

AMERICAN UNIVERSITY OF BEIRUT

A PRETREATMENT PROCESS FOR BRACKISH WATER
AND BRINE DESALINATION

by
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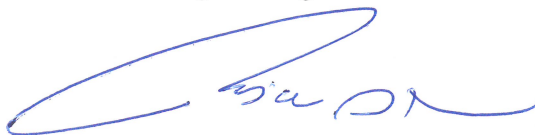
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Disclaimer:

The idea of using the principle of the process of alkalization and softening as a pretreatment for BWRO and a treatment for BWRO reject is initiated and developed by Prof. George Ayoub and consequently he is reserved all the rights and privileges pertaining to this idea.

AN ABSTRACT OF THE THESIS OF

Lea Georges Korban for Master of Science in Environmental Sciences
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Title: A Pretreatment Process for Brackish Water and Brine Desalination

In response to the increasing demand for fresh water worldwide, water reuse and desalination have been successfully employed as alternative methods of freshwater supply over the last few decades (Elimelech & Phillip, 2011). Specifically, reverse osmosis (RO) has gained significant appeal as one of the major processes for desalination, representing up to 80% of the total number of installed desalination plants globally (Greenlee et al., 2009; Valavala et al., 2011). Due to technological enhancements and reduction in cost requirements, RO is viewed as an energy-efficient process, especially for the desalination of brackish water (Lauer, 2006; Elimelech & Phillip, 2011). Nonetheless, the RO process has several limitations, the most hindering of which is membrane fouling due to particulate and colloidal matter, inorganic compounds, organic substances, and biological growth (Prihasto et al., 2009; Valavala et al., 2011). Not only does membrane fouling reduce the efficiency and lifetime of the RO membrane, but it also incurs additional costs to operate the system due to increased energy demand and frequent cleaning (Bodzek et al., 2011; Valavala et al., 2011). To prevent such drawbacks to the process, conventional as well as non-conventional pretreatment methods have been used, namely coagulation/ flocculation, sedimentation, granular media filtration, dissolved air flotation, ultrafiltration, microfiltration, and nanofiltration (Prihasto et al., 2009; Valavala et al., 2011). Within this context, precipitation softening is a conventional pretreatment process that contributes to the removal of a number of scale-producing and fouling pollutants, such as magnesium, calcium, silica, and strontium. The proposed research aims at assessing the effectiveness of precipitation softening as a pretreatment process for brackish water reverse osmosis. This was achieved by selecting the optimal softening chemicals and dosages, followed by examining the removal efficiency of a number of scaling and fouling contaminants under different pH and temperature conditions. The findings demonstrated a significant effect of pH on removals of key foulants like Ca, Mg, silica, and strontium in both water types, while temperature had a less significant impact. The pH values of 11.2 and 11.5 achieved the most desirable results in terms of parametric removals, with appropriate chemical addition. As for sludge settling, the best compaction rate was observed at pH=10.5, while floc formation was optimal between pH= 11 and pH= 11.5.

CONTENTS

FIGURES.....	xi
TABLES	xiii
ABBREVIATIONS	xv
1. INTRODUCTION	1
2. LITERATURE REVIEW	10
2.1. BWRO Reject	10
2.1.1. Brine Composition.....	10
2.1.2. Brine Management.....	11
2.1.2.1. Brine Disposal Options.....	11
2.1.2.2. Brine Treatment Options	12
2.2. Membrane Fouling.....	14
2.2.1. Fouling Effects.....	15
2.2.2. Types of Fouling in BWRO.....	16
2.2.2.1. Particulate and Colloidal Fouling	17
2.2.2.2. Inorganic Fouling or Scaling	19
2.2.2.3. Organic Fouling	22
2.2.2.4. Biological Fouling	24
2.2.3. Evaluation of Fouling Potential	27
2.3. Fouling Management and Pretreatment.....	28
2.3.1. Conventional Pretreatment	29
2.3.1.1. Pretreatment Practices.....	29

2.3.1.2.	Precipitation Softening	32
2.3.1.3.	Non-Conventional or Membrane Pretreatment.....	34
2.4.	Silica	36
2.5.	Barium and Strontium.....	38
2.6.	Boron	39
3.	MATERIALS AND METHODS.....	42
3.1.	Water Collection and Analysis	42
3.2.	Experimental Setup.....	44
3.3.	Titration Experiments	44
3.3.1.	Ca(OH) ₂	45
3.3.2.	NaOH.....	46
3.3.3.	Na ₂ CO ₃	47
3.3.4.	Combination of NaOH and Na ₂ CO ₃	48
3.3.5.	Combination of Ca(OH) ₂ and Na ₂ CO ₃	49
3.4.	Determination of the Optimal Alkalizing Agent	50
3.5.	Jar Testing.....	51
3.5.1.	Jar Testing Procedure.....	51
3.5.2.	Water Analysis.....	53
3.5.3.	Spiking.....	53
3.5.3.1.	Addition of Wastewater	54
3.5.3.2.	Addition of Iron	54
3.5.3.3.	Addition of Barium	55

3.6. Statistical Analysis.....	55
4. RESULTS AND DISCUSSION	56
4.1. Brackish Water and BWRO Brine Characterization	57
4.2. Jar Test Results	57
4.2.1. Effect of pH on Foulant Removal.....	59
4.2.2. Effect of Temperature on Foulant Removal	66
4.2.3. Combined Effect of pH and Temperature.....	76
4.2.4. Spiked Experiments	78
4.2.4.1. Addition of Wastewater	79
4.2.4.2. Addition of Iron	82
4.2.4.3. Addition of Barium.....	89
4.3. Settling Rate and Sludge Considerations.....	90
4.3.1. Settling Observation	90
4.3.2. Effect of pH, Temperature, and Spiking on Settling	93
4.4. Optimal Process Selection	96
4.4.1. Optimal Operating Conditions.....	96
4.4.2. Mass Balance	97
5. CONCLUSION AND RECOMMENDATIONS	100
BIBLIOGRAPHY	103
Appendix 1: Standard Methods Used For Water Analysis.....	113
Appendix 2: Matrix Of Experimental Conditions Of The Proposed Research	114

Appendix 3: Volumes Of The Optimal Combination Of Alkalizing Agents Under Different Experimental Conditions Of Temperature And pH	115
Appendix 4: Table Of Comparison Of BW Characteristics	116
Appendix 5: Table Of Comparison Of BWB Characteristics.....	118
Appendix 6: Calculations Of Mass Percentage And Sodium Concentration In The Optimal Softening Agents	119

FIGURES

Figure 1. 1 Membrane processes, corresponding particle sizes, and operating pressure ranges (El-Dessouky & Ettouney, 2002)	8
Figure 2. 1 Factors influencing colloidal fouling in RO membranes (Tang et al., 2011)	18
Figure 2. 2 CEOP and Concentration Polarization (a) before membrane fouling and (b) after membrane fouling (Tang et al., 2011).....	19
Figure 2.3 Descriptive scheme of the characteristics of the different membrane processes (Li et al., 2008).....	35
Figure 3.1 Titration curve of 100 mL (a) BW and (b) BWB with 1M Ca(OH) ₂	45
Figure 3.2 Titration curve of 100 mL (a) BW and (b) BWB with 1N NaOH	47
Figure 3.3 Titration curve of 100 mL (a) BW and (b) BWB with 1N Na ₂ CO ₃	48
Figure 3.4 Titration curve of 100 mL (a) BW and (b) BWB with 2:1 1N NaOH:1N Na ₂ CO ₃	49
Figure 3.5 Titration curve of 100 mL (a) BW and (b) BWB with 2:1 1M Ca(OH) ₂ :1N Na ₂ CO ₃	50
Figure 4.1 Average Percentage Removals of Ca, Mg, and Sr in BW at different experimental pH values at T≈25°C	61
Figure 4.2 Average Percentage Removals of Ca, Mg, and Sr in BWB at different experimental pH values at T≈25°C	62
Figure 4.3 Average Percentage Removals of Si and B in BW at different experimental pH values at T≈25°C	64
Figure 4.4 Average Percentage Removals of Si and B in BWB at different experimental pH values at T≈25°C	64
Figure 4.5 Average Percentage Removals of Ca in BW at different experimental pH values and temperatures.....	69
Figure 4.6 Average Percentage Removals of Ca in BWB at different experimental pH values and temperatures.....	70
Figure 4.7 Average Percentage Removals of Mg in BW at different experimental pH values and temperatures.....	70
Figure 4.8 Average Percentage Removals of Mg in BWB at different experimental pH values and temperatures.....	71

Figure 4.9 Average Percentage Removals of Sr in BW at different experimental pH values and temperatures.....	72
Figure 4.10 Average Percentage Removals of Sr in BWB at different experimental pH values and temperatures.....	72
Figure 4.11 Average Percentage Removals of B in BW at different experimental pH values and temperatures.....	73
Figure 4.12 Average Percentage Removals of B in BWB at different experimental pH values and temperatures.....	74
Figure 4.13 Interaction plots of pH and temperature SiO ₂ and H ₃ BO ₃ removals for a) BW and b)BWB.....	77
Figure 4.14 Average Percentage Removals of Fe in BW at different experimental pH values and temperatures.....	85
Figure 4.15 Average Percentage Removals of Fe in BWB at different experimental pH values and temperatures.....	86
Figure 4.16 Average Percentage Removals of Mg in BW with and without Fe Spiking at T≈23°C and different experimental pH values.....	87
Figure 4.17 Average Percentage Removals of Mg in BWB with and without Fe Spiking at T≈23°C and different experimental pH values.....	87
Figure 4.18 Average Percentage Removals of Mg in BW with and without Fe Spiking at T=30°C and different experimental pH values.....	88
Figure 4.19 Average Percentage Removals of Mg in BWB with and without Fe Spiking at T=30°C and different experimental pH values.....	88
Figure 4.20 Sludge Settling of BW vs. Time at T≈23°C with Spiking and different experimental pH values.....	91
Figure 4.21 Sludge Settling of BWB vs. Time at T≈23°C with Spiking and different experimental pH values.....	92
Figure 4.22 Sludge Settling of BW vs. Time at T≈25°C without Spiking and different experimental pH values.....	92
Figure 4.23 Sludge Settling of BWB vs. Time at T≈25°C without Spiking and different experimental pH values.....	93

TABLES

Table 2.1 Comparison of disinfection techniques used for RO membrane biofouling (Kim et al., 2009).....	26
Table 3.1 Composition of the sample BW and BWB samples collected for the experimental study.....	43
Table 3.2 Effect of 1M Ca(OH) ₂ on Ca and Mg Percentage Removals in (a) BW and (b) BWB	46
Table 3.3 Effect of 1N NaOH on Ca and Mg Percentage Removals in (a) BW and (b) BWB	47
Table 3.4 Effect of 1N Na ₂ CO ₃ on Ca and Mg Percentage Removals in (a) BW and (b) BWB	48
Table 3.5 Effect of 2:1 1N NaOH:1N Na ₂ CO ₃ on Ca and Mg Percentage Removals in (a) BW and (b) BWB	49
Table 3.6 Effect of 2:1 1M Ca(OH) ₂ :1N Na ₂ CO ₃ on Ca and Mg Percentage Removals in (a) BW and (b) BWB	50
Table 4.1 Treated BW Characteristics at experimental pH values and temperature T≈25°C	59
Table 4.2 Treated BWB at experimental pH values and temperature T≈25°C	60
Table 4.3 Single Linear Regression Analysis for Parametric Removals vs. pH at T=25°C for BW and BWB	65
Table 4.4 Treated BW Characteristics at experimental pH values and temperature T=10°C	66
Table 4.5 Treated BWB Characteristics at experimental pH values and temperature T=10°C	66
Table 4.6 Treated BW Characteristics at experimental pH values and temperature T=30°C	67
Table 4.7 Treated BWB Characteristics at experimental pH values and temperature T=30°C	68
Table 4.8 Single Linear Regression Analysis for Parametric Removals vs. pH at different temperatures for BW and BWB	74
Table 4.9 Two-way ANOVA results of parametric removal efficiencies vs. pH and temperature with their interaction.....	76

Table 4.10 Multiple linear regression equations for parametric removals vs. pH and temperature, with their interaction.....	78
Table 4.11 Results of Treatment of BW Spiked with wastewater at experimental pH values and temperature T=23°C	79
Table 4.12 Results of Treatment of BWB Spiked with wastewater at experimental pH values and temperature T=23°C	80
Table 4.13 Results of Treatment of BW Spiked with wastewater at experimental pH values and temperature T=30°C	81
Table 4.14 Results of Treatment of BWB Spiked with wastewater at experimental pH values and temperature T=30°C	81
Table 4.15 Results of Treatment BW Spiked with Iron at experimental pH values and temperature T≈23°C	82
Table 4.16 Results of Treatment of BWB Spiked with Iron at experimental pH values and temperature T=23°C	83
Table 4.17 Results of Treatment of BW Spiked with Iron at experimental pH values and temperature T=30°C	83
Table 4.18 Results of Treatment of BWB Spiked with Iron at experimental pH values and temperature T=30°C	84
Table 4.19 Single Linear Regression Analysis of Fe removal vs. pH and Temperature	86
Table 4.20 Results of Treatment of BW Spiked with Barium at experimental pH values and temperature T=23°C	89
Table 4.21 Results of Treatment of BWB Spiked with Barium at experimental pH values and temperature T=23°C	90
Table 4.22 Final Sludge Depth for both water types at different conditions of pH, temperature, and spiking.....	95
Table 4.23 Calculation of the total Na added to BW and BWB at T≈25°C	98
Table 4.24 Calculation of the mass balance of constituents in BW and BWB at T≈25°C	98
Table 4.25 Comparison of the mass balance and TDS decrease for BW and BWB at T≈25°C	98

ABBREVIATIONS

ACS	American Chemical Society
AMF	Sorption–membrane filtration hybrid processes
ANOVA	Analysis of Variance
APHA	American Public Health Association
AWWA	American Water Works Association
B	Boron
Ba	Barium
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
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
Fe	Iron

HAA	Halo Acetic Acids
IAP	Ionic Activity product
ICD	Intermediate Chemical Demineralization
IMS	Integrated Membrane Systems
LSI	Langelier Saturation Index
MD	Membrane Distillation
MEE	Multiple Effect Evaporation
MENA	Middle East and North Africa
MF	Microfiltration
MFI	Modified Fouling Index
Mg	Magnesium
MSF	Multistage Flash
Na-EDTA	Sodium Ethylenediaminetetraacetate
NF	Nanofiltration
NOM	Natural Organic Matter
NTU	Nephelometric Turbidity Units
PEUF	Polymer Enhanced Ultrafiltration
RO	Reverse Osmosis
SDI	Silt Density Index
SHMP	Sodium Hexametaphosphate
SI	Saturation Index
Si	Silica
Sr	Strontium
SWRO	Seawater Reverse Osmosis

TDS	Total Dissolve Solids
THMs	Trihalomethanes
TNTC	Too Numerous To Count
UAE	United Arab Emirates
UF	Ultrafiltration
USEPA	United States Environmental Protection Agency
UV	Ultraviolet
VSEP	Vibratory Shear Enhanced Process
WHO	World Health Organization
ZLD	Zero Liquid-Discharge

CHAPTER 1

INTRODUCTION

A substantial hurdle for economic growth and political stability for many countries is water scarcity, or in some cases, inaccessibility (Miller, 2003). Over the previous decade, an estimated 1 billion people did not have access to clean potable water, and the World Health Organization predicts that half of the global population will inhabit “water stressed areas” by 2025 (Service, 2006; World Health Organization, 2013). The problem of water shortage worldwide is exacerbated by population growth, rising living standards, agricultural development, ever-increasing urbanization, mismanagement and pollution of existing water resources, and climate change (Gleick, 2006; Elimelech & Phillip, 2011; Valavala et al., 2011). In particular, the Middle East and North Africa Region (MENA) is the area experiencing the highest levels of water scarcity, whereby it accounts for 6.3% of the global population while obtaining no more than 1.4% of the world’s freshwater (Gleick, 1993; Miller, 2003). To add, among the effects of anthropogenic activities on the supply of freshwater is environmental degradation, affecting precipitation rates and weather trends (El-Dessouky & Ettouney, 2002). As the demand for adequate potable water exceeds the current supply, the burden on human health is taking its toll on many communities, in terms of water-related diseases such as diarrhoea, typhoid, cholera, and dysentery (World Health Organization, 2013). Furthermore, traditional attempts, such as building dams, water conservation, and education and communication, have fallen short of single-handedly meeting the need for fresh water in communities (Greenlee et al., 2009).

Therefore, a solution was brought on with the emergence of water reuse and desalination as supplementing supply methods. Water reuse, or water reclamation, is the treatment of wastewater such that it meets water quality requirements and it may be used for functions like industrial processes, irrigation, recharging groundwater aquifers, or, in some countries, drinking water production (United States Environmental Protection Agency). For instance, in some nations municipal wastewater is treated, recovered, and reused, and polluted water sources such as saline wells are rehabilitated (Redondo, 2001; Kucera, 2014).

On the other hand, desalination is practiced as a treatment process directed at the removal of salts from water to yield water that is suitable for drinking and household usage, with TDS less than 1000 mg/L (Sandia, 2003). Desalination is by no means a novel field, whereby the practice was initially adopted on ships to provide drinking water, using a form of solar stills (distillation), when limited amounts could be stored on board (El-Dessouky & Ettouney, 2002; Greenlee et al., 2009). As well, during the second world war there was ongoing research on ways to desalinate water to supply clean water in areas where it was scarce (Cooley et al., 2006). Nowadays, it is extensively used to provide fresh drinking and domestic water in water-deprived areas; it is expected to provide more than 38 billion cubic meters of water worldwide by 2016, doubling its production rate of 2008 (Elimelech & Phillip, 2011).

Desalination consists of two types of processes: thermal and membrane. Thermal processes were developed early during the twentieth century, and they involve using heat to separate ions and water using evaporation-condensation or freezing-melting techniques. Multiple effect evaporation (MEE), multistage flash desalination/distillation (MSF), humidification-dehumidification, single effect vapor

compression, and solar stills are all thermal desalination methods. Of these, the MSF process, which accounts for 26% of the world's desalination capacity, is the most commonly used in the Arabian Gulf countries, where the first MSF desalination plants were installed in the late 1950's and early 1960's (Gleick, 2006; Lauer, 2006; IDA, 2012). Currently, the desalination industry in the Gulf states owes more than 85% of its capacity to MSF installations, mainly in Kuwait, Qatar, Oman, UAE, and Saudi Arabia (Lauer, 2006). This distillation method applies thermal energy evaporation followed by condensation to separate water from the rest of the salt mixture, and it is appealing because it lacks the concern of scaling in heat transfer tubes, unlike MEE. On the other hand, MEE can achieve enhanced thermal operation, with the possibility of performing at lower top boiling temperature thus reducing scaling potential (Miller, 2003; Cooley et al., 2006).

As for membrane desalination processes, they encompass reverse osmosis and electrodialysis (ED). As the name implies, these methods employ semi-permeable membranes to separate water and ions through the application of a gradient (Miller, 2003; Cooley et al., 2006). While ED involves the use of electrical energy with charge-selective membranes, RO uses mechanical energy (pressure). RO is of particular interest since it is more widely used, with more than 44% market share of the global desalination capacity (Greenlee et al., 2009). Reverse osmosis is the process of separating water from a solution with salinity between 1000 mg/L and 60,000mg/L in terms of TDS, using a semi-permeable membrane and a pressure exceeding the osmotic pressure of the saline solution (Miller, 2003; Greenlee et al., 2009). Seawater, TDS 30,000-45,000 mg/L, and brackish water, TDS 1,000-15,000 mg/L, can both undergo reverse osmosis to produce potable water. The differences in ion concentrations

between the various types of feed water necessitate the tailoring of the RO process. Commercial RO membranes were first produced in the early seventies, followed by much advancement in materials and membrane technology. There are two major types of membrane materials: Cellulose Acetate and Composite Polyamide. Composite Polyamide membranes are characterized by higher salt rejection, a wider range of pH tolerance, but a higher propensity to oxidation by free chlorine, when compared to Cellulose Acetate membranes (El-Dessouky & Ettouney, 2002; Soltanieh & Gill, 2007).

RO is a more energy-efficient desalination technique due to its advantages over thermal processes, leading to its market growth rate over the past 40 years. These advantages include: lower energy consumption, lower capital cost, smaller land requirements, and membrane technology development (Lauer, 2006; Elimelech & Phillip, 2011; Valavala et al., 2011). Evidently, RO requires no thermal energy, which represents up to 50% of the total costs in a thermal desalination plant (Cooley et al., 2006). Also, the advances in energy recovery devices and their use in RO plants have proven significant compensation for energy (Miller, 2003; Mezher et al., 2011). As a result, RO has become the standard process in desalination, providing domestic water for communities at a more affordable price than other (thermal) desalination methods.

The pollution of water resources through anthropogenic activities, coupled with fresh water depletion in inland regions, has contributed to the increased need for supplemental sources of domestic water (Hastuti & Wardiha, 2012; Kucera, 2014). Relevantly, with the increase in seawater intrusion in coastal areas where groundwater is a major source of domestic supply, such as the Greater Beirut Area, Lebanon, brackish water RO is a rather appealing option. Brackish water has a salinity (TDS) lower than that of seawater, but higher than that of freshwater. It is either found in

groundwater aquifers, naturally saline or due to salt water intrusion, or in estuaries, and sometimes in inland surface water bodies (Greenlee et al., 2009). Brackish water RO (BWRO), with lower feed water salinity and a generally higher recovery rate, consumes less energy than seawater RO (SWRO), partly because it requires lower operating pressures, ranging from 15 to 25 bar (Al-Handhaly et al., 2003; Miller, 2003; Greenlee et al., 2009). Unsurprisingly, only 11% of the costs in brackish water RO are allocated to electrical energy consumption, whereas for seawater RO, this energy attributes 44% of the overall costs (Miller, 2003). So, given its quite convenient cost, brackish water RO is currently gaining momentum as the desalination method of choice (Miller, 2003; Greenlee et al., 2009; Pandey et al., 2012). For example, most of the US desalination capacity consists of brackish and surface water RO (Miller, 2003).

