term performance as affected by membrane fouling
3. Performing additional experiments under the same condition, thus increasing the number of trials and lowering standard deviations.
4. Using at least 4 Simultaneous RO apparatus and running under similar conditions with different types of water to obtain a more accurate result for fouling of RO membrane surfaces.
5. Intensive pilot-testing program interfaced with focused and supporting bench testing.
6. Further characterization and elemental analysis for elements such as Na+, which will enable the calculation of osmotic pressure change at different pH levels.
7. Performing a detailed feasibility study after determining the benefit from utilizing the RO in hospitals around Lebanon, which should also include a breakeven analysis in comparison to buying water and/or health risks associated with the absence of such a system

8. Comparing the cost of the studies system to that of conventional and membrane pretreatment.

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APPENDIX A

Parameter	Method of Analysis	Method Reference (APHA/ HACH)
pH	Electrometric Method	4500-H^+
Temperature	Thermometric Method	2550
Turbidity	Nephelometric Method	2130
TDS	Gravimetric Method	2540-C
TSS	Gravimetric Method	2540-D
VSS	Gravimetric Method	2540-E
Alkalinity	Titrimetric Method	2320
Calcium Hardness	EDTA TitrimetricMethod	3500-Ca
Total Hardness	EDTA Titrimetric Method	2340-C
Sodium	Flame Emission Photometric Method	3500-Na
Iron	Flame Emission Photometric Method	3500-Fe
Sulfates	Spectrophotometric Method	4500-$SO4^{2-}$
Chlorides	Argentometric Method	4500-Cl^-
Boron	Carmine Method	4500-B
Silica	Molybdosilicate Method	4500-SiO_2-C
Strontium	Flame Emission Photometric Method	3500-Sr
Barium	Turbidimetric Method	HACH Method 8014
Fecal Coliforms	Fecal Coliform Membrane Filter Procedure	9222-D
Total Coliforms	Total Coliform Membrane Filter Procedure	9222-B

APPENDIX B

Phase	pH 8.5	pH 9.5	pH 10	pH 10.5	pH 11	pH 11.5	pH 12	Species
Aragonite	0.5	1.38	1.5	1.8	2.02	0	0	$CaCO_3$
Calcite	0.65	1.53	1.5	1.95	2.16	0	0	$CaCO_3$
Cerrusite	0.46	-0.76	-0.4	0	0	0	0	$PbCO_3$
Chalcedony	-0.45	-0.65	-0.8	-1.49	0	0	0	SiO_2
Chrysotile	3.96	9.51	11	13.6	0	0	0	$Mg_3Si_2O_5(OH)_4$
CO2(g)	-3.58	-4.67	-5	-6.2	-6.91	-7.59	-8.59	CO_2
Dolomite	2.25	4.02	4.22	4.86	5.28	0	0	$CaMg(CO_3)_2$
Fe(OH)3(a)	1.49	0.95	0	0	0	0	0	$Fe(OH)_3$
Goethite	7.38	6.84	3	0	0	0	0	FeOOH
H2(g)	-25.05	-27	-28	-29	-30.05	-31.05	-32.05	H_2
H2O(g)	-1.51	-1.51	-1.51	-1.51	-1.51	-1.5	-1.5	H_2O
Halite	-3.54	-3.54	-3.54	-3.54	-3.55	-3.55	-3.37	NaCl
Hausmannite	-0.48	4.3	2	0	0	0	0	Mn_3O_4
Hematite	16.77	15.69	5	0	0	0	0	Fe_2O_3
Manganite	-0.99	0.94	0	0	0	0	0	MnOOH
O2(g)	-33.19	-29.19	-27	-25.19	-23.19	-21.19	-19.19	O_2
Pb(OH)2	0.91	0.72	0	0	0	0	0	$Pb(OH)_2$
Pyrochroite	-3.35	-2.42	0	0	0	0	0	$Mn(OH)_2$
Pyrolusite	-4.53	-1.61	0	0	0	0	0	$MnO_2{:}H_2O$
Quartz	-0.02	-0.22	-0.8	-1.06	0	0	0	SiO_2
Rhodochrosite	1.25	1.09	0.5	0	0	0	0	$MnCO_3$
Sepiolite	1.67	5.05	5.25	6.42		0	0	$Mg_2Si_3O_7.5OH{:}3H_2O$
Sepiolite(d)	-1.23	2.15	2.5	3.52	0	0	0	$Mg_2Si_3O_7.5OH{:}3H_2O$
Siderite	-3.94	-6.57	0	0	0	0	0	$FeCO_3$
SiO2(a)	-1.29	-1.48	-1.5	-2.32	0	0	0	SiO_2
Strontianite	-0.01	0.89	1.02	1.07	0	0	0	$SrCO_3$
Sylvite	-5.03	-5.01	-5.03	-5.03	-5.03	-5.02	-4.93	KCl
Talc	6.76	11.92	12	14.41	0	0	0	$Mg_3Si_4O_{10}(OH)_2$
Witherite	-2.53	-1.93	-1.7	-1.47	0	0	0	$BaCO_3$