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 (Malaeb & Ayoub, 2011; Miller, 2003). Among these, the issues of concentrate disposal expense and feasibility, and scaling/ fouling remain as major limitations to the brackish RO process. As feed water is desalinated, the remaining salt solution makes up the concentrate or brine. Depending on the initial feed water characteristics, RO recovery rate, and pretreatment options, the brine stream may contain all the rejected salts in addition to a number of adverse contaminants from pretreatment that can prove problematic and ultimately costly to manage (Cooley et al., 2006; Al-Handhaly et al., 2003). The RO reject is sometimes treated before being discharged, conditional on relevant regulations and the further designated use, such as irrigation. Disposal practices can vary by location of the RO plant and availability of capital and land resources, and thus consist

of the following: discarding in the wastewater stream, construction of evaporation ponds, deep well injection, and disposal in surface water bodies, which in the case of brackish water may affect the overall salinity of a lake or a river (Ahmed et al., 2002; Greenlee et al., 2009).

Fouling occurs through four mechanisms: particulate and colloidal fouling, inorganic fouling/ scaling, organic fouling, and biological growth (biofouling) (Li et al., 2008; Prihasto et al., 2009; Valavala et al., 2011). Generally, the principal fouling contaminants relating to brackish water RO are primarily dissolved inorganic material and scaling compounds as well as biofouling conaminants, rather than suspended particulates and organic material. Fouling leads to the degradation of the RO membrane performance by increasing the frequency of cleaning, reducing the membrane lifetime which imposes more frequent changing of membanes, increasing the pressure drop across the membrane, increasing the salt passage, and decreasing permeate flux. This, in turn, contributes to higher maintenance and operating costs (Prihasto et al., 2009; Valavala et al., 2011). Consequently, pretreatment of the feed water is commonly practiced in RO desalination plants, in the intent of maximizing the membrane functions (Shahalam et al., 2002).

Two types of pretreatment methods have been practiced: conventional pretreatment and non-conventional or membrane pretreatment. Conventional pretreatment entails the use of disinfection, carbon adsorption, coagulation/flocculation, filtration, precipitation, and pH adjustment, to name a few. Disinfection inactivates bacteria and other microorganisms, and carbon adsorption serves to remove the residual chlorine from the feed water. Coagulation flocculation allows the removal of particulate matter, while granular media filtration can be used for the removal of suspended solids

and colloids. Further, conventional media filtration has been widely used for brackish groundwater, as well as chemical addition, disinfection, and cartridge filtration as a final pretreatment step before RO (Afonso et al., 2004; Greenlee et al., 2009). As for precipitation prevention, dosing of antiscalants and pH decrease are common practices to control scale formation of compounds like calcium carbonate, calcium sulfate, magnesium sulfate, and silica compounds, among others (El-Dessouky & Ettouney, 2002). However, a disadvantage is that the excessive addition of antiscalants could actually lead to fouling and is harmful to aquatic environments when improperly disposed of with the brine (El-Manharawy & Hafez, 2001; Cooley et al., 2006). Other choices for brackish water pretreatment include ion exchange for boron reduction or Ca and Mg scale control, and precipitation softening using lime, soda ash, and/or caustic for Ca, Mg, and Si removal (Sheikholeslami & Bright, 2002; Venkatesan & Wankat, 2011; Ayoub et al., 2013).

Non-conventional or membrane pretreatment processes, such as microfiltration (MF), nanofiltration (NF), and ultrafiltration (UF), have been increasingly used lately, depending on the feed water quality and product water characteristics required (Afonso et al., 2004; M'nifa et al., 2007). As depicted in Figure 1.1, these membranes have larger pore sizes than RO membranes, require lower operating pressures, and have demonstrated successful removal of foulants from a wide range of feed water types. This flexibility in their performance has rendered membrane processes appealing for RO pretreatment (El-Dessouky & Ettouney, 2002; Cooley et al., 2006). Also, membrane pretreatment options have been considered as more feasible than their conventional counterparts due to their improved costs and product water quality in some cases, and especially since they can reduce the volume of brine without adding

unfavorable chemicals to it (Cooley et al., 2006; Greenlee et al., 2009; Schrotter et al., 2010; Pandey et al., 2012).

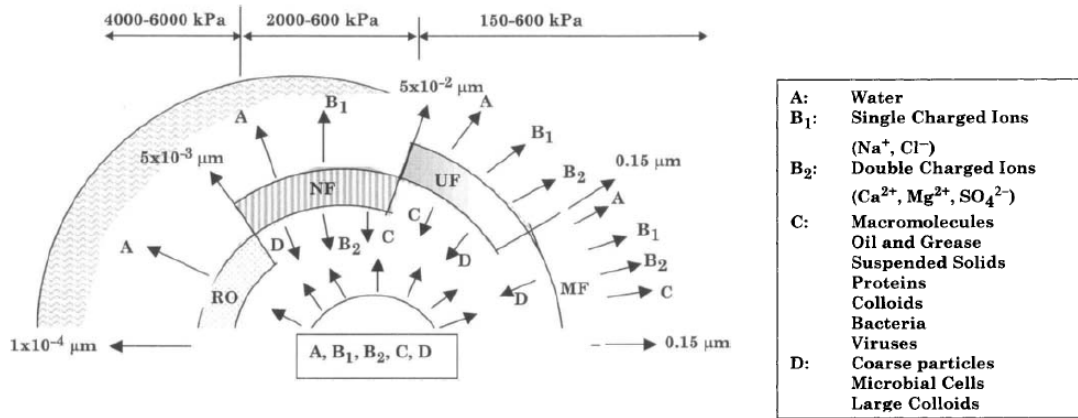


Figure 1. 1 Membrane processes, corresponding particle sizes, and operating pressure ranges (El-Dessouky & Ettouney, 2002)

It is important to mention that the quality of the feed water affects the type and consequent costs of pretreatment, which can reach up to 30% of the overall operational costs of the RO desalination procedure with very poor feed water quality (Miller, 2003; Pandey et al., 2012). So, considering the potential energy consumption and cost of pretreatment of feed water, minimizing the requirements for pretreatment, such as reducing chemical and material usage, is an important step in reducing its negative environmental impacts (Prihasto et al., 2009; Elimelech & Phillip, 2011). Within this context, not only does an effective pretreatment reduce post-treatment requirements, but it also minimizes the amount of adverse chemicals and residues that ultimately end up in the brine stream. Moreover, pretreatment of RO feed water will decrease membrane fouling and cut the need for cleaning and replacement, which normally constitutes up to 5% of the total costs in an RO plant, ultimately improving the membrane's lifetime and the RO system's overall performance (Cooley et al., 2006; Prihasto et al., 2009;

Valavala et al., 2011; Mogheir et al., 2013). Furthermore, an effective brine treatment process would allow volume reduction and potential recycling of the BWRO concentrate, thus reducing the brine disposal costs that can comprise up to 33% of the total cost of desalination (Mohamed et al., 2005).

Pertaining to this subject, the proposed research investigates the process of precipitation softening as a pretreatment stage for brackish water RO and as a post-treatment stage for brackish water RO brine. The effectiveness of precipitation softening is assessed by measuring the removal efficiencies of the pollutants of interest, through a series of experiments using three softening agents (caustic soda, lime, and soda ash). The removal of scale-producing and fouling components of water, such as iron, silica, barium, strontium, calcium, and magnesium, is expected, along with the simultaneous elimination of bacteria and organic matter for both types of water. This impact is achieved through coagulation/flocculation and disinfection, by the effect of pH increase. Additionally, the anticipated reduction of harmful RO concentrate would lower post-treatment requirements, thereby further lowering the related expenditure. Moreover, the significance of such a study lies in its universality and in the positive implications of the suggested process, the improved quality of feed water to the RO system, and the decreased RO concentrate stream. These positive impacts are exhibited in terms of lower chemical consumption, reduction in energy demand, improved RO membrane performance and characteristics (longer lifetime, decreased cleaning frequency), and possibly less harmful brine/ concentrate (less post-treatment requirements). It is needless to say that by reducing pretreatment and post-treatment requirements, operational costs are definitely cut down, whereby it has been proven that as the feed water quality deteriorates the costs of pretreatment can appreciably increase.

CHAPTER 2

LITERATURE REVIEW

In response to the unremitting advance in population size, industrial technologies, infrastructure, and living standards, water demand and consumption have soared in recent years, leaving renewable water sources at low quantity and raw water resources at low quality (Redondo, 2001; Mohamed et al., 2005). As an alternative source, brackish water has been increasingly used in RO desalination in the last two decades, especially in inland regions where seawater is not easily available (Kucera, 2014). Not unlike thermal desalination processes, RO has some significant drawbacks, namely brine disposal and membrane fouling due to the presence of constituents like calcium, microorganisms, silica, strontium, and barium (El-Dessouky & Ettouney, 2002; Lauer, 2006). To add, the deterioration in feed water quality only adds to the problem of fouling, thus increasing the need for pretreatment of raw water prior to RO desalination.

2.1. BWRO Reject

2.1.1. Brine Composition

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; and the brine stream usually constitutes 10 to 35% of the feed water as BWRO recovery rate varies between 65 and 90% (Ahmed et al., 2002; Mohamed et al., 2005; Greenlee et al., 2010). As determined by the characteristics and pretreatment needs of the feed water and the desalination process employed, the concentrate stream may contain initial water

components and salts (e.g. boron, silica, barium...), coagulants, antiscalants, antifoaming agents, residues from membrane cleaning with industrial chemicals, excess biocides or disinfection byproducts, toxic substances like fluoride, ammonia and hydrogen sulfide found in brackish groundwater, and traces of heavy metals from equipment deterioration such as copper, nickel and lead (Campbell & Jones, 2005; ESCWA, 2005; Mohamed et al., 2005; Greenlee et al., 2009).

2.1.2. Brine Management

2.1.2.1. Brine Disposal Options

The two major aspects of concern in concentrate management are environmental and economical; whereby evaporation ponds, for example, 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 (Ahmed et al., 2002; Cooley et al., 2006; Khedr, 2012). While irrigation using RO concentrate is a convenient option, it can adversely affect plant growth and salt levels in the soil (Mohamed et al., 2005; Greenlee et al., 2009). Similarly, discharge into surface waters like estuaries or lakes 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 (Sandia, 2003; Cooley et al., 2006; Subramani et al., 2012). 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 (Mohamed et al., 2005).

Unlike other desalination methods, BWRO plants seldom discharge brine at high temperatures, so thermal pollution to the receiving habitat is not a serious concern (Mezher et al., 2011). 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 (Arnal et al., 2005; Rahardianto et al., 2010).

As well, costs of brine disposal are subject to regulatory enforcement, and they are affected by the quality and quantity of the concentrate (Mohammadesmaeili et al., 2010b; Malaeb & Ayoub, 2011). 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 (Mohamed et al., 2005).

2.1.2.2. Brine Treatment Options

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 (Mickley, 2006). The ideal target would be to minimize liquid effluent and recover useful or valuable products from the brine, transforming the waste into commodity (Ahmed et al., 2002; Arnal et al., 2005; Mohammadesmaeili et al., 2010a; Ibáñez et al., 2013). 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) (Ahmed et al., 2002; Sandia, 2003; Ning et al., 2006; ESCWA, 2009). ZLD can be achieved once the recovery reaches 100% approximately,

where all the salts are retrieved and good-quality water is produced (Greenlee et al., 2009; Mohammadesmaeili et al., 2010a). 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. (2011) 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 (Komgold et al., 2005; Turek et al., 2009; Mohammadesmaeili et al., 2010a; Mezher et al., 2011; Perez Gonzalez et al., 2012; Jiang et al., 2014). 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 (Greenlee et al., 2011; Perez Gonzalez et al., 2012; Rahardianto et al., 2012). Experiments have been conducted using membrane distillation (MD), a cross between membrane and thermal processes, to effectively concentrate a groundwater RO reject (Qu et al., 2009; Kesime et al., 2013).

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 (Gabelich et al., 2007; Mohammadesmaeili et al., 2010a; Comstock et al., 2011). Moreover, carbon dioxide air stripping was explored as a method to enhance calcium precipitation by pH increase for BWRO concentrates with high carbonate concentrations (Hasson et al., 2011). Assessments of combining precipitation, MF, or NF treatment with secondary RO, followed by concentration through evaporation demonstrated a considerable reduction

in sludge volume (Mohammadesmaeili et al., 2010b; Gabelich et al., 2011; Khedr, 2012; Subramani et al., 2012).

Moreover, chemically-enhanced seeded precipitation (CESP) of concentrate using gypsum has been evaluated, as a step prior to secondary RO treatment (Rahardianto et al., 2010; McCool et al., 2013). Similar attempts of accelerated precipitation softening with a second RO pass for brackish water resulted in favorable reduction of major scalants like silica, barium, and strontium (Rahardianto et al., 2007; Zhu et al., 2010). Relevantly, using bittern, a solution rich in magnesium, to increase magnesium levels and thus induce coagulation and flocculation phenomena has been used as an effective treatment option for the removal of several foulants including suspended and colloidal material (Ayoub et al., 2000; Ayoub et al., 2001; Semerjian & Ayoub, 2003).

Still, many pilot-scale trials are conducted in the aim of evaluating reject management options, including reprocessing the concentrate stream with the primary RO, ion exchange, vibratory shear enhanced process (VSEP), MF, and UF (Khedr, 2012; Perez Gonzalez et al., 2012; Subramani et al., 2012; Wang et al., 2014). However, as environmentally viable as the ZLD alternative is, it is still among the most costly brine management options. Therefore, as costs seem to increase and environmental laws become progressively more severe, more feasible and environmentally sustainable brine treatment options are sought after (Ahmed et al., 2002; Khedr, 2012).

2.2. Membrane Fouling

Common to all membrane processes, fouling is the accumulation of organic and inorganic contaminants onto the surface or the pores of a membrane, but mainly on

the surface in the case of RO membranes, leading to an increase in pressure drop and salt passage across the membrane (Melián-Martel et al., 2012). This buildup can appear through three different scenarios: narrowing of the membrane pores, blocking of the pores, or developing a gel or cake layer (Pandey et al., 2012). For RO operation, the most likely means of fouling is the latter, since such membranes have very small pore size, nearing a “nonporous” quality (Song & Tay, 2011).

In part, fouling and decreased permeate flux are attributed to the phenomenon of concentration polarization (CP), whereby the relative concentration of salts tends to increase near the membrane surface or “boundary layer” compared to that in the bulk solution, and this eventually causes an increase in salt passage across the membrane (van de Lisdonk et al., 2001; Soltanieh & Gill, 2007; Greenlee et al., 2009). Just as important, fouling is also a function of the feed water quality, operating pressure, and membrane characteristics (Tang et al., 2011; Zhao et al., 2013). It is well recognized that surface roughness of the RO membrane can be a driving force in fouling of colloidal particles, minerals, and organic material (Ramon & Hoek, 2013).

2.2.1. Fouling Effects

Fouling can be reversible or irreversible, and it is undoubtedly a major impediment in the development of RO desalination (Pandey et al., 2012). The undesirable deposition of certain constituents near the membrane surface reduces the permeate flow and imposes RO operation at a lower recovery. Relevantly, the osmotic-resistance filtration model, described by Chong et al. (2007), explains the effect of fouling by calculating the flux for a clean membrane J_0 and for a fouled membrane J_f through 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 ΔP is the pressure difference across the membrane, $\Delta \Pi_b$ is the osmotic pressure difference between the bulk feed water and the product water, and μ is the feed water viscosity. R_m and R_f are the hydraulic resistance and the additional hydraulic resistance from the cake layer, respectively. M_0 and M_f are the CP modulus for the clean membrane and the fouled membrane (Tang et al., 2011).

The loss of performance quality and efficiency of the membrane caused by fouling necessitates mitigation measures like operating the RO system at greater pressures, recurrent membrane cleaning, and pretreatment of the feed water. Not only do these measures increase energy consumption of RO plants, but they also incur further operation costs and adversely affect the product water quality as well as the membrane lifetime (Sheikholeslami & Ong, 2003; Prihasto et al., 2009). As a result, it is reported that membrane replacement of up to 8% every year is needed to sustain water production objectives, representing about 7% of the total costs of a BWRO plant (between 1 and 5\$/m²-yr) (Miller, 2003; Cooley et al., 2006; Zhu et al., 2010; Melián-Martel et al., 2012).

2.2.2. Types of Fouling in BWRO

Fouling can occur in four different types: particulate fouling, inorganic scaling, organic fouling, and biological fouling. In BWRO, which mainly treats groundwater or inland surface water, membranes are fouled primarily by inorganic scaling and biofouling, since brackish feed water contains less amounts of colloids and organics (Greenlee et al., 2011; Pandey et al., 2012).

2.2.2.1. Particulate and Colloidal Fouling

Colloidal fouling is attributable to the accumulation of colloids, ranging from 1 to 10^3 nm in size, onto the membrane surface (Pandey et al., 2012). Knowledge about colloidal fouling is still insufficient, but it is well established that colloids can be organic or inorganic (Ning et al., 2005; Song & Tay, 2011). Inorganic colloids include clay particles, aluminosilicates, metal oxides (e.g. iron oxide), elemental sulfur (originating from sulfate-reducing bacteria in some aquifers), and colloidal silica; whereas organic colloids encompass a range of compounds, such as humic substances, polysaccharides from cell walls, proteins, and some biofoulants like cell fragments and debris (Ning R. Y., 1999; AWWA Membrane Technology Research Committee, 2005; Sutzkover-Gutman & Hasson, 2010; Tang et al., 2011). It is worthy to note that most of the naturally occurring colloids are negatively charged at the source water pH range (Song & Tay, 2011; Tang et al., 2011).

As contaminants are retained by the membrane, colloidal particles accumulate near the membrane and can deposit on it, compacting due to their increased concentration, or by interacting with the membrane surface. As well, some colloids like ferric and aluminum hydroxide can form polymers with other organic or inorganic foulants, resulting in a gel-like formation (Ning R. Y., 1999; Tang et al., 2011). Colloids have the ability to interact with the membrane surface as well as other colloidal agglomerations. The possible interactions can be expressed as the totality of the Van der Waals force, acid-base interaction, and the electrostatic interaction force, also known as the electrical double layer (EDL) force. Colloidal fouling and interactions are driven by several factors that are schematically represented in Figure 2.1 (Tang et al., 2011).

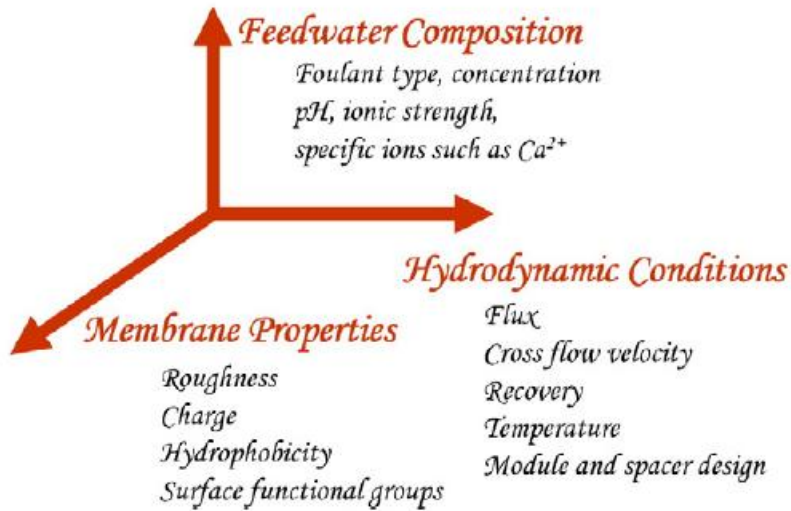


Figure 2. 1 Factors influencing colloidal fouling in RO membranes (Tang et al., 2011)

The deposition of colloids at the membrane surface contributes to a cake-like fouling layer, which not only decreases permeate flux by adding hydraulic resistance but also aggravates concentration polarization at the layer itself. This, in turn, necessitates higher operating pressure because of the phenomenon of cake-enhanced osmotic pressure (CEOP) from the solute accumulation near the membrane surface. This process is illustrated in Figure 2.2, adapted from Tang et al. (2011).

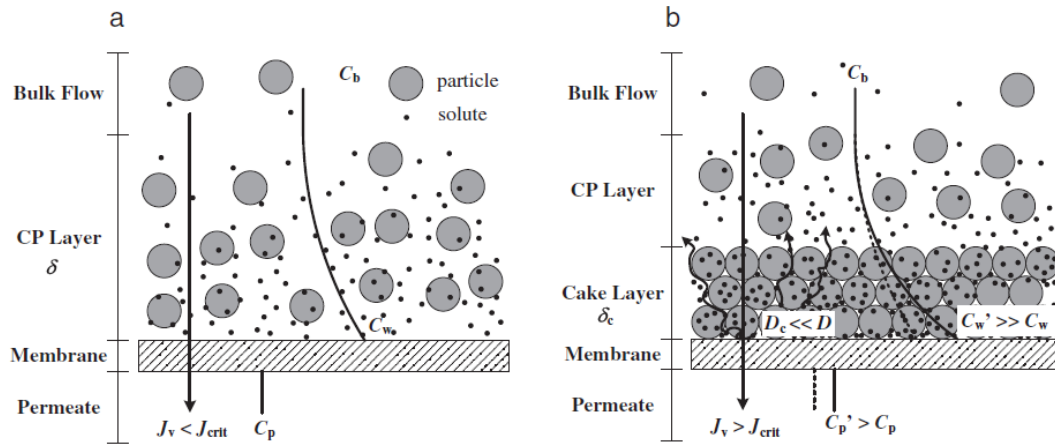


Figure 2. 2 CEOP and Concentration Polarization (a) before membrane fouling and (b) after membrane fouling (Tang et al., 2011)

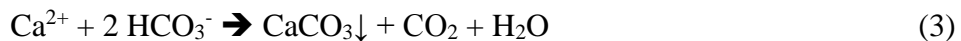
2.2.2.2. Inorganic Fouling or Scaling

During RO operation, as permeate is recovered and the concentrate stream becomes increasingly concentrated, inorganic fouling occurs when the solubility product of a sparingly soluble salt is exceeded at the feed water side of the membrane (van de Lisdonk et al., 2001). The main components that have a tendency to precipitate in BWRO systems are silica (SiO_2), calcium carbonate (CaCO_3), calcium sulphate (CaSO_4), barium sulphate (BaSO_4), strontium sulphate (SrSO_4), calcium fluoride (CaF_2), and to a lesser extent magnesium hydroxide ($\text{Mg}(\text{OH})_2$) (Greenlee et al., 2010; Greenlee et al., 2011). Some heavy metals that can exhibit fouling in RO are iron (Fe) and aluminum (Al) (Ning & Netwig, 2002). The abundance of inorganic scalants in the feed water is highly dependent on the source, whether surface or subterranean, and silica and calcium fouling are certainly the most problematic (Saavedra et al., 2012).

Scaling occurs in three stages, beginning with nucleation. It refers to the arrangement of inorganic molecules in a pattern creating a core for crystal formation, effected by the rise in ionic concentration at the retentate side (Mercer et al., 2005). This

allows more particles to deposit at the active sites of the nuclei and assemble into a basic crystalline shape. Finally, the crystal growth resumes, provided that the inorganic salts exceed their solubility limit (Zuddas & Mucci, 1998; Al-Rawajfeh & Al-Shamaileh, 2007).

The most frequent scale in BWRO is that of CaCO₃, followed by gypsum (CaSO₄) precipitation, among others (Melián-Martel et al., 2012). The precipitation of CaCO₃ and Mg(OH)₂ is promoted by increased pH, increased temperature, and high Ca²⁺, Mg²⁺, HCO₃⁻ and CO₃²⁻ concentrations (Zhang & Dawe, 1998; El-Dessouky & Ettouney, 2002). CaCO₃ starts to precipitate at pH values higher than 8, where carbonate ions are abundant, while Mg(OH)₂ precipitates at much higher pH values, beginning around 10.5-11 (Greenlee et al., 2010; Ayoub et al., 2013). Studies have shown that abundance of Mg²⁺ ions has an impact on the nucleation, quality, and growth of CaCO₃ crystals (Chen et al., 2005; Chen et al., 2006). The reactions for CaCO₃ equilibrium as well as the precipitation of Mg(OH)₂ in the abundance of OH⁻ ions are described as follows (El-Dessouky & Ettouney, 2002; Semerjian & Ayoub, 2003):



In this regard, the impact bicarbonate and carbonate concentrations goes back to the dependence of precipitation on CO₂ concentration; whereby gaseous CO₂ dissociates in water into carbonic acid, then contributes bicarbonate and carbonate alkalinity, according to the following reactions adapted from Al-Rawajfeh et al. (2008):



The equilibrium of gaseous CO₂ and dissolved CO₂ is governed by the Henry's law relationship (Chao & Westerhoff, 2002).

Unlike calcium carbonate, gypsum (CaSO₄) solubility is poorly related to pH, whereas the abundance of sulfate ions (SO₄²⁻) over carbonate ions has a partial positive effect on CaSO₄ solubility (Chong & Sheikholeslami, 2001; Rahardianto et al., 2008).

As for iron, it occurs naturally in many water sources, as dissolved ferrous iron(II) and as insoluble ferric iron(III). The latter is less problematic in membrane processes since it is easily filtered out after aeration and before reaching the membrane, but the former has the ability to foul the RO membrane. When present in groundwater, a common feed water source for BWRO, it exists in the reduced ferrous form and can be oxidized into the ferric form when in contact with oxygen (Teunissen et al., 2008). When it exceeds its solubility limit, ferric iron can precipitate in the system, and it is known to co-precipitate with Ca (Masarwa et al., 1997). The oxidation reaction of iron is adapted from Lerk (1965), as follows (Teunissen et al., 2008):



Iron can be precipitated as ferric hydroxide by lime-soda softening (Sheikholeslami & Bright, 2002). Other options for ferrous iron removal is adsorption in the presence of oxygen or oxidation into insoluble Fe(OH)₃ (Masarwa et al., 1997; Teunissen et al., 2008).

Another fouling precursor, fluoride, whose WHO maximum allowable concentration is 1.5 mg/L, can be found in many brackish waters in the MENA region. If not reduced, excessive amounts in potable water can lead to adverse health effects such as dental and skeletal fluorosis (Amor et al., 2001; Mogheir et al., 2013).

Another concern is the possibility of “biological precipitation”, which refers to the interaction between inorganic ions like Ca^{+} with ionizable groups that are carried in the biofouling film, such as negatively charged COO^{-} , CO_3^{2-} , SO_4^{2-} , PO_4^{3-} , OH^{-} , and the carboxylic acid functional group R-COOH (AWWA Membrane Technology Research Committee, 2005; Meng et al., 2009; Tang et al., 2011). This yields a gel-like structure and renders the fouling layer denser, aggravating the flux decline caused by fouling.

Many researchers have emphasized the impact of water composition on the kinetics and morphology of the scales formed on the membrane, primarily due to the coexistence of different scaling ions that could have synergistic or antagonistic effects (Chong & Sheikholeslami, 2001; Rahardianto et al., 2008). Therefore, co-precipitation is a valid assumption when several sparingly soluble salts are present in the water; whereby initially precipitating species can provide nucleation sites for other inorganic components (El-Dessouky & Ettouney, 2002; Sheikholeslami, 2011).

Inorganic scaling is treated in a variety of ways, but mainly anti-scaling agents and acid dosing are practiced. As for fluoride removal from potable water, several defluoridation techniques have been evaluated, like ion exchange, precipitation, and adsorption, but they remain costly options, thus limiting their use in the desalination industry (Amor et al., 2001). Other processes that target inorganic fouling include precipitation softening using alkalizing chemicals and NF membrane treatment. These options, their advantages and disadvantages, are more thoroughly discussed in the following sections.

2.2.2.3. Organic Fouling

Organic fouling occurs due to the presence of Natural Organic Matter (NOM), which is a mixture of a variety of components: humic substances, biopolymers (i.e. polysaccharides and proteins), and macromolecules from living organisms' decomposition and breakdown (Song & Tay, 2011). Organic constituents tend to easily adsorb onto the RO membrane, forming a fouling layer rich in proteins, humic substances and colloids (Meng et al., 2009). This causes a quick drop in water flux that tends toward a steady rate (Sutzkover-Gutman & Hasson, 2010).

As previously noted, research has shown that high ionic strength and high concentration of foulants, especially Ca^{2+} and Mg^{2+} , intensify fouling of humic substances, partly because of the affinity of Ca^{2+} to the carboxyl group in humic substances (Tang et al., 2011). Another influencing factor is feed water temperature, where membrane permeability is altered and salt rejection declines at higher temperatures (Jin et al., 2009). Moreover, the characteristics of the organic foulants in the feed water (e. g. molecular weight) as well as membrane properties highly affect the propensity of organic fouling. This is partly because organic material has a high affinity to positively charged and hydrophobic membrane surfaces (Sutzkover-Gutman & Hasson, 2010).

This type of fouling can be mitigated by removing organic components through coagulation-flocculation, carbon adsorption, and ion exchange (El-Dessouky & Ettouney, 2002). Lime-soda precipitation is a potential process that successfully removes soluble organics, such as fulvic acids and other humic substances, from groundwater by the effect of increased pH. This is also facilitated in the presence of sufficient Mg^{2+} concentrations, where some organic compounds tend to adsorb onto precipitating flocs like $\text{Mg}(\text{OH})_2$ (Randtke et al., 1982). Membrane surface modification

has also been suggested in the literature to effectively decrease fouling tendency in RO (Ramon & Hoek, 2013; Hegab et al., 2015).

2.2.2.4. Biological Fouling

A complex process, biological fouling is a serious concern in RO desalination, due to the varying characteristics of microorganisms and their persistence, where even after highly successful pretreatment, the slightest of bacterial concentration remaining can trigger biofouling (Flemming et al., 1997; AWWA Membrane Technology Research Committee, 2005). Biofouling refers to the attachment, growth, and multiplication of microorganisms onto the RO membrane.

The tendency for biofouling is governed by a multitude of factors, mainly the availability of nutrients and biodegradable material in the feed water, the count and species present, and water temperature (Sutzkover-Gutman & Hasson, 2010). Additionally, the affinity and physical-chemical interactions between bacterial cells and the membrane surface are major determinants of the formation of a biofilm (Meng et al., 2009).

As microorganisms are carried with the feed water to the membrane surface, they adhere to it and start proliferating and producing extracellular polymeric substances (EPS). The EPS matrix is made up of polysaccharides, proteins and other microbial molecules, making up a gel-like slime layer that facilitates the attachment of bacterial cells onto the surface and protects them from shear forces of the water flux (Flemming et al., 1997; Pandey et al., 2012). This can be considered as the ‘induction phase’ of biofouling, which is followed by the ‘logarithmical growth phase’ as described by Matin et al. (2011). Once the bacterial cells are attached, they use the

nutrients found in the water to further multiply and colonize the membrane, thus developing a matrix of polymers that resembles a mucus layer. As growth continues, this biofilm layer becomes increasingly stable and can retain colloids, organic material, and other particles; this is where the 'plateau phase' takes over (Sutzkover-Gutman & Hasson, 2010). After the biofilm matrix becomes mature, cells start detaching and disperse to new locations where new film formation is initiated (Matin et al., 2011). Once the biofilm starts significantly affecting RO operation, a limit which varies between different systems, the process is labeled as biofouling (Flemming et al., 1997).

Ultimately, uncontrolled biofouling can increase membrane selectivity as well as drastically reduce the water flux and salt rejection; this is basically caused by the biofilm functioning as a second membrane under increased operating pressure (Matin et al., 2011; Melián-Martel et al., 2012). Due to the nature of the EPS matrix, the biofilm can biodegrade membrane polymers and deteriorate the penetrability and effectiveness of biocides (Song & Tay, 2011). This exacerbates the possibility of complete biofilm removal through membrane cleaning, and the need for flux compensation implies more energy and cost expenditure (Matin et al., 2011).

The management of biological fouling is usually done either through prevention by feed water pretreatment and membrane treatment or through control by chemical cleaning. Membrane adjustments include the improvement of the surface's hydrophilic trait and roughness as well as increasing its negative charge (Matin et al., 2011). As for membrane cleaning, it is generally aimed at degenerating the fouling layer by disrupting the different interactions between the biofilm molecules (including Van der Waals interactions), in order to remove it using shear forces. However, the resulting improvement in membrane permeability has been shown to last only for a limited period

after cleaning because of the difficulty to completely remove the biofilm, thus enabling new bacterial growth (Flemming et al., 1997). Relevantly, the cost of cleaning can account up to 20% of operational costs (Matin et al., 2011).

Consequently, prevention is widely practiced, using disinfection techniques like chlorination, ozonation, and UV treatment. A summary adapted from Kim et al. (2009) is presented in Table 2.1 showing the different disinfection methods and their pros and cons. Chlorination is the most common disinfectant, where it was shown by Lechevallier et al. (1988) that chloramines (e.g. monochloramine (NH₂Cl) and chlorine dioxide (ClO₂)) were more effective in penetrating the biofilm layer than free chlorine (e.g. HOCl, OCl⁻) (Lechevallier et al., 1988; Malaeb & Ayoub, 2011; Matin et al., 2011). Aside from disinfectants, pH adjustment has been extensively examined as a complementary or stand-alone process, whereby it was established that a sufficient decrease or increase in pH can effectively inactivate bacteria and viruses (Rincón & Pulgarin, 2004; Ayoub et al., 2013).

Table 2.1 Comparison of disinfection techniques used for RO membrane biofouling (Kim et al., 2009)

	Disinfection	Advantage	Disadvantage
Physical	UV	<ul style="list-style-type: none"> • Easy installation and maintenance • Effective inactivation • Oxidation of organic matter 	<ul style="list-style-type: none"> • Scale formation • No residual effect
	Membrane	<ul style="list-style-type: none"> • Combined with membrane pretreated 	<ul style="list-style-type: none"> • High capital and operation cost
	Sand filtration	<ul style="list-style-type: none"> • Low installation and operation cost 	<ul style="list-style-type: none"> • Low bacterial removal efficiency
Chemical	HOCl, OCl ⁻	<ul style="list-style-type: none"> • High inactivation efficiency • Organic matter removal • Relatively low cost 	<ul style="list-style-type: none"> • Chemical corrosion of RO membrane • THMs, HAAs formation
	NH ₂ Cl	<ul style="list-style-type: none"> • Less harmful on membrane than HOCl • Residual inactivation 	<ul style="list-style-type: none"> • Relatively low efficiency
	ClO ₂	<ul style="list-style-type: none"> • No damage on membrane 	<ul style="list-style-type: none"> • Chlorite toxicity
	Ozone	<ul style="list-style-type: none"> • Effective inactivation • High oxidation potential for organic matter 	<ul style="list-style-type: none"> • Bromate formation • Very small half life • Damage by residual ozone

2.2.3. Evaluation of Fouling Potential

It is crucial to determine and quantify the principal fouling species in the source water in order to properly manage their effects, in terms of selecting the proper pretreatment (Melián-Martel et al., 2012). Schemes for prediction and protection against fouling have been developed by many researchers, each having its own pros and cons. Primarily, a comprehensive chemical and microbiological analysis of the feed water is useful. A widespread measure of fouling tendency is the Silt Density Index (SDI), which is based on running feed water through a 0.45 μm pore-size membrane at a steady pressure and calculating the decrease in flow per unit time. An acceptable value for feed water is a SDI value less than 3 (Li et al., 2008; Greenlee et al., 2009). Despite its extensive use in the industry, this technique presents some discrepancies when it comes to correcting for water temperature, accounting for contaminants smaller than 0.45 μm , and underestimating fouling propensity.

Consequently, the Modified Fouling Index (MFI) was developed with the corrective features of temperature consideration and linearly correlating the fouling tendency with the concentration of colloidal particles. It holds the assumption of cake layer formation as the governing process, whereby it acts as a filter then blocks the membrane. Nevertheless, the adequacy of this index to RO systems has also been questioned (Song & Tay, 2011; Salinas-Rodriguez et al., 2015). Thus, an alteration of the MFI using UF membranes (MFI-UF) with smaller pore size has been examined by several researchers and is being adopted for assessing fouling and pretreatment efficacy in RO plants (Greenlee et al., 2009).

As for estimating scaling potential for specific mineral salts, the saturation index (SI) can be calculated as follows:

$$SI_x = IAP / K_{sp,x} \quad (9)$$

where x is the sparingly soluble salt of interest, IAP is its ionic activity product, and $K_{sp,x}$ is its solubility product (Zhang & Dawe, 1998; Sobhani et al., 2012). When the solubility of a salt is exceeded by its ionic activity in the solution, the SI is greater than one, indicating potential for precipitation. For lower salinity feed waters, the Langelier Saturation Index (LSI), which is the logarithm of the SI, is commonly used, specifically for CaCO_3 precipitation (Alhadidi et al., 2009; Hchaichi et al., 2012).

Furthermore, turbidity, measured in Nephelometric Turbidity Units (NTU), is a rough indicator of particulate contaminants like algae, colloids, and humic substances (Sutzkover-Gutman & Hasson, 2010). Still, emphasis remains on developing a reliable and appropriate index for evaluating fouling tendency, especially for RO application (Alhadidi et al., 2013).

2.3. Fouling Management and Pretreatment

Membrane cleaning is crucial to restore RO performance and extend the membrane's lifetime, and it is usually carried out once the pressure differential increases by 15- 20% or water production decreases by 10%. It is categorized into physical cleaning, which involves the application of vibration and shear force, and chemical cleaning (AWWA Membrane Technology Research Committee, 2005; Schrotter et al., 2010). The chemicals commonly used are acidic solutions like citric acid and hydrochloric acid, followed by basic agents like sodium ethylenediaminetetraacetate (Na-EDTA), and sodium hydroxide, in order to remove the

cake layer formed by the different types of foulants (Song & Tay, 2011). Additionally, considerable research continues to be conducted to develop membranes that are more resistant to fouling and require less cleaning by altering their surface properties (AWWA Membrane Technology Research Committee, 2005; Elimelech & Phillip, 2011; Zhao et al., 2013; Hegab, Wimalasiri et al., 2015). Nonetheless, pretreatment is broadly practiced in order to minimize the need for membrane cleaning and replacement. The two types of pretreatment are: conventional pretreatment, involving the use of chemicals and filtration mainly, and non-conventional pretreatment which entails the use of low-pressure membrane (such as MF and UF) as well as high-pressure (such as NF) membrane processes.

2.3.1. Conventional Pretreatment

2.3.1.1. Pretreatment Practices

RO plants practice several pretreatment steps before feeding the water into the system, in order to avoid membrane fouling and loss of efficiency and, in some cases, to comply with certain water quality standards for the product water. If the feed water contains undesirable dissolved gases, such as hydrogen sulfide or carbon dioxide, degasification through stripping towers is conducted for their removal (Ning & Netwig, 2002).

For disinfecting the feed water, chlorine is mostly adopted even though it must be followed by the use of activated carbon for the purpose of de-chlorination to protect RO membranes from oxidation (Prihasto et al., 2009). Other biocides like formaldehyde and ozone are less commonly used because they are either less efficient or more costly (El-Dessouky & Ettouney, 2002; Sutzkover-Gutman & Hasson, 2010). Aside from

carbon adsorption, a possible step after chlorination is the application of chemicals like sodium bisulfate, sodium metabisulfite, and copper sulfate to protect the RO membrane from residual chlorine (Al-Mutaz, 2001; Khawaji et al., 2008; Melián-Martel et al., 2012). A major drawback of chlorination is that it is likely to produce some disinfection byproducts (DBP) in the presence of bromine and organic matter, such as trihalomethanes (THMs) and halo acetic acids (HAA), some of which are possible carcinogens (Matin et al., 2011; CDC, 2014).

To reduce colloidal material, organic matter, turbidity, and even some microorganisms, coagulation, flocculation, and sedimentation are widely practiced (Sutzkover-Gutman & Hasson, 2010). Coagulation involves the use of chemicals like ferric salts (e.g. ferric sulfate or ferric chloride) or other polymers along with rapid mixing, to induce the destabilization and agglomeration of colloids and suspended particles by neutralizing their negative surface charges. It is followed by flocculation, which consists of slow mixing and further aggregation of the non-settleable particles to allow them to settle (Marquardt, 1984; Koohestanian et al., 2008; Prihasto et al., 2009). In this regard, aluminum sulfate is less frequently used because it is less effective and, if present in sufficient amounts, their residues pose the risk of irreparable fouling (Li et al., 2008; Valavala et al., 2011).

Granular media filtration consists of several layers of different materials, such as gravel, anthracite, and sand, with their corresponding effective sizes; it can be operated by gravity or under pressure. The latter is more common in RO practices, and this pretreatment step can remove turbidity-causing contaminants (Greenlee et al., 2009).

As well, to prevent scaling of constituents like silica and calcium, antiscalants are applied to the feed water; these include negatively charged polymers, polyphosphates, polycarboxylate, or sodium hexametaphosphate (SHMP) compounds, (El-Dessouky & Ettouney, 2002). They have been extensively used due to the relatively low doses needed and their convenient costs (Sutzkover-Gutman & Hasson, 2010). These chemicals control scaling by adsorbing onto active sites of precipitates during the nucleation phase, thus preventing or hindering crystal growth (Greenlee et al., 2010; Sutzkover-Gutman & Hasson, 2010).

The limitations of antiscalants remain, in that they can cause fouling themselves due to the possible presence of phosphate ions, and harmful amounts can be found in the brine and even in the permeate, raising environmental and health concerns (Sheikholeslami, 1999; Ning & Netwig, 2002; Shahalam et al., 2002; Greenlee et al., 2009). Further research is currently carried out on electrolytic processes and the use of Zinc (Zn) to remove scaling components (Sutzkover-Gutman & Hasson, 2010).

Sometimes in combination with antiscalants or alone, dosing of acids like sulfuric or hydrochloric acid, decreases the pH and effectively removes bicarbonate alkalinity to prevent the precipitation of sparingly soluble salts like CaCO_3 and Mg(OH)_2 (El-Dessouky & Ettouney, 2002; Ning & Netwig, 2002; Sutzkover-Gutman & Hasson, 2010). Even though these acids are rather inexpensive, their handling and storage poses safety and environmental risks as they are corrosive and hazardous. Also, the potential of scaling of calcium, barium, and strontium due to the presence of sulfate must be considered (El-Dessouky & Ettouney, 2002; Ning & Netwig, 2002). Another drawback of acid addition is that it is more effective in controlling calcium carbonate

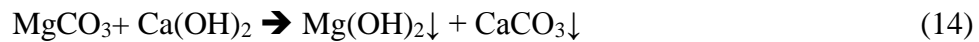
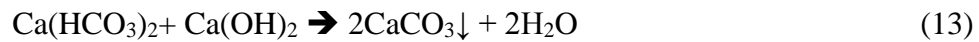
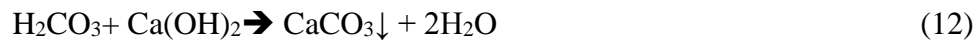
precipitation than that of sulfates or calcium fluoride (Ning & Netwig, 2002; Rahardianto et al., 2006).

Cartridge filtration is normally the final refining step before RO treatment, removing any contaminants larger than 5 or 10 μm that might have passed through previous stages (El-Dessouky & Ettouney, 2002; Shahalam et al., 2002; Greenlee et al., 2009).

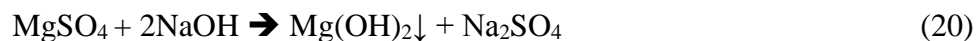
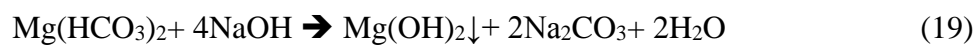
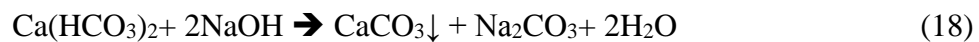
2.3.1.2. Precipitation Softening

Softening is the process of removing hardness caused by Ca and Mg in water, either by adding lime and soda ash or by employing ion exchange (Roalson et al., 2003; Venkatesan & Wankat, 2011). Relevant to the proposed research, lime-soda softening works by increasing the pH to ultimately reduce the solubility and induce the precipitation of salts like calcium carbonate (CaCO_3) and magnesium hydroxide ($\text{Mg}(\text{OH})_2$). Lime ($\text{Ca}(\text{OH})_2$) mainly contributes the hydroxyl ions (OH^-) for pH increase, and soda ash (Na_2CO_3) contributes the additional carbonates (CO_3^{2-}) to react with excess Ca (Chao & Westerhoff, 2002; Dey et al., 2007). Moreover, caustic soda (NaOH) is also used as a substitute source of hydroxyl ions to achieve a higher pH (Semerjian & Ayoub, 2003). This pretreatment technique has been demonstrated to efficiently remove Ca and Mg hardness as well as other contaminants like iron and boron (Ayoub et al., 2013). Other attempts for the removal of hardness causing elements include aeration and partial sludge recirculation combined with lime-soda softening, which demonstrated lower chemical consumption (Chao & Westerhoff, 2002).

In softening feed water for Ca and Mg removal, it should be taken into account that CaCO₃ reaches its lowest solubility at around pH 10.5 and Mg(OH)₂ requires operation at a pH of 11-11.5 to be effectively removed by softening (Chao & Westerhoff, 2002). However, it was reported by Semerjian and Ayoub (2003) and Ayoub et al. (2013) that while precipitation of carbonates is expected to occur between pH 9.3 and 10, the precipitation of hydroxide began between pH 10.5 and 11 in seawater. Other research demonstrated that Mg was removed, to a certain extent, at pH above 9.7 (Gabelich et al., 2007). The main precipitation reactions for Ca and Mg that occur upon addition of the alkalizing agent quicklime (CaO) or hydrated lime (Ca(OH)₂) are depicted as follows (Culp et al., 1978; Tchobanoglous & Burton, 1991; Semerjian & Ayoub, 2003):



The precipitation reactions when using NaOH as an alkalizing agent are as follows:



When Na₂CO₃ is used, the following reactions take place:



2.3.1.3. Non-Conventional or Membrane Pretreatment

Membrane filtration techniques (MF, UF, and NF) are used in different industries for purification of liquids, namely the production of drinking water, and recently they have been the subjects of research for the pretreatment of RO feed water (M'nifa et al., 2007; Hastuti & Wardiha, 2012). Figure 2.3 presents the different pore sizes, operating pressures, and rejected components of these membranes (Li et al., 2008). MF membranes can decrease turbidity and remove suspended solids and bacteria. UF membranes are able to eliminate color-causing impurities, organic molecules like humic acids, silt, as well as some bacteria and viruses (Wolf et al., 2005). As for NF membranes, they can reduce water hardness caused by divalent ions (Ca²⁺ and Mg²⁺), organic matter, sulfates, viruses, and even some heavy metals and pesticides (El-Dessouky & Ettouney, 2002; Cooley et al., 2006). The most commonly used is UF since its pore size is smaller than MF (Greenlee et al., 2009).

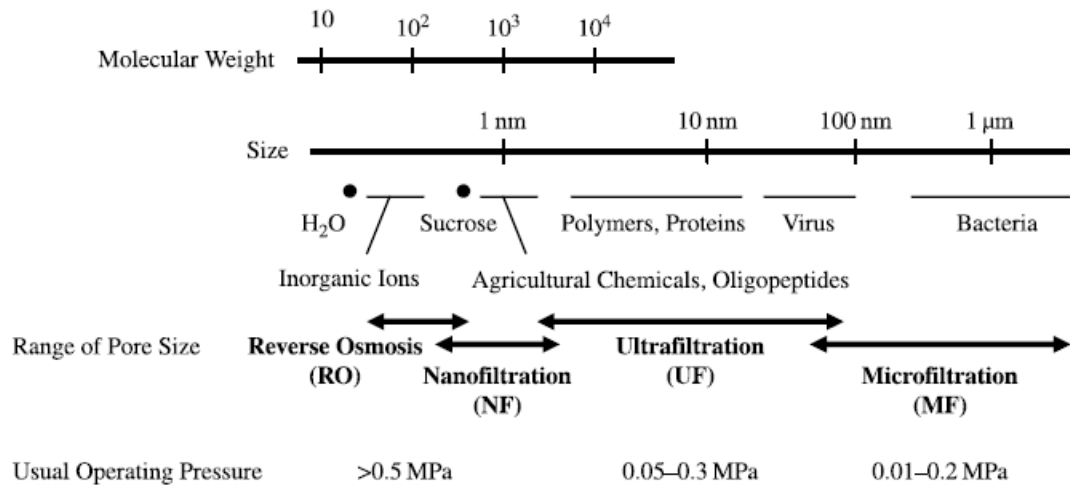


Figure 2.3 Descriptive scheme of the characteristics of the different membrane processes (Li et al., 2008)

Additionally, certain large-scale desalination plants employ integrated membrane systems (IMS) by utilizing MF and/or UF as a highly effective pretreatment step for RO. This resilient process can be consistent in providing significant control and reduction of particular parameters like turbidity, TSS, and harmful microorganisms. However, IMS lacks the ability to eliminate organic matter, dissolved substances, and disinfection by products (DBP), and could likely incur additional pretreatment costs (Redondo, 2001). Another membrane process, ED, was successfully attempted for excess fluoride removal, along with other inorganic foulants, with and without chemical addition, resulting in product water that complies with WHO drinking water standards (Amor et al., 2001).

The greatest disadvantage of membrane pretreatment is that they are subject to fouling on the surface and in the pores and, in turn, require backwashing and frequent cleaning using additional chemicals (Sheikholeslami, 1999; Li et al., 2008; Valavala et al., 2011).

2.4. Silica

Silicon (Si) exists in the form of free silica (SiO_2) in nature, rather than in its elemental form (Xie, 2011). At natural water pH, silica is usually present in the dissolved unionized form of monosilicic acid ($\text{Si}(\text{OH})_4$), and its solubility decreases with pH and temperature decrease (EI-Manharawy & Hafez, 2001). Average levels of silica are 7- 45 mg/L in groundwater and 1- 20 mg/L in surface waters. In some brackish sources and reject water, silica concentrations can be above 1000 mg/L (Arar et al., 2013). Silica (SiO_2) is dissolved in water according to the following reaction:



When exceeding its solubility limit, dissolved silica ($\text{Si}(\text{OH})_4$) can condense and polymerize, forming a high molecular weight type of silicic acid, which can precipitate onto an RO membrane, causing irreversible fouling. As well, colloidal silica can deposit to form a cake layer on the surface of the membrane, but this type can be more easily controlled by pretreatment or membrane cleaning (Badruzzaman et al., 2011; Xie, 2011).

The presence of certain heavy metals like iron and manganese as well as elevated Ca and Mg concentrations are known to enhance silica fouling. This is due to the fact that silica is known to adsorb onto the surface of precipitating metal hydroxides, namely magnesium hydroxide and ferric hydroxide (Sheikholeslami & Bright, 2002). To further complicate silica scaling, residues from aluminum-containing pretreatment chemicals can initiate aluminum silicate precipitation (Greenlee et al., 2009). Hence, silica deposits are quite problematic and difficult to control without causing membrane damage (Sheikholeslami et al., 2002; Arar et al., 2013).

To prevent dissolved silica from fouling, chemicals are commonly used, either to inhibit the formation of silica polymers or to scatter the particles and prevent their accumulation onto the membrane (Den & Wang, 2008; Badruzzaman et al., 2011; Xie, 2011). The removal of silica can be attributed to two mechanisms, adherence of dissolved silica Si onto $\text{Mg}(\text{OH})_2$ or other flocs and the formation of magnesium silicates (Chao & Westerhoff, 2002; Gabelich et al., 2007). Precipitation softening has been practiced for silica removal using lime and soda ash, giving successful results but adding to the calcium levels in the solution (Sheikholeslami & Bright, 2002). This removal can be in the form of magnesium silicate (Mg_2SiO_4) or calcium silicate (Ca_2SiO_4), and it can also be due to co-precipitation with insoluble iron and other metal hydroxides (Masarwa et al., 1997; Parks & Edwards, 2007). Moreover, silica elimination by the application of $\text{Mg}(\text{OH})_2$ showed that silica effectively adsorbs onto the surface of magnesium hydroxide flocs, and in some cases the $\text{Mg}(\text{OH})_2$ allows the effective polymerization of silica (Ayoub et al., 2001; Sheikholeslami & Bright, 2002; Ning et al., 2006).

Similarly, the use of coagulation- flocculation processes can also assist in colloidal silica removal, since silica has a negatively charged surface. Additionally, electrocoagulation, the process of coagulating suspended solids and metals by the effect of applying electrical charge, has been studied extensively (Sanfan & Qinlai, 1987; Den & Wang, 2008). Furthermore, Cheng et al. (2009) studied in-line coagulation followed by ultrafiltration as a pretreatment process for brackish water with a considerable level of silica. As well, significant silica removal was achieved using electrodeionization from water with high silica content (Arar et al., 2013).

2.5. Barium and Strontium

Barium and strontium are alkaline earth elements that naturally occur as the divalent cations Ba^{2+} and Sr^{2+} . Barium normally exists in the form of barite $BaSO_4$ in sediments, and barium compound solubility decreases with pH increase. The average level of barium in groundwater ranges from negligible concentrations up to 2.5 mg/L (World Health Organization, 2004). Ba^{2+} and Sr^{2+} are both able to react with carbonate, hydroxide, and sulfate, but the most common membrane scaling forms are $BaSO_4$ and $SrSO_4$ (Parks & Edwards, 2006). However, in waters with sufficient carbonate alkalinity, the scaling precursors can combine with the carbonate ion and precipitate as $BaCO_3$ and $SrCO_3$. $SrSO_4$ has lower solubility than $BaSO_4$ in natural water pH, but they are both less worrisome in BWRO membrane operation because they are usually present in trace amounts with respect to Ca and Mg (Greenlee et al., 2009; Alhadidi et al., 2013). Still, barium and strontium scaling can occur if present in sufficient concentrations, when RO water recovery is increased (Rahardianto et al., 2007).

Despite the lack of knowledge about health effects of strontium, a recommended level of 4 mg/L in drinking water has been set by the USEPA (USEPA, 2012). As for barium, there has been no considerable evidence of carcinogenicity in animals, but high exposure can lead to peristalsis, paralysis, and vasoconstriction (World Health Organization, 2004; Parks & Edwards, 2006). Consequently, the WHO set a guideline value of 0.7 mg/L of barium in drinking water (World Health Organization, 2004).

The treatment of feed water to eliminate barium and strontium is usually conducted by softening or the use of additional chemicals, such as aluminum salts or zinc compounds (Masarwa et al., 1997; Sheikholeslami et al., 2002; Parks & Edwards,

2006). It is noteworthy that NF pretreatment has the ability to remove such divalent ions. Although research on the mechanisms of Ba^{2+} and Sr^{2+} precipitation is rather scarce, they are known to be highly related to Ca scaling at elevated pH (EI-Manharawy & Hafez, 2001). Some studies state that these ions have the ability to co-precipitate, by integration into the crystalline network of $CaCO_3$ or by sorption onto the surface of the $CaCO_3$ crystals (Parks & Edwards, 2006; Gabelich et al., 2007). While maximum barium removals were reported at around pH of 11- 11.5 in feed water and RO reject, the addition of $Mg(OH)_2$ yielded 64% barium removal (Ning et al., 2006).

2.6. Boron

Boron is an essential element to living organisms, and it is abundant in rocks, soil, and water usually in the form of boric acid or borate salts (Zerze et al., 2013). It occurs in water either naturally from silts and rock weathering, or due to anthropogenic activity, such as the use and disposal of boron-containing detergents (Prats et al., 2000; Wolska & Bryjak, 2013). It is found in lower to moderate concentrations in groundwater (ranging from 0.3 to 0.6 mg/L) and surface water (less than 0.5mg/L), so it is more of a limiting factor in the desalination of seawater because it has an average concentration between 4.5 and 6 mg/L in seawater (Cooley et al., 2006; Li et al., 2008; Greenlee et al., 2009; Tu et al., 2013; Wang et al., 2014; Güler et al., 2015). At normal source water pH, boron is present as unionized boric acid $B(OH)_3$, which has a relatively low molecular weight and is therefore hard to reject by standard RO membranes (Greenlee et al., 2009; Mel'nik, 2010). Boric acid dissociates around pH= 9 (dissociation constant $pka \approx 9.24$), converting to borate $B(OH)_4^-$, whereby the

equilibrium reaction governing the speciation of boron in water is as follows (Wang et al., 2014; Güler et al., 2015):



Boron rejection by a RO membrane was reported at pH 9.5 and above, and it approached complete rejection at pH around 10.5 (Prats et al., 2000). Therefore, boron removal is highly dependent on the water temperature and pH as well as ionic strength (Oo & Ong, 2010; Schrotter et al., 2010; Arias et al., 2011).

Even though boron is necessary for vegetation, it is known to have harmful effects on plants, like growth inhibition and reduced fruit production, if present at levels above 1 mg/L (Zerze et al., 2013). As well, it adversely affects the male reproductive system in animals after oral intake. In case of chronic exposure to boron in humans, it can lead to problems in development and in the nervous system (Wang et al., 2014). As of 2011, the WHO set the maximum recommended level for boron in drinking water at 2.4 mg/L (Wolska & Bryjak, 2013).

When high boron concentrations are a concern for certain brackish water sources, many RO plants practice base dosing, which raises the pH in order to transform boric acid into the borate ion, which enhances its retention by the RO membrane (Sutzkover-Gutman & Hasson, 2010). However, the increased pH implies the problematic precipitation of numerous scalants at the RO membrane (Prats et al., 2000). Moreover, another pretreatment choice is the ion exchange process using specific resins that remove boron (Greenlee et al., 2009). However, the resin used for ion exchange must be regularly regenerated, which entails further use of chemicals like acids and bases and the production of highly contaminated wastewater with only limited

efficiency (Miller, 2003). This, in turn, necessitates chemical storage space and treatment of the water used for resin regeneration (Hu et al., 2015).

The use of a seawater RO membrane as a second pass has also been successful at removing boron, while simultaneously increasing the overall recovery rate of the RO system (Glueckstern & Priel, 2007; Alghoul et al., 2009; Farhat et al., 2013; Teychene et al., 2013). Further, precipitation softening has been studied as a removal technique; whereby significant boron reduction was observed at higher concentrations of Si and Mg, showing that boron adsorbs onto the precipitating magnesium silicates (Parks & Edwards, 2007; Zerze et al., 2013). Other boron removal methods that have been tested include the following:

- Polymer enhanced ultrafiltration (PEUF) (Zerze et al., 2013)
- Adsorption (Wolska & Bryjak, 2013)
- Sorption–membrane filtration hybrid processes (AMF), combining ion exchange with MF or UF (Tu et al., 2013; Güler et al., 2015)
- Electrocoagulation (Wolska & Bryjak, 2013)
- Electrodeionization (EDI) (Arar et al., 2013)
- Liquid–liquid extraction (Zerze et al., 2013)
- ED (Oren et al., 2006; Bodzek et al., 2011; Dydo & Turek, 2013; Wang et al., 2014)
- NF (Güler et al., 2015)

CHAPTER 3

MATERIALS AND METHODS

3.1. Water Collection and Analysis

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 (Afonso et al., 2004; Greenlee, et al., 2009). Four 500L tanks were used to collect and transfer the brackish water from the sampling location to the American University of Beirut, where the water was stored in 20L gallon containers at 23°C. It is important to mention that the tanks as well as the gallons were all adequately cleaned and rinsed twice with the sample water itself before filling and storage. Furthermore, brackish water RO reject samples were acquired by running a large fraction of the brackish water through a BWRO membrane at the AUB Chemical Engineering Lab FS1 at around 30% recovery rate. The resulting brine was also collected and stored at 23°C in 20L gallon containers that were cleaned and rinsed with the brine twice beforehand.

Within the objectives of the research at hand, both types of the sample water were analyzed frequently based on the standard methods (APHA et al., 2012) as presented in Appendix 1 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 9 months of uninterrupted laboratory work. The characteristics of the collected brackish water (BW) and the brackish water brine (BWB) are shown in Table 3.1.

Table 3.1 Composition of the sample BW and BWB samples collected for the experimental study

Parameter	Unit	BW			BWB		
		Number of Observations	Mean	Standard Deviation	Number of Observations	Mean	Standard Deviation
pH	pH units	11	7.54	0.1	11	7.4	0.1
Temperature	°C	11	25.30	1.7	11	25.5	1.9
Conductivity	mS	2	10.62	0.1	2	15.3	0.3
TDS (electrochemical)	mg/L	2	5305	49.5	2	7675	162.6
TDS (gravimetric)	mg/L	6	6357.5	244.2	6	9053.3	539.9
TSS	mg/L	4	34	15.5	4	44	24
VSS	mg/L	4	33.33	20.8	5	20.0	9.6
Alkalinity (hydroxide)	mg/L as CaCO ₃	7	0	0	7	0	0
Alkalinity (carbonate)	mg/L as CaCO ₃	7	0	0	7	0	0
Alkalinity (bicarbonate)	mg/L as CaCO ₃	7	113.2	25.9	7	117	59.1
Ca Hardness	mg/L as CaCO ₃	18	920.6	115.02	18	1197	130.7
Mg Hardness	mg/L as CaCO ₃	18	1625.6	168.8	18	2111	182.0
Total Hardness	mg/L as CaCO ₃	18	2524.4	148.9	18	3273	166.5
Chlorides	mg/L	14	3812.9	80.4	14	5489	216.0
Silica	mg/L as Si	17	4.2	1.3	17	6	1.4
	mg/L as SiO ₂	17	9.02	2.5	17	13.1	4.6
Fe	mg/L	4	0.04	0.004	4	0.041	0.004
Boron	as B (mg/L)	6	1.92	0.4	6	2.1	0.2
	as H ₃ BO ₃ (mg/L)	6	10.93	2.5	6	11.9	1.4
Strontium	mg/L	7	5.56	1.5	7	7.5	2.2
Barium	mg/L	4	BDL	BDL	4	BDL	BDL
Na	mg/L	5	1695.96	216.5	5	2842.7	349.7
K	mg/L	2	18.49	4.2	2	35.2	1.4
Fecal Coliforms	CFU in 100 mL After 24 hrs	3	0	0	3	0	0
Total Coliforms	CFU in 100 mL After 24 hrs	3	0	0	3	0	0

3.2. Experimental Setup

With the intention of assessing the efficacy of precipitation softening as both, a pretreatment step for BW desalination by reverse osmosis and as a brine treatment step, a series of titration experiments were conducted on the two types of sample water at room temperature (23 ± 1.4 °C and 22.8 ± 1.2 °C, for BW and BWB respectively). The titrations led to determining the optimal alkalizing agent. This was followed by examining the removal of scale-forming ions under different operating conditions of pH and temperature. These experimental conditions were chosen to be consistent with findings from the literature and previous work done in this field of study (Appendix 2).

3.3. Titration Experiments

The effectiveness of three softening chemicals, lime ($\text{Ca}(\text{OH})_2$), caustic soda (NaOH), and soda ash (Na_2CO_3), as well as combinations of $\text{Ca}(\text{OH})_2$ and Na_2CO_3 and of NaOH and Na_2CO_3 , in the removal of scaling and other fouling components was investigated in this study. To achieve this, a series of 6 titrations were carried out on the sample water with each of the proposed alkalizing agents, followed by the evaluation of Ca and Mg removal efficiencies. The initial and final water temperatures and pH values were recorded during the titrations, and the calcium and total hardness were analyzed. Ultimately, the agent or combination of agents that best achieved the required pH and optimal scalant removal was adopted as the final alkalizing agent/ agents for the consequent experiments. This selected softening agent was then used in successive titrations at different temperatures of 10°C and 30°C. Finally, the titrations allowed the calculation of the optimal softener volumes needed to reach the different experimental pH values, as presented in Appendix 3.

3.3.1. $\text{Ca}(\text{OH})_2$

Calcium oxide powder (ACS reagent, $\geq 99\%$ purity), in the amount of 56g in 1L of deionized water, was used to prepare 1M (= 1 mol/L) $\text{Ca}(\text{OH})_2$, and the resulting solution served as the source of hydroxyl ions (OH^-) to raise the sample water pH (Ayoub & Koopman, 1986; Ayoub et al., 1992; Ayoub, G. M., 1994; Ayoub et al., 1999; Chao & Westerhoff, 2002; Mercer et al., 2005). The prepared $\text{Ca}(\text{OH})_2$ solution was then used to titrate 100 mL of BW and BWB separately, as shown in Figures 3.1a and 3.1b.

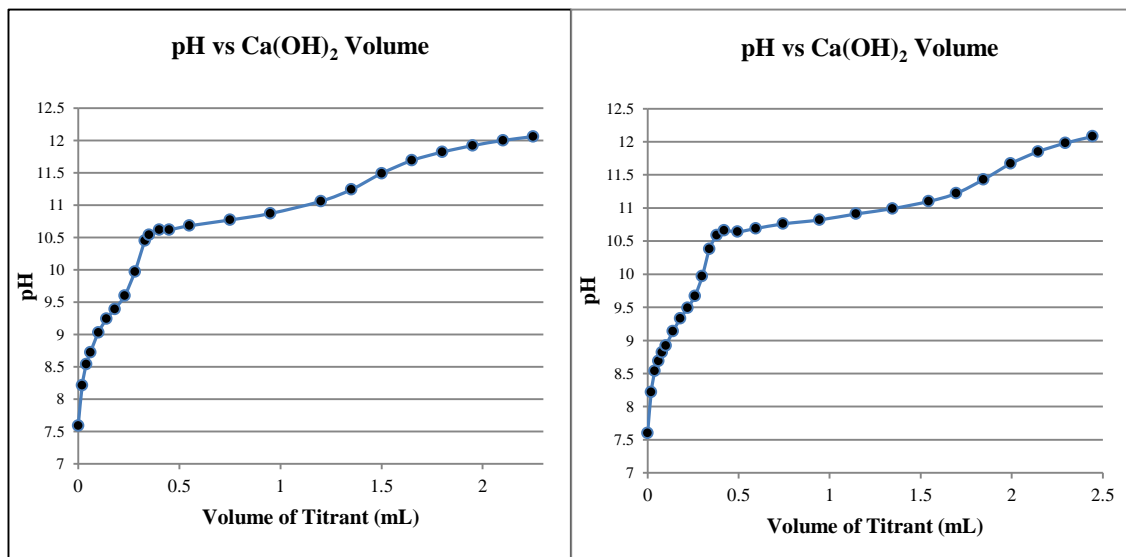
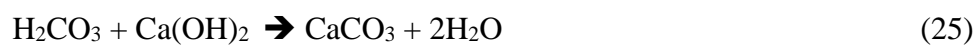


Figure 3.1 Titration curve of 100 mL (a) BW and (b) BWB with 1M $\text{Ca}(\text{OH})_2$

It is noteworthy that the dissolved CO_2 , present as carbonic acid, is expected to react with $\text{Ca}(\text{OH})_2$ according to the reaction below, but this does not contribute to additional hardness (Dey et al., 2007):



The results of titrating the sample water with respect to hardness removal is presented in Table 3.2.

Table 3.2 Effect of 1M Ca(OH)₂ on Ca and Mg Percentage Removals in (a) BW and (b) BWB

Water Type	BW		BWB	
Titrant Used	Ca(OH) ₂		Ca(OH) ₂	
Titrant Concentration	1M		1M	
Parameter	Mean	Standard Deviation	Mean	Standard Deviation
Sample Temperature	21.7	2.3	20.7	0.5
pH	12.1	0.1	12.12	0.07
Ca % Removal	-87.9	29.6	-100.8	11.6
Mg % Removal	76.1	8.5	84.8	6.9
Titrant Volume (mL) added to 100 mL of sample water	2.12		2.56	

3.3.2. NaOH

1N caustic soda, which is equal to 1 mol/L concentration, was prepared using 40 g of NaOH pellets (ACS reagent, ≥97% purity) and deionized water. NaOH is known to be a useful source of OH⁻ ions in softening (Semerjian & Ayoub, 2003; Mercer et al., 2005; Ayoub et al., 2013). 100 mL samples of both water types were titrated and the pH variation as a function of the titrant volume is presented in Figures 3.2a and 3.2b. It is necessary to consider that, upon the addition of NaOH to the water, CO₂ can react with it to form sodium carbonate, as per the following reaction:



Furthermore, the removals of Ca and Mg as a result of titrating with NaOH are represented in Table 3.3.

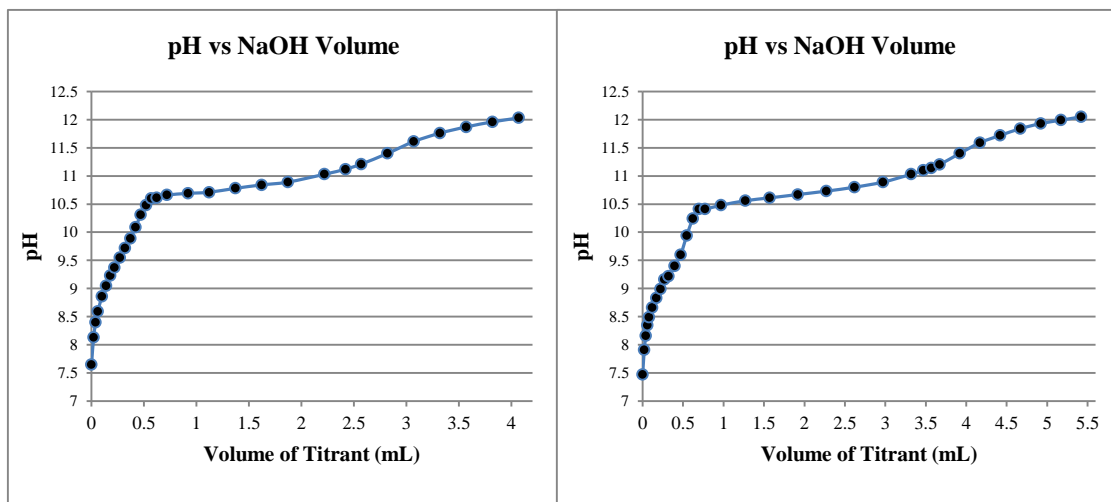


Figure 3.2 Titration curve of 100 mL (a) BW and (b) BWB with 1N NaOH

Table 3.3 Effect of 1N NaOH on Ca and Mg Percentage Removals in (a) BW and (b) BWB

Water Type	BW		BWB	
Titrant Used	NaOH		NaOH	
Titrant Concentration	1N		1N	
Parameter	Mean	Standard Deviation	Mean	Standard Deviation
Sample Temperature	22.6	1.6	23.7	0.5
pH	12.1	0.1	12.13	0.16
Ca % Removal	77.8	8.0	65.5	3.5
Mg % Removal	95.3	1.6	91.0	6.0
Titrant Volume added to 100 mL of sample water	4.48		5.51	

3.3.3. Na_2CO_3

To make 1N soda ash (=0.5 mol/L), 53 g of Na_2CO_3 powder (ACS reagent, $\geq 99.5\%$ purity) was mixed with 1L deionized water. During softening, the increase in pH results in the formation of carbonate ions from bicarbonate ions, thus removing Ca hardness to some extent. However, once all the carbonate ions are consumed in the precipitation of $CaCO_3$, Na_2CO_3 provides additional carbonate ions CO_3^{2-} to allow the

precipitation of the remaining calcium from the water (Chao & Westerhoff, 2002; Mercer et al., 2005). The titration results are portrayed in Figure 3.3, and the impact of Na_2CO_3 addition on hardness removal is shown in Table 3.4.

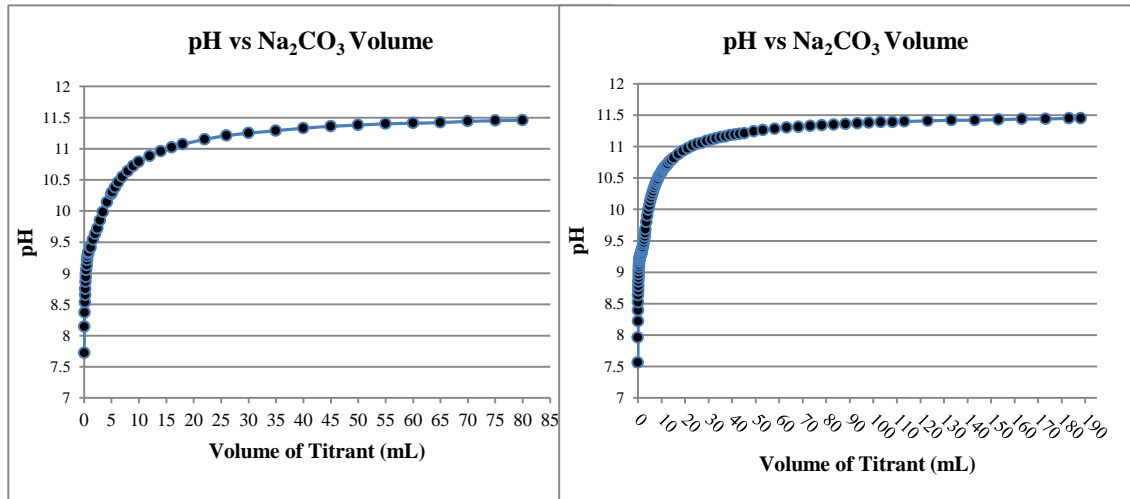


Figure 3.3 Titration curve of 100 mL (a) BW and (b) BWB with 1N Na_2CO_3

Table 3.4 Effect of 1N Na_2CO_3 on Ca and Mg Percentage Removals in (a) BW and (b) BWB

Water Type	BW		BWB	
Titrant Used	Na_2CO_3		Na_2CO_3	
Titrant Concentration	1N		1N	
Parameter	Mean	Standard Deviation	Mean	Standard Deviation
Sample Temperature	22.8	0.8	23.5	1.8
pH	11.3	0.2	11.33	0.2
Ca % Removal	100.0	0.0	100	0
Mg % Removal	52.4	5.2	66.4	6.4
Titrant Volume added to 100 mL of sample water	134.01		265.92	

3.3.4. Combination of NaOH and Na_2CO_3

Titration experiments were conducted using a combination of 1N NaOH and 1N Na_2CO_3 , in a 2:1 volumetric ratio, to assess the mixture as a potential alkalinizing

agent for the experimental study. The titration results are depicted in Figure 3.4, and the resulting removal percentages are shown in Table 3.5.

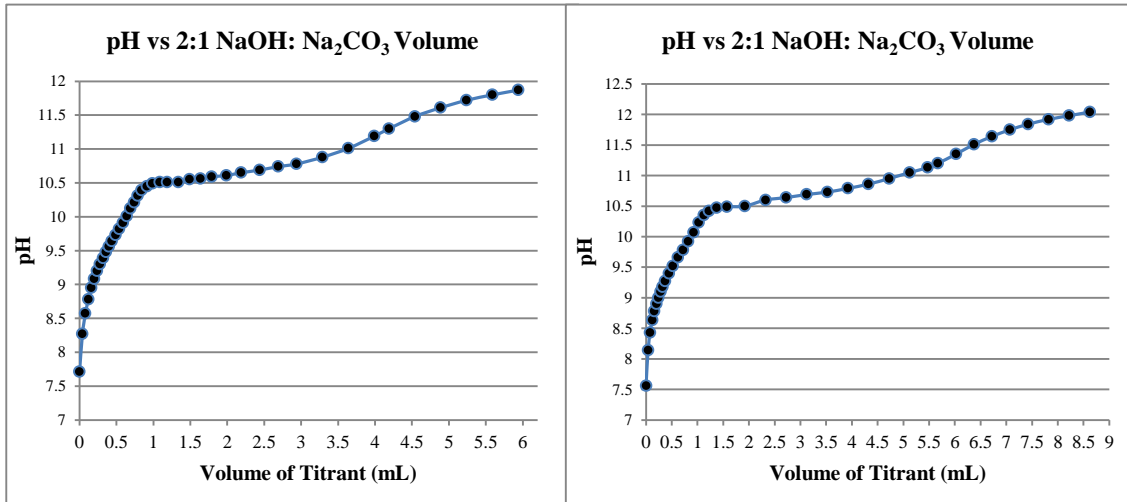


Figure 3.4 Titration curve of 100 mL (a) BW and (b) BWB with 2:1 1N NaOH:1N Na₂CO₃

Table 3.5 Effect of 2:1 1N NaOH:1N Na₂CO₃ on Ca and Mg Percentage Removals in (a) BW and (b) BWB

Water Type	BW		BWB	
Titrant Used	2:1 NaOH:Na ₂ CO ₃		2:1 NaOH:Na ₂ CO ₃	
Titrant Concentration	1N: 1N		1N: 1N	
Parameter	Mean	Standard Deviation	Mean	Standard Deviation
Sample Temperature	23.7	0.6	23.6	0.7
pH	11.9	0.1	12.02	0.05
Ca % Removal	99.9	0.1	99.9	0.1
Mg % Removal	95.9	0.1	97.1	0.4
Titrant Volume added to 100 mL of sample water	6.07		8.43	

3.3.5. Combination of Ca(OH)₂ and Na₂CO₃

Since Ca(OH)₂ alone is not totally effective in hardness removal, a 2:1 volumetric mixture of 1M Ca(OH)₂ with 1 N Na₂CO₃ was used to titrate 100 mL water samples.

The titrations are represented in Figures 3.5a and 3.5b, and Ca and Mg removals are depicted in Table 3.6.

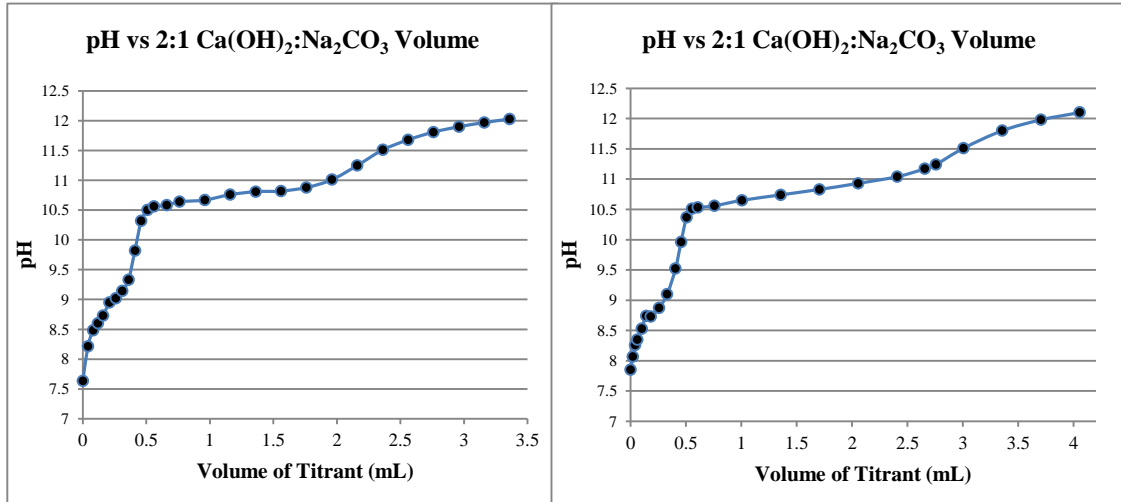


Figure 3.5 Titration curve of 100 mL (a) BW and (b) BWB with 2:1 1M Ca(OH)_2 :1N Na_2CO_3

Table 3.6 Effect of 2:1 1M Ca(OH)_2 :1N Na_2CO_3 on Ca and Mg Percentage Removals in (a) BW and (b) BWB

Water Type	BW		BWB	
Titrant Used	2:1 Ca(OH)_2 : Na_2CO_3		2:1 Ca(OH)_2 : Na_2CO_3	
Titrant Concentration	1M: 1N		1M: 1N	
Parameter	Mean	Standard Deviation	Mean	Standard Deviation
Sample Temperature	23.1	1.2	23.1	1.3
pH	12.1	0.2	12.02	0.09
Ca % Removal	-33.2	22.3	-19.4	4
Mg % Removal	66.0	2.9	73.5	4.3
Titrant Volume added to 100 mL of sample water	3.20		4.26	

3.4. Determination of the Optimal Alkalinizing Agent

It is clear that the final titrant volumes needed to achieve the same pH value were higher for the BWB. This is partly due to the increased buffering capacity of the

BWB derived from increased alkalinity. As seen in Table 3.2, the use of $\text{Ca}(\text{OH})_2$ alone as the titrant added considerable amounts of Ca to the water that are potentially problematic, rendering it the least favorable alkalizing agent.

As for NaOH, it resulted in higher Mg removals than Ca removals, mainly because of the contribution of hydroxyl ions and the shortage of carbonate ions to precipitate excessive Ca. Na_2CO_3 , however, yielded complete Ca removal for both water types but was incapable of removing Mg significantly. This makes it an unreasonable alkalizing agent, especially with regard to the extremely high volumes of 265.92 mL for 100 mL BW and 134.01 mL for 100 mL BWB added to attain an average pH around 11.3. To add, the mixture of $\text{Ca}(\text{OH})_2$ and Na_2CO_3 still contributed excessive Ca hardness, proving that it will not give optimal hardness removals in the subsequent softening experiments.

The 2:1 volumetric combination of 1N NaOH and 1N Na_2CO_3 gave the highest removals of both Ca and Mg hardness, with moderate volumes of titrant added to 100 mL of each water sample. Therefore, it was selected as the optimal alkalizing agent for the jar testing experiments. Since the effect of temperature on pH is undeniable, additional titration experiments were conducted with the selected agent at the experimental temperatures of 10 and 30°C, in order to determine the optimal doses required to attain the experimental pH values (Al-Rawajfeh et al., 2008). The corresponding results are depicted in Appendix 3.

3.5. Jar Testing

3.5.1. Jar Testing Procedure

A series of experiments were conducted at 3 different temperatures and 4 different pH values (Appendix 1), in order to explore the effect of these two factors on the removal of key contaminants, especially since there has been significant proof of their important role in the formation of Ca and Mg scale (Al-Rawajfeh et al., 2008). The experiments were carried out using the standard jar test apparatus (Phipps and Bird Model 7790-300 Six Paddle Stirrer), at 10, 25, and 30°C, since RO plants operate at similar temperatures depending on the source type and geographical location of the feed brackish water. It is worthy to note that the literature emphasizes that RO plants can exhibit optimal water production around temperatures of 27-28°C; therefore the experimental temperatures selected in this research can provide relevant insight to existing systems (Jin et al., 2009). At every temperature, the test pH values were 10.5, 11, 11.2, and 11.5; whereby a statistically significant difference in specific removals was expected. Specifically, Mg precipitation is known to occur at higher pH than that of Ca, and it can considerably affect the removal of other foulants (Randtke et al., 1982; Tang et al., 2011; Ayoub et al., 2013). Ultimately, this would allow the selection of optimal pH and temperature values for parametric removals, by choosing the conditions that primarily achieved superior removals of Ca and Mg, which are the main foulants of concern in this study.

The experiments were done on 2L samples of both water types, starting with a rapid mixing phase of 1 minute at 100 rpm, followed by slow mixing at 30 rpm for 20 minutes. Then, the treated samples were left to settle for around 60 minutes, while settling interface height measurements were taken to assess the sludge settling rate at 25°C for the different tested pH values.

When the jar tests were conducted at 10°C and 30°C, fitted polystyrene jackets were used to insulate every jar and maintain the experimental temperature for the required time (Ayoub et al., 2013). pH and temperature were monitored at regular intervals throughout the experimental time. In this regard, slight pH decreases were observed, mainly due to the dissolved CO₂ which takes the form of carbonic acid H₂CO₃, which results in reducing the pH (Chao & Westerhoff, 2002; Al-Rawajfeh et al., 2008; Ayoub et al., 2013).

3.5.2. *Water Analysis*

Samples were withdrawn after the completion of settling, such that the settled layer is not disturbed. The samples were analyzed, according to Standard methods, as shown in Appendix 1 (APHA et al., 2012). The main analysis parameters tested included: pH, temperature, conductivity, TDS, TSS, VSS, calcium, magnesium, silica, iron, boron, strontium, barium, sodium ions, and fecal and total coliform. The final concentrations of key parameters along with their initial concentrations were used to calculate their corresponding removal percentages.

3.5.3. *Spiking*

Even though the composition of the BW and BWB used is comparable to the typical chemical characteristics of these water types found in the literature, important constituents like iron, barium, and bacteria were deficient. So, in order to evaluate the effectiveness of the suggested softening process in removing such foulants, the sample water was spiked, and at least 3 spiking runs were conducted for each parameter. Percentage removals were calculated following every experiment, and this was used to

establish the effect of experimental conditions on the removal of these key contaminants.

3.5.3.1. Addition of Wastewater

Total coliform and fecal coliform are indicator microorganisms of a possible bacterial contamination of a water source. One of the most common types of total coliform is the *Escherichia coli* bacteria, which grow in the natural water pH range of 6 to 8 (Rincón & Pulgarin, 2004; Oram, 2014). To simulate the conditions of a contaminated water sample, municipal wastewater was used to spike BW (0.005-0.0075% by volume) and BWB (0.0065-0.01% by volume). The spiking runs were operated at room temperature ($\approx 25 \pm 2^\circ\text{C}$) and at 30°C , and the treated samples were analyzed for total and fecal coliform in the same day as the experiment.

3.5.3.2. Addition of Iron

Since the BW and BWB in this experimental study have negligible levels of iron, as depicted in Table 3.1, additional spiking runs were conducted at 30°C and at room temperature ($\approx 25 \pm 2^\circ\text{C}$). Ferrous sulfate (FeSO_4) was used to spike the samples, in order to replicate the occurrence of iron in natural brackish water, which ranges between 0.1 and 28.87 mg/L, emphasizing that this level can be twice as concentrated in RO brine (Alghoul et al., 2009; Stuyfzand & Raat, 2010; Saavedraa et al., 2013). The amounts of FeSO_4 added to 2L of sample water ranged between 17.2-18.6 mg for BW and 30.2- 31.9 mg for BWB, yielding concentrations of 3.16- 3.42 mg/L for BW and 5.55- 5.86 mg/L for BWB.

3.5.3.3. Addition of Barium

As previously noted, Barium can exist in brackish water in toxic levels, jar tests were carried out at room temperature ($\approx 25 \pm 2^\circ\text{C}$) while spiking with barium chloride dehydrate ($\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$). Barium concentrations in BW have been reported between 0.014 mg/L and 2.5 mg/L (Ning & Netwig, 2002; World Health Organization, 2004; Rahardianto et al., 2006). To achieve concentrations of 4.53- 7.03 mg/L for BW and 9.33- 13.44 mg/L for BWB, the quantities of $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ used for 2L of each, BW and BWB, were 16.1- 25 mg and 33.2- 47.8 mg, respectively.

3.6. Statistical Analysis

After calculating the percentage removals for key contaminants, such as calcium, magnesium, silica, iron, boron, strontium, barium, and fecal and total coliform, a statistical analysis was conducted to assess the effect of the proposed softening treatment on BW and BWB water quality. One way ANOVA testing was done to evaluate the separate impact of pH and temperature on removal efficiency as well as on final sludge depth. Two-way ANOVA allowed the assessment of the combined effect of pH and temperature on removals and final sludge depth. Furthermore, to test for any correlation and interaction between pH, temperature, and removal efficiency, single and multiple linear regressions were employed.

CHAPTER 4

RESULTS AND DISCUSSION

With the increasing prevalence of water source pollution and depletion, desalination is currently a viable solution for water-scarce communities. Specifically, RO is a quite appealing option for desalination in terms of energy consumption and membrane technology advancement. In that regard, brackish water is gaining attention as the feed water of choice for RO, especially in inland areas where seawater is not readily available, since among the other advanced desalination processes it requires the least amount of electric energy. Relevantly, BW constitutes up to 19% of the global feed water used in desalination (ESCWA, 2009).

Nevertheless, the overall efficacy of BWRO systems is still questionable because of the burden of membrane fouling and brine management and costs. This issue is exacerbated by the shortcomings in developing fouling resistant membranes as well as the degradation of source water quality. Thus, all BWRO systems require effective pretreatment of the feed water to minimize fouling, and this adds to the operation expenses. The experimental study at hand attempts the evaluation of a one-step process for the pretreatment of BW and the treatment of BWB, to finally determine its optimal operating conditions in terms of removing various foulants, such as Ca, Mg, Si, Fe, Ba, and bacteria. This process is based on the precipitation softening that is commonly used in water treatment, and it involves the use of one type or a mixture of chemicals to achieve the simultaneous removal of the water components that are known to cause fouling.

4.1. Brackish Water and BWRO Brine Characterization

Water samples investigated in this research, Table 3.1, have characteristics comparable to BW and BWB reported in the literature (Appendix 4 and Appendix 5). As expected for BW and BWB, the types of fouling that are anticipated are primarily inorganic due to the high concentrations of scaling salts represented by the following:

- Ca (920.6 ± 115.02 mg/L as CaCO_3 for BW; 1197 ± 130.7 mg/L as CaCO_3 for BWB)
- Mg (1625.6 ± 168.8 mg/L as CaCO_3 for BW; 2111 ± 182 mg/L as CaCO_3 for BWB)
- Si (4.2 ± 1.3 mg/L as Si for BW; 6 ± 1.4 mg/L as Si for BWB)

Also, although to a lesser degree, other fouling types are expected, namely organic (VSS: 33.33 ± 20.8 mg/L for BW; 20 ± 9.6 mg/L for BWB) and colloidal (TSS: 34 ± 15.5 mg/L for BW; 44 ± 24 mg/L for BWB).

To alleviate any possible fouling, pretreatment in this case is mandatory. As pointed earlier, precipitation softening is the process to be investigated in order to assess its efficacy in controlling such fouling. In order to test the removal efficiencies of some fouling materials present in low concentrations or missing in the samples, spiking of these foulants was deemed necessary so as to more accurately arrive at their removal levels. In this case spiking was performed with Fe (3.82 ± 1.38 mg/L for BW and 7.5 ± 4.42 mg/L for BWB), Ba (6.05 ± 1.02 mg/L for BW and 11.85 ± 1.75 mg/L for BWB), and bacteria (TNTC).

4.2. Jar Test Results

The experiments of this research involved the use of the selected optimal alkalizing combination of agents 1N NaOH and 1N Na₂CO₃ with volumetric ratio 2:1. Specific volumes of this combination of softening agents were used in different jars to achieve the desired pH, which in turn allowed the precipitation of the inorganic salts (Appendix 3). The jar tests were conducted under various experimental conditions of pH and temperature, and settling rate was observed and samples were withdrawn and analyzed for the different parameters of interest. The experimental temperatures were 10°C, ≈23- 25°C, and 30°C, and the test pH values at each temperature were 10.5, 11, 11.2, and 11.5 (Appendix 2).

After the calculation of the parametric removal efficiencies, the data was used to conduct a statistical analysis using the R project for Statistical Computing. The Shapiro-Wilk test for normality of data was used, along with the Bartlett test for the homogeneity of variances. As well, one-way and two-way ANOVA tests were performed on every parameter, and the null and alternative/ experimental hypotheses were defined as follows:

- H₀: The suggested treatment (pH and/ or temperature) has no effect on the parametric removal efficiency
- H_a: The suggested treatment (pH and/ or temperature) has an effect on the parametric removal efficiency

After significant findings were extracted from the Analysis of Variance, single and multiple linear regressions were conducted as well with the aim to assess the linear relationship between the predictor variables of pH and temperature and the response variable, which is the removal efficiency of the key contaminants. It is important to mention the assumptions maintained for the statistical analysis, including the linear

relationship between parametric removal and pH and/ or temperature, normal distribution of removal percentages, and homogeneous variances of removals under each pH and temperature condition.

4.2.1. Effect of pH on Foulant Removal

It is well established that pH can have a significant impact on the precipitation of inorganic salts like Ca and Mg, as such the effect of pH was assessed at room temperature ($\approx 25 \pm 2^\circ\text{C}$) operating at four pH values of 10.5, 11, 11.2, and 11.5. The results of the jar test experiments, with the mean removal percentages and the standard deviations (sd) are presented in Tables 4.1 and 4.2.

Table 4.1 Treated BW Characteristics at experimental pH values and temperature $T \approx 25^\circ\text{C}$

Parameter	Unit	Initial BW Mean \pm sd	Treated Water at pH \approx 10.5 Mean \pm sd	Treated Water at pH \approx 11 Mean \pm sd	Treated Water at pH \approx 11.2 Mean \pm sd	Treated Water at pH \approx 11.5 Mean \pm sd
Experimental pH	pH units	7.54 \pm 0.1	10.4 \pm 0.1	10.9 \pm 0.1	11.1 \pm 0.1	11.5 \pm 0.1
Temperature	$^\circ\text{C}$	25.30 \pm 1.7	24.4 \pm 1.5	24.4 \pm 1.5	25.8 \pm 0.7	24.7 \pm 1.7
Ca Hardness	mg/L as CaCO ₃	920.56 \pm 115.0	452.5 \pm 49.9	80.75 \pm 16.5	13.7 \pm 0.6	3.8 \pm 7.5
Ca Removal	%	N/A	50.84 \pm 5.42	91.23 \pm 1.79	98.52 \pm 0.06	99.59 \pm 0.81
Mg Hardness	mg/L as CaCO ₃	1625.6 \pm 353.3	1350.0 \pm 55.68	208.5 \pm 16.50	86.33 \pm 34.44	69.50 \pm 15.59
Mg Removal	%	N/A	16.95 \pm 3.43	87.17 \pm 3.47	94.69 \pm 2.12	95.72 \pm 0.96
Silica	mg/L as Si	4.17 \pm 1.6	0.98 \pm 0.83	0.50 \pm 0.36	0.60 \pm 0.56	1.38 \pm 0.76
	mg/L as SiO ₂	9.02 \pm 3.2	2.10 \pm 1.82	1.10 \pm 0.71	1.27 \pm 1.17	2.95 \pm 1.59
Silica Removal	% as Si	N/A	76.62 \pm 19.81	88.01 \pm 8.53	85.61 \pm 13.35	67.03 \pm 18.30
	% as SiO ₂	N/A	76.73 \pm 20.21	87.81 \pm 18.30	85.96 \pm 12.94	67.31 \pm 17.60
Boron	as B (mg/L)	1.92 \pm 0.5	0.60 \pm 0.10	0.40 \pm 0.36	0.67 \pm 0.42	1.43 \pm 0.51
	as H ₃ BO ₃ (mg/L)	10.93 \pm 3.2	3.47 \pm 0.49	2.13 \pm 1.96	3.80 \pm 2.38	8.07 \pm 2.89
Boron Removal	% as B	N/A	68.70 \pm 5.22	79.13 \pm 18.81	65.22 \pm 21.72	40.00 \pm 11.07
	% as c	N/A	68.29 \pm 4.51	80.49 \pm 17.88	65.24 \pm 21.78	40.55 \pm 12.93
Strontium	mg/L	5.56 \pm 1.8	4.34 \pm 0.87	3.04 \pm 0.23	2.42 \pm 0.20	1.71 \pm 0.25
Strontium Removal	%	N/A	22.03 \pm 15.58	45.39 \pm 4.12	56.50 \pm 3.51	69.18 \pm 4.56

Table 4.2 Treated BWB at experimental pH values and temperature T≈25°C

Parameter	Unit	Initial BWB Mean ± sd	Treated Water at pH≈ 10.5 Mean ± sd	Treated Water at pH≈ 11 Mean ± sd	Treated Water at pH≈ 11.2 Mean ± sd	Treated Water at pH≈ 11.5 Mean ± sd
Experimental pH	pH units	7.4 ± 0.1	10.4 ± 0.1	10.9 ± 0.1	11 ± 0.1	11.4 ± 0.1
Temperature	°C	25.5 ± 1.9	24.6 ± 1.8	24.5 ± 1.5	25.7 ± 0.8	24.7 ± 1.5
Ca Hardness	mg/L as CaCO ₃	1197.2 ± 130.7	537.5 ± 42.7	103.3 ± 10.0	14.3 ± 1.5	2.8 ± 5.5
Ca Removal	%	N/A	55.10 ± 3.57	91.38 ± 0.84	98.80 ± 0.13	99.77 ± 0.46
Mg Hardness	mg/L as CaCO ₃	2110.6 ± 417.8	1410 ± 130.8	244.0 ± 42.9	100.7 ± 14.5	71.5 ± 13.1
Mg Removal	%	N/A	33.19 ± 6.20	88.44 ± 2.03	95.23 ± 0.69	96.61 ± 0.62
Silica	mg/L as Si	6.12 ± 2.1	0.6 ± 0.4	0.6 ± 0.4	0.6 ± 0.8	2.1 ± 0.9
	mg/L as SiO ₂	13.1 ± 4.6	1.3 ± 0.8	1.2 ± 0.8	1.4 ± 1.7	4.4 ± 1.9
Silica Removal	% as Si	N/A	90.61 ± 5.72	90.61 ± 6.02	89.66 ± 12.68	66.52 ± 14.51
	% as SiO ₂	N/A	90.46 ± 5.86	91.03 ± 6.28	89.57 ± 13.14	66.79 ± 14.23
Boron	as B (mg/L)	2.1 ± 0.6	0.5 ± 0.3	0.4 ± 0.3	0.8 ± 0.2	1.4 ± 0.5
	as H ₃ BO ₃ (mg/L)	11.9 ± 3.1	2.7 ± 1.3	2.4 ± 1.5	4.6 ± 0.97	7.6 ± 2.5
Boron Removal	% as B	N/A	77.4 ± 12.2	79.0 ± 12.2	59.7 ± 7.4	33.9 ± 21.8
	% as H ₃ BO ₃	N/A	77.1 ± 10.6	80.1 ± 12.7	61.1 ± 8.2	35.9 ± 20.6
Strontium	mg/L	7.5 ± 2.7	5.7 ± 0.8	3.9 ± 0.3	2.99 ± 0.4	2.1 ± 0.2
Strontium Removal	%	N/A	24.16 ± 10.5	48.4 ± 3.4	60.2 ± 5.6	71.6 ± 2.6

It was clear that for Ca, Mg, and Sr, the percentage removals increased with pH increase from 10.5 to 11.5, reaching their maximum removals of 99.59%, 95.72%, and 69.18% respectively for BW and 99.77%, 96.61%, and 71.6% respectively for BWB at pH=11.5. Consistently, the one-way ANOVA conducted showed that pH had a significant effect on the removal efficiency of Ca (p-value: $2e^{-16}$ for BW and $2e^{-16}$ for BWB), Mg (p-value: $3.7e^{-07}$ for BW and $2.87e^{-08}$ for BWB), and Sr (p-value: $1.45e^{-05}$ for BW and $1.02e^{-06}$ for BWB).

The increase in Ca and Mg removal with pH is in agreement with previous research reported on BW, BWB, and seawater (Gabelich et al., 2007; Rahardianto et al., 2007; Ayoub et al., 2013). The removal of strontium is attributed to its precipitation as SrSO₄, and it paralleled the removal of Ca with respect to pH variation. Thus, it is possible that Sr co-precipitated with CaCO₃, yielding better removal at pH higher than 10, which was reported in the literature to reach up to 88–95% (Gabelich et al., 2007). A comparative graph of these average removals is demonstrated for each, BW and BWB, in Figures 4.1 and 4.2.

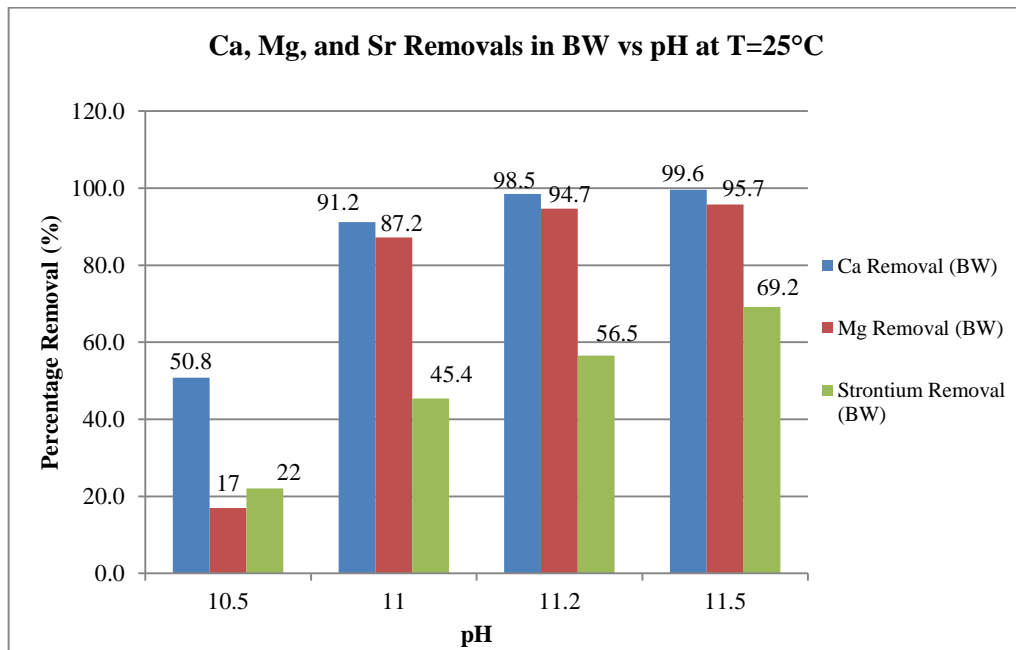


Figure 4.1 Average Percentage Removals of Ca, Mg, and Sr in BW at different experimental pH values at T≈25°C

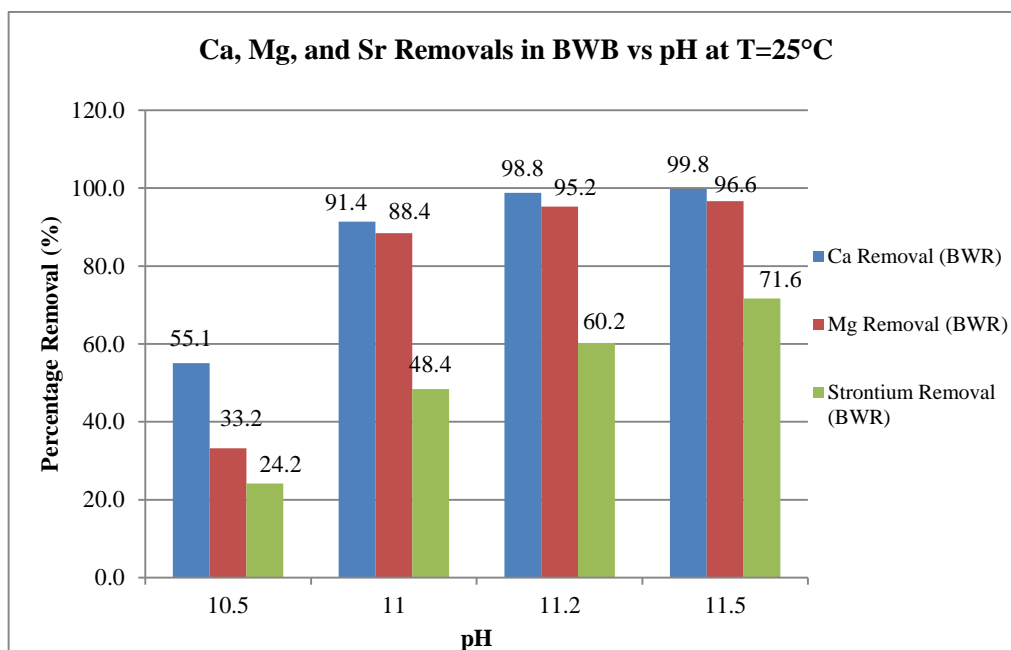


Figure 4.2 Average Percentage Removals of Ca, Mg, and Sr in BWB at different experimental pH values at T≈25°C

For the two water types, boron and silica removals were the least at pH 11.5 (Si as SiO₂: 67.31% for BW and 66.79% for BWB; B as H₃BO₃: 40.55% for BW and 35.9% for BWR) and the highest at pH= 11 (Si as SiO₂: 87.81% for BW and 91.03% for BWR; B as H₃BO₃: 80.49% for BW and 80.1% for BWR). According to the Analysis of Variance test, no statistically significant differences were observed in SiO₂ removal efficiencies between the different pH values tested at T=25°C, whereby the p-value was 0.352 for BW and for 0.868 BWB. However, the difference in H₃BO₃ removal between the experimental pH values was statistically significant for BWB only (p-value= 0.0123).

Though silica removal is normally expected to be in congruence with Mg removal, the optimal percentage of removal exhibited is similar to that reported by earlier studies that demonstrated maximum Si removal at pH around 11 (Gabelich et al., 2007). The removal of Si originates from two scenarios: the production of magnesium

silicate, and the abundance of the hydroxyl ion at elevated pH values, which facilitates the formation of metal hydroxides (of Mg and Fe) providing more adsorption sites for Si (Masarwa et al., 1997; Gabelich et al., 2007; Teunissen et al., 2008).

As for the removal of boron, it is quite similar to the removal of Si, as seen in Figures 4.3 and 4.4. This is reinforced by the hypothesis that boron removal is favored in the presence of both Mg and Si, which co-precipitate, since it attaches to the insoluble magnesium silicate formed. A plausible explanation of reduced boron removal beyond this pH value could be the competitive sorption by carbonate and hydroxyl ions on magnesium silicate flocs (Parks & Edwards, 2007).

Comparing the removal values for Silica and Boron, it is noted that the percentage removal of these two metals in BWB appreciably exceeds the removal in BW, and this is more obvious at pH 10.5 where the difference in removal stands at about 14% and 9% respectively. This behavior tends to strengthen and moreover justify the hypothesis that removal is favored by the presence Mg, where in this case the concentration of Mg in BWB is much higher than in BW. Thus, more magnesium silicate is formed, which will enhance the settling of more Si and in turn will enhance the removal of B even at lower pH values (10.5 compared 11.0 and 11.5).

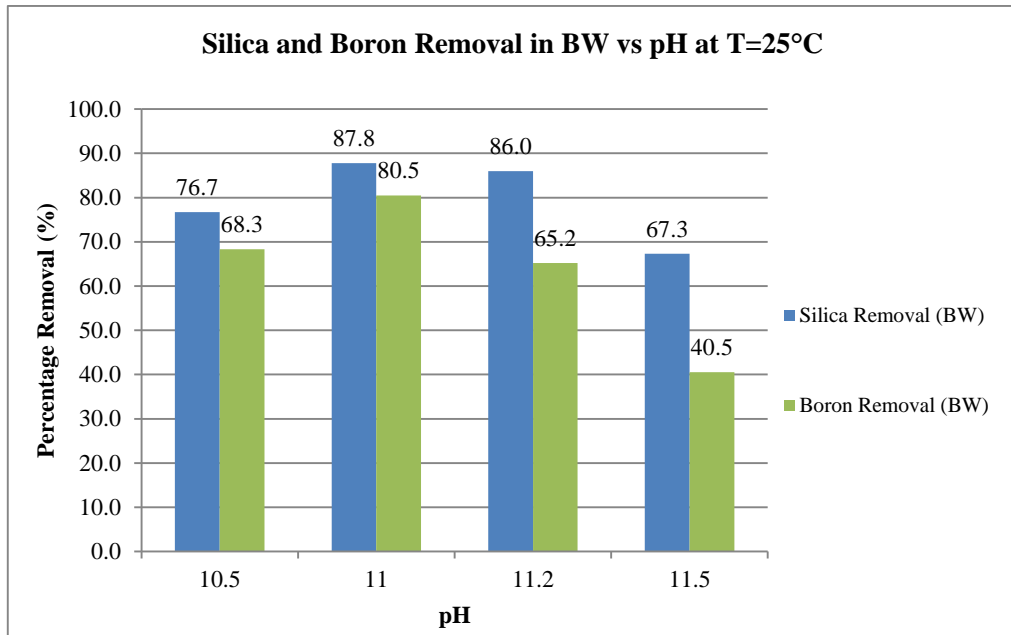


Figure 4.3 Average Percentage Removals of Si and B in BW at different experimental pH values at T≈25°C

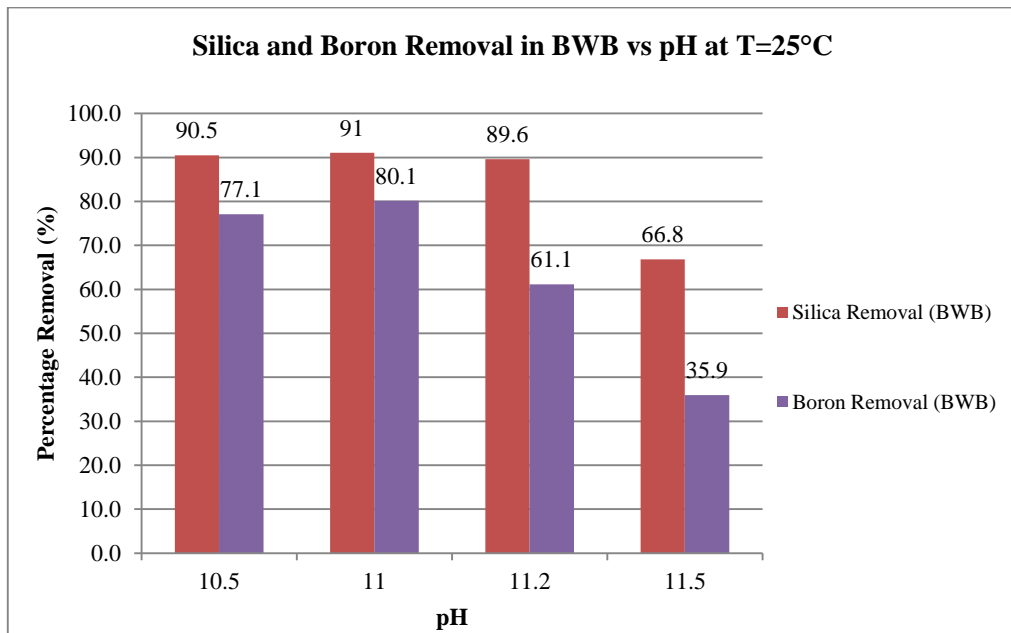


Figure 4.4 Average Percentage Removals of Si and B in BWB at different experimental pH values at T≈25°C

Moreover, the single regression analysis for the key parameters produced the equations in Table 4.3, where R^2 and adjusted R^2 (between 0 and 1) represent the proportion of variability in parametric removal that is accounted for by pH, and the p-

value is an indicator of the significance level α . In coherence with the ANOVA results for SiO₂, the linear relationship of its removal versus pH is not significant, with the lowest coefficient of determination (R^2) and p-value.

Table 4.3 Single Linear Regression Analysis for Parametric Removals vs. pH at T=25°C for BW and BWB

Water Type	Parameter % Removal	Regression Equation	R ²	R ² _{adj}	P-value
BW	Ca	-539.186 + 56.287 pH	0.8626	0.8589	< 2.2e ⁻¹⁶
	Mg	-648.86 + 64.12 pH	0.5373	0.5237	3.704e ⁻⁰⁷
	SiO ₂	-9.439 + 7.785 pH	0.02346	-0.002933	0.3519
	H ₃ BO ₃	301.50 - 21.41 pH	0.1679	0.07547	0.2107
	Sr	-477.573 + 47.588 pH	0.8591	0.845	1.453e ⁻⁰⁵
BWB	Ca	-540.165 + 56.358 pH	0.843	0.8387	2.2e ⁻¹⁶
	Mg	-582.711 + 58.800 pH	0.6007	0.5889	2.873e ⁻⁰⁸
	SiO ₂	95.4482 - 0.9151 pH	0.0007557	-0.02625	0.8681
	H ₃ BO ₃	502.39 - 39.71 pH	0.4817	0.4298	0.01229
	Sr	-481.796 + 48.227 pH	0.9168	0.9085	1.016e ⁻⁰⁶

The abovementioned results prove that a precipitation softening process using the combination of 2:1 volumetric ratio of 1N NaOH with 1N Na₂CO₃ respectively can successfully remove inorganic contaminants that are capable of fouling an RO membrane. It can be said that the optimal pH for Ca, Mg, and Sr removal is 11.5, followed by pH=11.2. As for silica and boron, their highest removals were achieved at pH= 11. Nevertheless, at pH=11.2 Si removal experiences a 1.8% and a 1.4% decrease for BW and BWB respectively. However, B removal declines as pH increases, as previously pointed out. Moreover, the variation in boron removal as a function of pH somewhat supports previous work in precipitative softening; whereby optimal boron removal was attained at pH=10.8 and it was insignificant below pH of 10.4 (Parks & Edwards, 2007). Still, it is necessary to evaluate and quantify the effect of temperature and pH and their possible interaction. This is discussed in the following sections.

4.2.2. Effect of Temperature on Foulant Removal

Since temperature is known to play a significant role in the precipitation of key scalants, similar jar tests were carried out at 10°C and 30°C, with four experimental pH values at each temperature. The resulting parametric removals in BW and BWB are demonstrated in Tables 4.4 and 4.5 respectively at T= 10°C and in Tables 4.6 and 4.7 respectively at T= 30°C.

Table 4. 4 Treated BW Characteristics at experimental pH values and temperature T=10°C

Parameter	Unit	Initial BW Mean ± sd	Treated Water at pH≈ 10.5 Mean ± sd	Treated Water at pH≈ 11 Mean ± sd	Treated Water at pH≈ 11.2 Mean ± sd	Treated Water at pH≈ 11.5 Mean ± sd
Experimental pH	pH units	7.54 ± 0.1	10.56 ± 0.09	10.96 ± 0.04	11.16 ± 0.03	11.43 ± 0.02
Temperature	°C	25.30 ± 1.7	11.0 ± 0.4	10.8 ± 0.3	11.0 ± 0.4	10.5 ± 0.9
Ca Hardness	mg/L as CaCO ₃	920.56 ± 115.0	580 ± 26.5	546.7 ± 32.1	396.7 ± 32.1	220 ± 26.5
Ca Removal	%	N/A	37 ± 2.9	40.6 ± 3.5	56.9 ± 3.5	76.1 ± 2.9
Mg Hardness	mg/L as CaCO ₃	1625.6 ± 353.3	1585 ± 21.2	1523.3 ± 66.6	1140 ± 95.4	826.7 ± 68.1
Mg Removal	%	N/A	2.5 ± 1.3	6.3 ± 4.1	29.9 ± 5.9	49.1 ± 4.2
Silica	mg/L as Si	4.17 ± 1.6	3.6 ± 0.6	2.0 ± 0.9	0.7 ± 0.5	0.5 ± 0.2
	mg/L as SiO ₂	9.02 ± 3.2	7.7 ± 1.3	4.3 ± 1.9	1.6 ± 1.0	1 ± 0.5
Silica Removal	%	N/A	13.7 ± 13.6	52.8 ± 21.5	82.4 ± 11.8	88.8 ± 4.99
	%	N/A	14.7 ± 14.1	52.7 ± 21.4	82.6 ± 10.9	88.9 ± 5.1

Table 4. 5 Treated BWB Characteristics at experimental pH values and temperature T=10°C

Parameter	Unit	Initial BWB Mean ± sd	Treated Water at pH≈ 10.5 Mean ± sd	Treated Water at pH≈ 11 Mean ± sd	Treated Water at pH≈ 11.2 Mean ± sd	Treated Water at pH≈ 11.5 Mean ± sd
Experimental pH	pH units	7.4 ± 0.1	10.49 ± 0.07	10.91 ± 0.03	11.14 ± 0.03	11.42 ± 0.03
Temperature	°C	25.5 ± 1.9	10.3 ± 0.5	10.2 ± 0.7	10.1 ± 0.8	10.5 ± 0.8
Ca Hardness	mg/L as CaCO ₃	1197.2 ± 130.7	773.3 ± 30.6	733.3 ± 23.1	486.7 ± 20.8	243.3 ± 49.3

Ca Removal	%	N/A	35.4 ± 2.6	38.7 ± 1.9	59.4 ± 1.7	79.7 ± 4.1
Mg Hardness	mg/L as CaCO ₃	2110.6 ± 417.8	2110.0 ± 70.7	1906.7 ± 47.3	1176.7 ± 15.3	856.7 ± 25.2
Mg Removal	%	N/A	2.4 ± 0.0	9.7 ± 2.2	44.2 ± 0.7	59.4 ± 1.2
Silica	mg/L as Si	6.12 ± 2.1	4.8 ± 0.1	2.2 ± 1.0	0.4 ± 0.1	0.5 ± 0.1
	mg/L as SiO ₂	13.1 ± 4.6	10.2 ± 0.3	4.7 ± 2.1	0.8 ± 0.3	1.0 ± 0.3
Silica Removal	% as Si	N/A	22.2 ± 1.9	64.1 ± 16.1	93.5 ± 1.6	92.4 ± 1.9
	% as SiO ₂	N/A	22.1 ± 2.0	63.9 ± 16	93.6 ± 2.3	92.6 ± 2.2

Table 4. 6 Treated BW Characteristics at experimental pH values and temperature T=30°C

Parameter	Unit	Initial BW Mean ± sd	Treated Water at pH≈ 10.5 Mean ± sd	Treated Water at pH≈ 11 Mean ± sd	Treated Water at pH≈ 11.2 Mean ± sd	Treated Water at pH≈ 11.5 Mean ± sd
Experimental pH	pH units	7.54 ± 0.1	10.4 ± 0.1	10.9 ± 0.0	11.2 ± 0.0	11.5 ± 0.1
Temperature	°C	25.30 ± 1.7	30.5 ± 0.5	30.2 ± 0.9	29.7 ± 1.0	29.6 ± 1.1
Ca Hardness	mg/L as CaCO ₃	920.56 ± 115.0	410.0 ± 70.7	85.0 ± 9.9	8.0 ± 2.8	0.0 ± 0.0
Ca Removal	%	N/A	55.5 ± 7.7	90.8 ± 1.1	99.1 ± 0.3	100.0 ± 0.0
Mg Hardness	mg/L as CaCO ₃	1625.6 ± 353.3	1330.0 ± 183.8	116.0 ± 1.4	75.5 ± 2.1	62.0 ± 1.4
Mg Removal	%	N/A	18.2 ± 11.3	92.9 ± 0.1	95.4 ± 0.1	96.2 ± 0.1
Silica	mg/L as Si	4.17 ± 1.6	0.4 ± 0.4	0.6 ± 0.1	1.6 ± 0.8	1.2 ± 0.2
	mg/L as SiO ₂	9.02 ± 3.2	0.8 ± 0.8	1.3 ± 0.2	3.4 ± 1.6	2.5 ± 0.4
Silica Removal	% as Si	N/A	90.4 ± 10.2	85.6 ± 3.4	62.8 ± 18.7	72.4 ± 5.1
	% as SiO ₂	N/A	91.1 ± 9.4	86.1 ± 2.4	62.9 ± 18.0	72.3 ± 4.7
Boron	as B (mg/L)	1.92 ± 0.5	0.5 ± 0.3	0.9 ± 0.1	1.3 ± 0.2	2.5 ± 1.2
	as H ₃ BO ₃ (mg/L)	10.93 ± 3.2	2.7 ± 1.9	5.3 ± 0.4	7.1 ± 0.7	14.1 ± 7.1
Boron Removal	% as B	N/A	73.9 ± 15.7	51.3 ± 3.0	33.9 ± 8.0	8.7 ± 3.7
	% as H ₃ BO ₃	N/A	75.0 ± 16.9	51.2 ± 3.7	35.1 ± 6.6	8.5 ± 5.2
Strontium	mg/L	5.56 ± 1.8	4.9 ± 0.5	3.1 ± 0.5	2.3 ± 0.8	1.7 ± 0.7
Strontium Removal	%	N/A	11.4 ± 9.5	43.6 ± 8.9	58.5 ± 14.7	69.1 ± 12.6

Table 4. 7 Treated BWB Characteristics at experimental pH values and temperature T=30°C

Parameter	Unit	Initial BWB Mean ± sd	Treated Water at pH≈ 10.5 Mean ± sd	Treated Water at pH≈ 11 Mean ± sd	Treated Water at pH≈ 11.2 Mean ± sd	Treated Water at pH≈ 11.5 Mean ± sd
Experimental pH	pH units	7.4 ± 0.1	10.4 ± 0.1	10.9 ± 0.1	11.1 ± 0.1	11.4 ± 0.1
Temperature	°C	25.5 ± 1.9	30.4 ± 0.5	30.1 ± 0.7	30.8 ± 0.7	29.8 ± 0.6
Ca Hardness	mg/L as CaCO ₃	1197.2 ± 130.7	475.0 ± 7.1	111.0 ± 15.6	9.0 ± 1.4	0.0 ± 0.0
Ca Removal	%	N/A	60.3 ± 0.6	90.7 ± 1.3	99.2 ± 0.1	100.0 ± 0.0
Mg Hardness	mg/L as CaCO ₃	2110.6 ± 417.8	1550.0 ± 84.9	200.0 ± 36.8	80.0 ± 7.1	67.5 ± 2.1
Mg Removal	%	N/A	26.6 ± 4.0	90.5 ± 1.7	96.2 ± 0.3	96.8 ± 0.1
Silica	mg/L as Si	6.12 ± 2.1	0.6 ± 0.4	0.9 ± 0.4	1.3 ± 0.1	1.3 ± 0.4
	mg/L as SiO ₂	13.1 ± 4.6	1.1 ± 0.7	1.9 ± 0.6	2.7 ± 0.3	2.8 ± 0.9
Silica Removal	% as Si	N/A	91.0 ± 5.8	86.1 ± 5.8	78.8 ± 2.3	78.8 ± 6.9
	% as SiO ₂	N/A	91.6 ± 5.4	85.9 ± 4.9	79.4 ± 2.2	79.0 ± 7.0
Boron	as B (mg/L)	2.1 ± 0.6	0.3 ± 0.2	1.0 ± 0.2	1.8 ± 0.5	1.9 ± 0.3
	as H ₃ BO ₃ (mg/L)	11.9 ± 3.1	1.8 ± 1.0	5.7 ± 1.1	8.4 ± 0.8	10.1 ± 0.6
Boron Removal	% as B	N/A	83.9 ± 7.4	50.0 ± 10.1	27.4 ± 6.8	15.3 ± 3.4
	% as H ₃ BO ₃	N/A	84.9 ± 8.0	52.4 ± 9.5	29.5 ± 7.1	15.2 ± 4.7
Strontium	mg/L	7.5 ± 2.7	6.1 ± 0.4	3.8 ± 0.6	3.1 ± 1.3	2.2 ± 0.9
Strontium Removal	%	N/A	19.2 ± 4.7	49.7 ± 7.5	59.2 ± 16.8	70.7 ± 12.1

For both BW and BWB, Ca and Mg removals showed a general trend of improvement with temperature increase, especially at pH 10.5, 11.2, and 11.5, and this is exhibited in Figures 4.5 and 4.6 at 10°C and Figures 4.7 and 4.8 at 30°C. Statistically significant differences in Ca and Mg removals between different operating temperatures were recorded (p-value < 0.05) for BW and BWB. Additionally, Ca, Mg, and Si removals were the absolute lowest at pH=10.5 and temperature T=10°C. Therefore, it was established that an operating temperature of 10°C is far from being an optimum

condition. It was also observed that there was a trend of increase in silica elimination with the rise in temperature between 10 and 25°C at pH values less than 11.2 to 11.5. This is coherent with findings in the literature, whereby silica was found to exhibit improved polymerization with increased temperature (Sheikholeslami et al., 2002). Nonetheless, the effect of temperature on SiO₂ removal was statistically significant for BWB only (p-value= 0.0336).

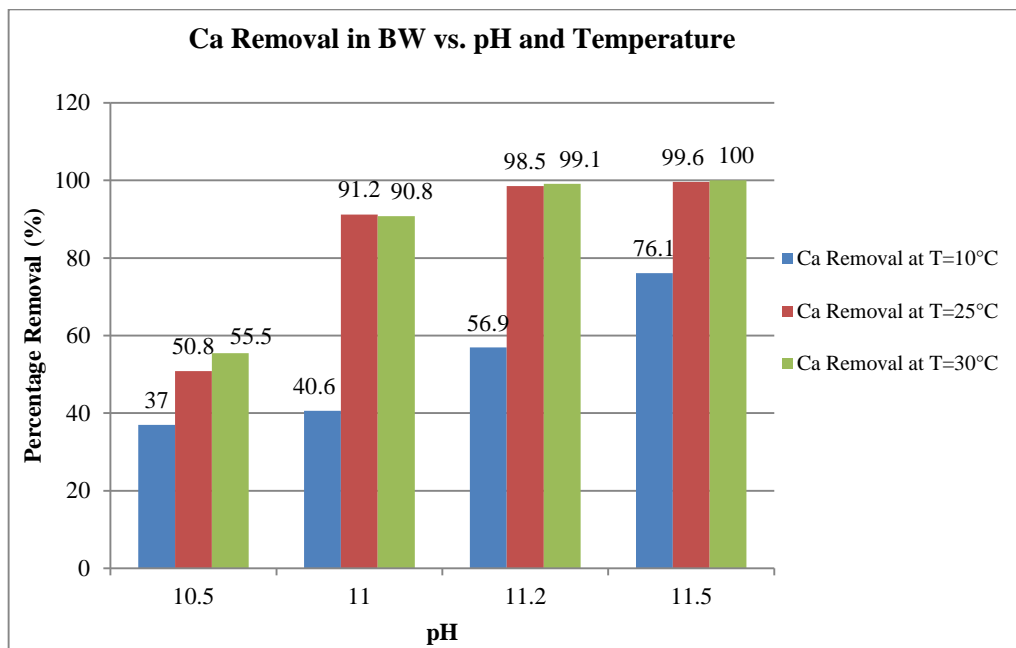


Figure 4.5 Average Percentage Removals of Ca in BW at different experimental pH values and temperatures

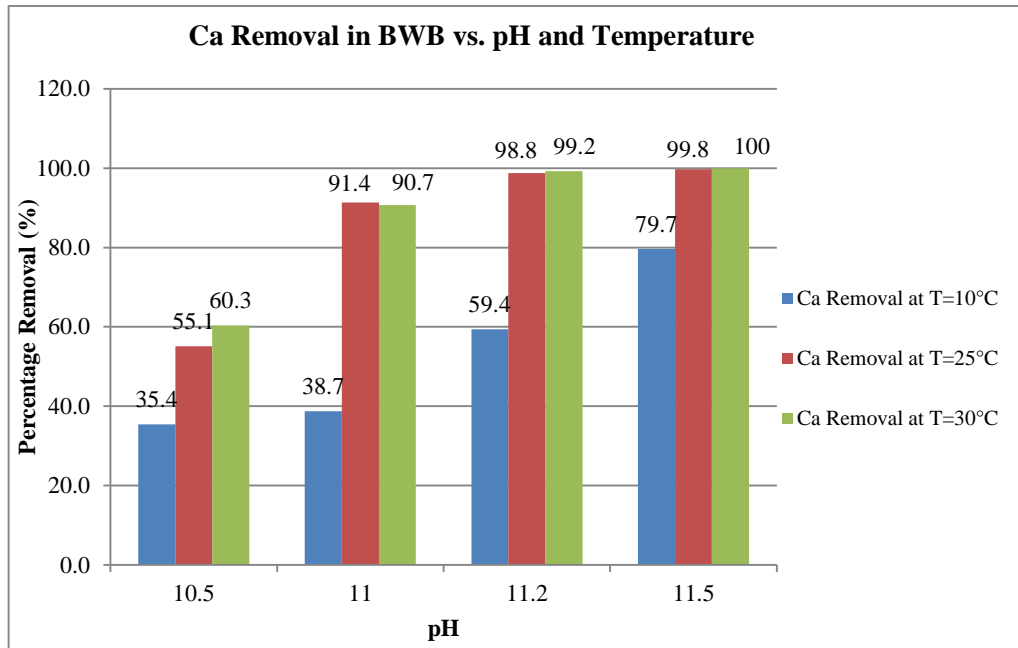


Figure 4.6 Average Percentage Removals of Ca in BWB at different experimental pH values and temperatures

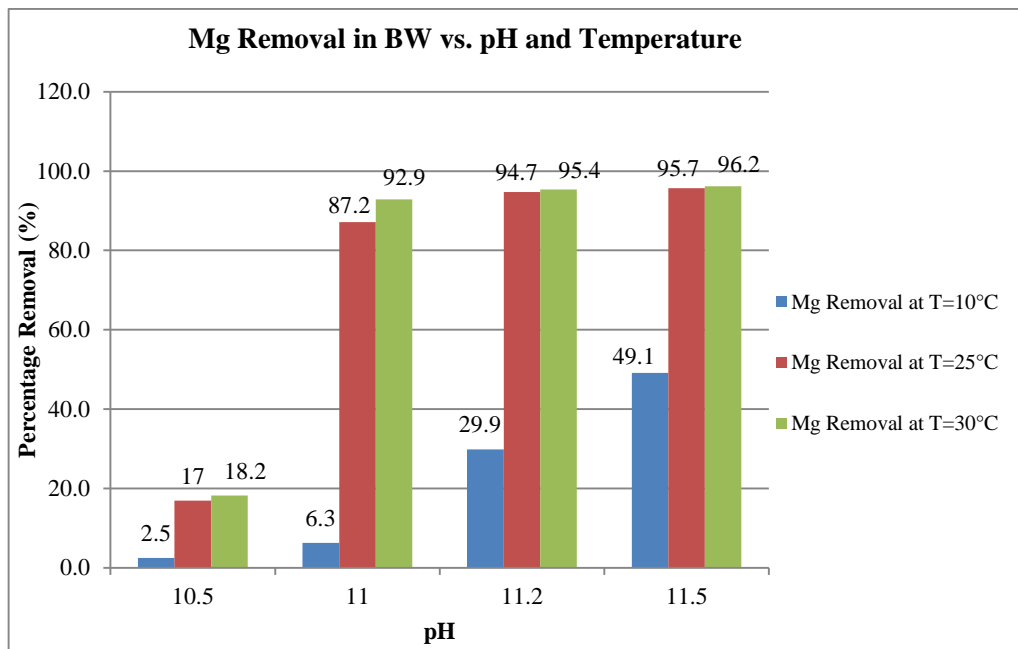


Figure 4.7 Average Percentage Removals of Mg in BW at different experimental pH values and temperatures

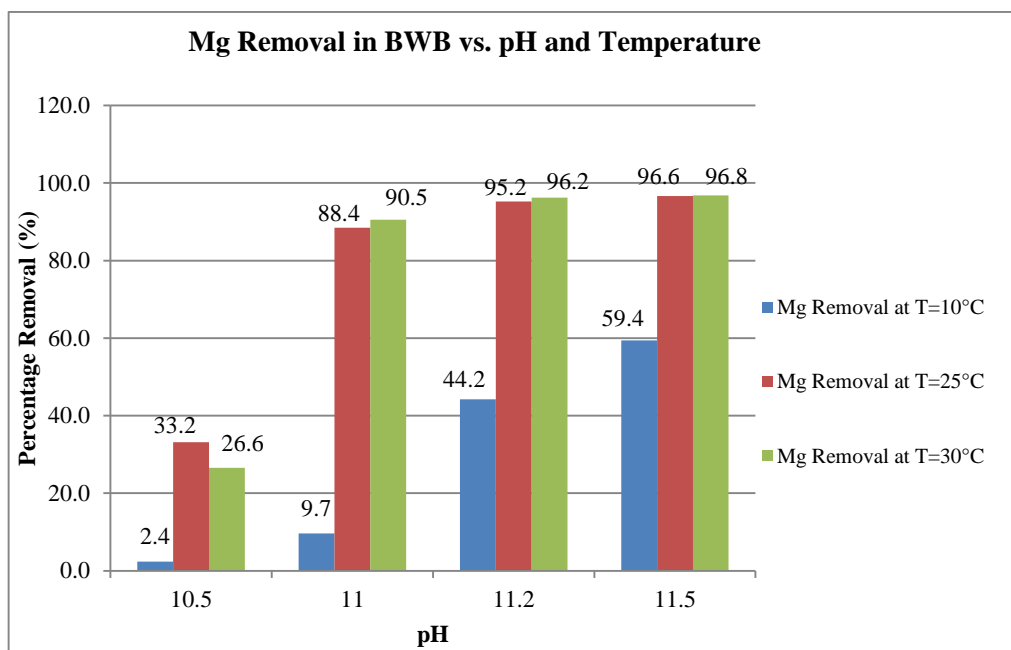


Figure 4.8 Average Percentage Removals of Mg in BWB at different experimental pH values and temperatures

Given that the temperature of 10°C produced undesirable removals for the major scalants Ca and Mg, strontium and boron removals were compared between 25°C and 30°C, and this showed that the optimal removal of Sr in both water types was accomplished at pH=11.5. Nevertheless, the removal percentage was slightly higher at 25°C than it was at 30°C (average difference of 0.08% for BW and 0.9% for BWB), but the difference was not statistically significant (p-value: 0.776 for BW and 0.867 for BWB). A graphical comparison of Sr removal efficiency under different temperature and pH conditions is shown in Figures 4.9 and 4.10.

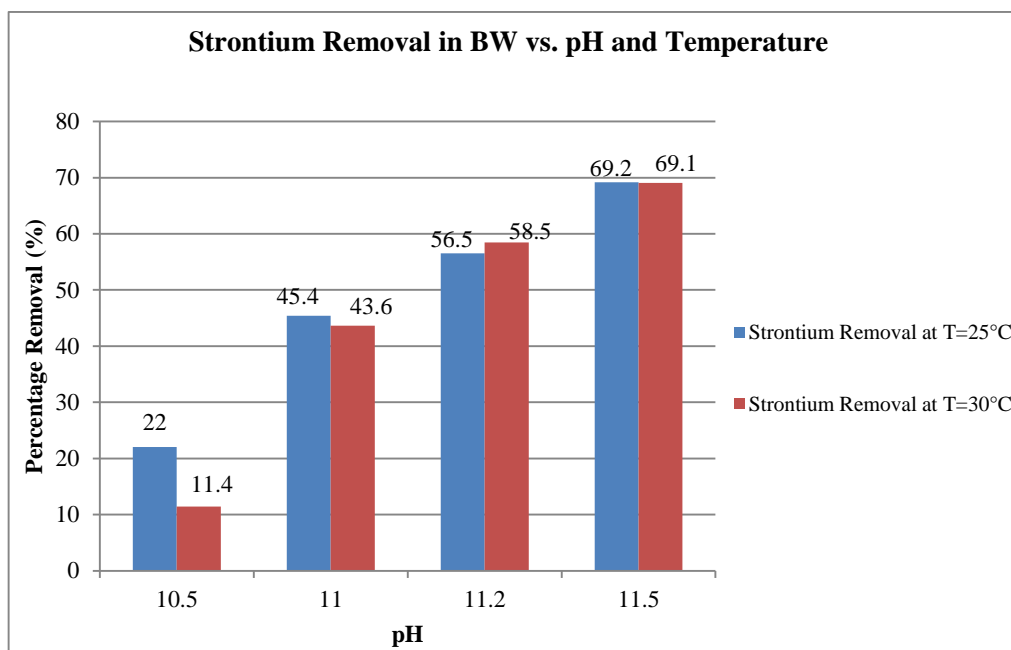


Figure 4.9 Average Percentage Removals of Sr in BW at different experimental pH values and temperatures

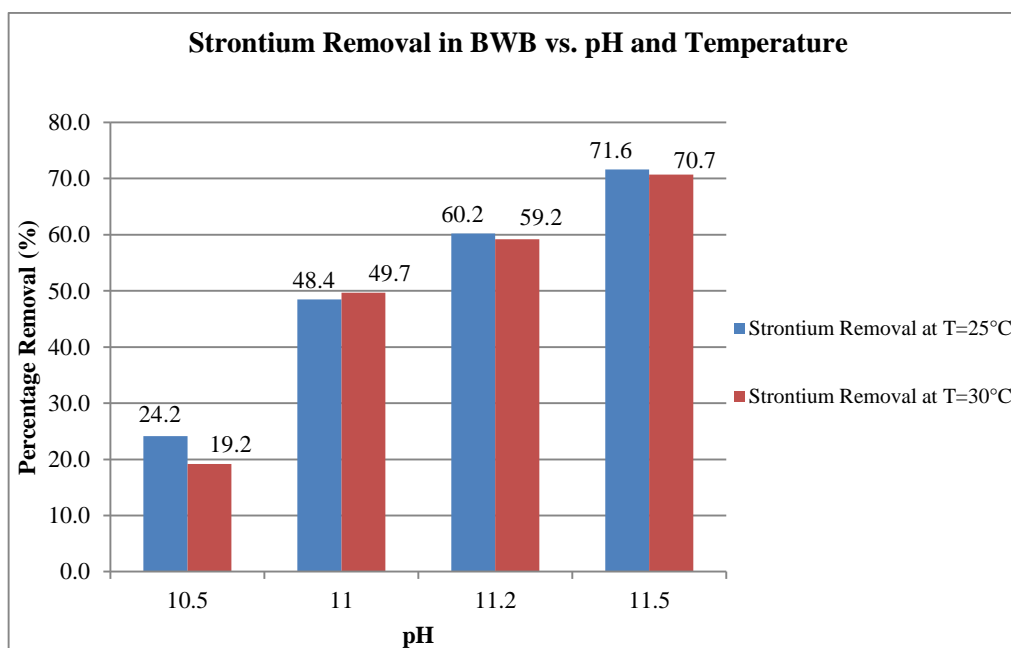


Figure 4.10 Average Percentage Removals of Sr in BWB at different experimental pH values and temperatures

As for boron, its removal showed a decline with increasing temperature above pH of 10.5, showing an inversely proportional relationship between B removal and

temperature; but the ANOVA test proved the effect of temperature to be barely significant for BW (p -value= 0.049) and not significant at all for BWB (p -value= 0.225) . It is important to note that this relationship between temperature and boron removal is consistent with findings from the literature (Ayoub et al., 2013).

At $T=30^{\circ}\text{C}$, the highest removal of boron was recorded at $\text{pH}=10.5$, followed by $\text{pH}=11$ with a difference greater than 20% for BW and BWB. However, at 25°C the optimal boron removal was observed at $\text{pH}=11$. In comparison, previous results by Ayoub et al. for seawater, boron removal was the highest at $\text{pH}=10.5$ at temperatures 10, 20, 25, and 30°C . The graphs in Figures 4.11 and 4.12 show the variation of boron removal as a function of temperature.

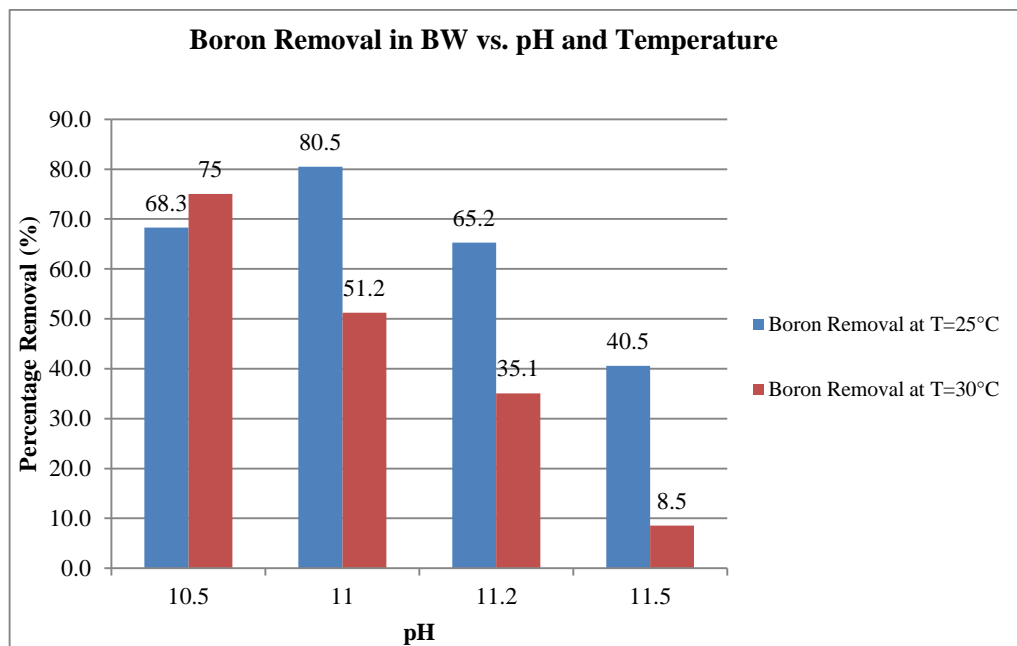


Figure 4.11 Average Percentage Removals of B in BW at different experimental pH values and temperatures

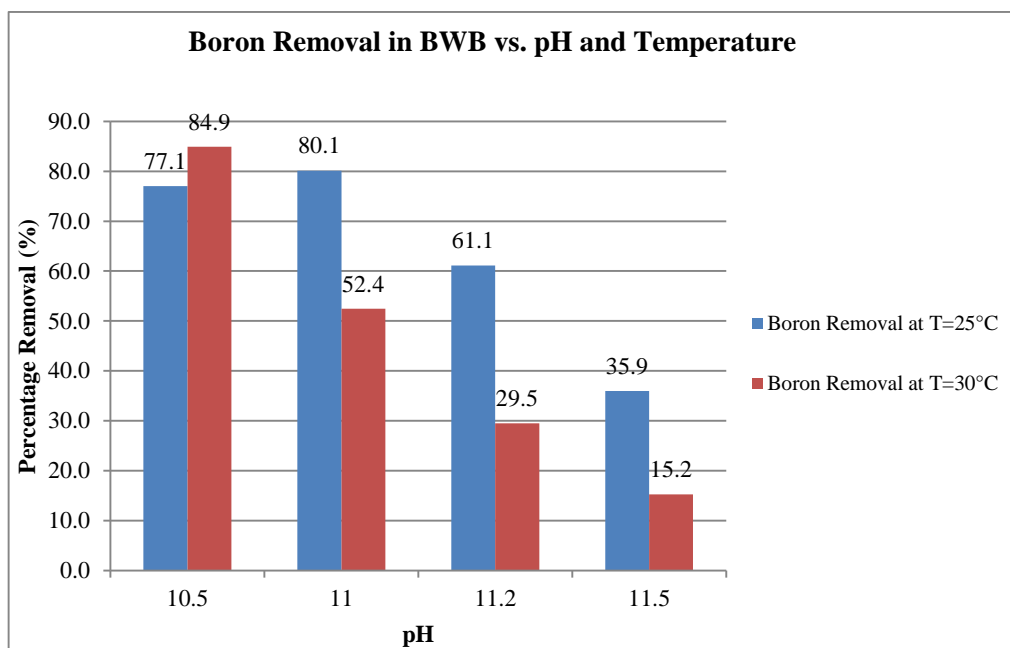


Figure 4.12 Average Percentage Removals of B in BWB at different experimental pH values and temperatures

A regression analysis was performed to assess the linear relationship between parametric removals and pH at every experimental temperature and it is presented in Table 4.8. The results were analogous with the findings from the Analysis of Variance for all the parameters.

Table 4.8 Single Linear Regression Analysis for Parametric Removals vs. pH at different temperatures for BW and BWB

Parameter % Removal	Water Type	Temperature (°C)	Regression Equation	R2	R2adj	P-value
Ca	BW	10	-372.747 + 38.498 pH	0.7972	0.777	9.25e ⁻⁰⁵
		25	-539.186 + 56.287 pH	0.8626	0.8589	< 2.2e ⁻¹⁶
		30	-452.362 + 48.761 pH	0.835	0.8232	7.56e ⁻⁰⁷
	BWB	10	-433.417 + 44.046 pH	0.8006	0.7807	8.49e ⁻⁰⁵
		25	-540.165 + 56.358 pH	0.843	0.8387	2.20 e ⁻¹⁶
		30	-392.046 + 43.471 pH	0.8125	0.7991	1.87e ⁻⁰⁶
Mg	BW	10	-531.750 + 50.042 pH	0.7879	0.7644	0.0002652
		25	-648.86 + 64.12 pH	0.5373	0.5237	3.70e ⁻⁰⁷
		30	-577.78 + 58.08 pH	0.554	0.5221	0.0009443
	BWB	10	-736.68 + 69.08 pH	0.8179	0.7951	0.0003256

		25	-582.711 + 58.800 pH	0.6007	0.5889	2.87e ⁻⁰⁸
		30	-611.547 + 61.744 pH	0.7511	0.7333	1.40e ⁻⁰⁵
SiO₂	BW	10	-800.22 + 77.84 pH	0.7983	0.7759	0.0002104
		25	-9.439 + 7.785 pH	0.02346	-0.00293	0.3519
		30	547.71 - 43.21 pH	0.4989	0.4631	0.002225
	BWB	10	-773.315 + 76.143 pH	0.862	0.8483	1.31e ⁻⁰⁵
		25	95.4482 - 0.9151 pH	0.0007557	-0.02625	0.8681
		30	432.838 - 31.978 pH	0.4555	0.4166	0.004125
H₃BO₃	BW	25	301.50 - 21.41 pH	0.1679	0.07547	0.2107
		30	748.96 - 63.90 pH	0.8623	0.847	3.66e ⁻⁰⁵
	BWB	25	502.39 - 39.71 pH	0.4817	0.4298	0.01229
		30	838.007 - 71.688 pH	0.9344	0.9263	5.19e ⁻⁰⁶
Sr	BW	25	-477.573 + 47.588 pH	0.8591	0.845	1.45e ⁻⁰⁵
		30	-608.47 + 59.20 pH	0.8257	0.8083	4.28e ⁻⁰⁵
	BWB	25	-481.796 + 48.227 pH	0.9168	0.9085	1.02e ⁻⁰⁶
		30	-526.868 + 52.176 pH	0.8021	0.7823	8.18e ⁻⁰⁵

As previously noted, Ca and Mg removals tended to increase significantly with increased temperatures and pH, reaching their optimal removals at T=30°C between pH 11.2 and 11.5. Strontium exhibited its optimal removal for both BW and BWB at pH=11.5 and T=25°C, with a minor decrease at T=30°C and the same pH. The higher removals of Ca and Mg at increased temperatures and pH can be explained by the fact that under such conditions, the equilibrium of the carbonate system shifts towards the alkaline mechanism of CO₂ hydration-dehydration (Al-Rawajfeh et al., 2008). In other words, more bicarbonates, carbonates and hydroxyl ions are supplied in the water, thus promoting precipitation. As well, the formation of Mg(OH)₂ flocs at the higher pH values definitely contributed to the removal of other contaminants (Ayoub et al., 2013).

Further, silica was optimally removed at pH=10.5 and T=30°C in BW, but at pH=11.2 and T=10°C for BWB, with a mere 2% difference in removal at pH=10.5 and T=30°C. Boron removal was optimal at T=25°C and pH=11 for BW (80.5%) and at T=30°C and pH=10.5 for BWB (84.9%). Nevertheless, boron removals at T=25°C an

pH=11.2 were 65.2% and 61.1% for BW and BWB respectively, which can be considered acceptable if the treated water complies with the WHO maximum recommended level of 2.4 mg/L for boron in drinking water (Wolska & Bryjak, 2013).

4.2.3. Combined Effect of pH and Temperature

Even though pH and temperature can each affect the removal of key foulants, it is necessary to measure their combined effect and whether there is a significant interaction between these independent factors. This was achieved by performing a two-way ANOVA test for each parameter's removal, and the resulting p-values are presented in Table 4.9. The findings demonstrated a significant interaction between pH and temperature in the case of SiO₂ at the 99% confidence level and H₃BO₃ at the 90% confidence level. The interaction plots for SiO₂ and H₃BO₃ are represented in Figures 4.13a and 4.13b for BW and BWB respectively, where the combined effect of pH and temperature is noted since the lines are not all parallel.

Table 4.9 Two-way ANOVA results of parametric removal efficiencies vs. pH and temperature with their interaction

Parameter	Source of Variation	BW	BWB
		2-way ANOVA P-value	2-way ANOVA P-value
% Removal Ca	Temperature	2e ⁻¹⁶	7.88e ⁻¹⁶
	pH	2e ⁻¹⁶	2e ⁻¹⁶
	Interaction	0.112	0.63
% Removal Mg	Temperature	2.71e ⁻⁰⁷	4.34e ⁻⁰⁸
	pH	5.72e ⁻¹²	4.68e ⁻¹⁵
	Interaction	0.594	0.825
% Removal SiO ₂	Temperature	0.191	0.00343
	pH	0.406	0.23261
	Interaction	6.44e ⁻⁰⁷	4.5e ⁻¹¹
% Removal H ₃ BO ₃	Temperature	0.005215	0.0299
	pH	0.000166	1.62e ⁻⁰⁶
	Interaction	0.029967	0.0555

% Removal Sr	Temperature	0.502	0.679
	pH	2.54e ⁻⁰⁹	1.02e ⁻⁰⁹
	Interaction	0.284	0.679

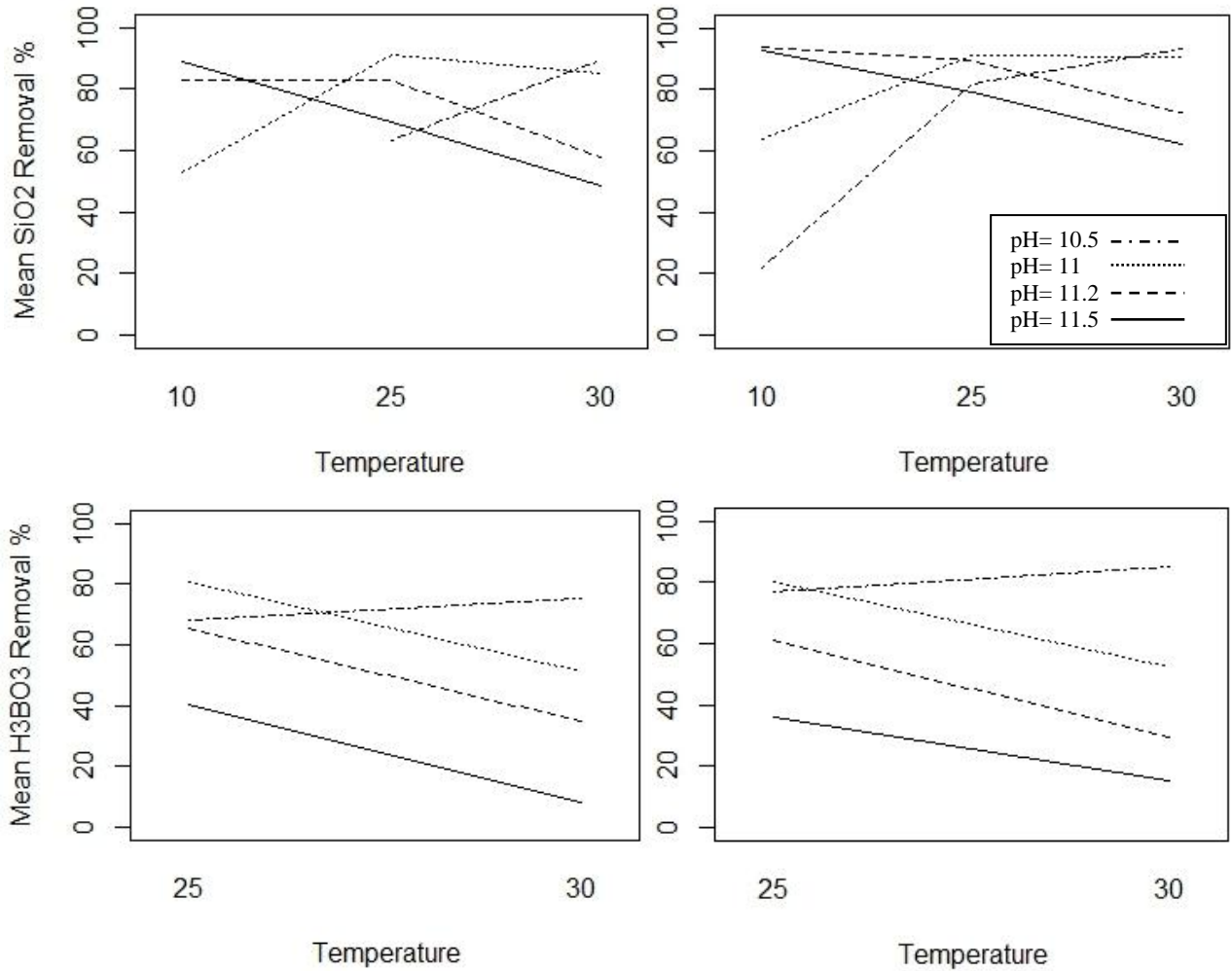


Figure 4.13 Interaction plots of pH and temperature SiO₂ and H₃BO₃ removals for a) BW and b)BWB

Furthermore, the linearity of the relationship between parametric removal and pH and temperature, including their combined effect, is explored in Table 4.10 by performing a multiple linear regression on the experimental data. The strength of the linear relationship between parametric removal and pH and temperature is below 90%

for all parameters, implying a moderate level of linearity with all p-values less than 0.05.

Table 4.10 Multiple linear regression equations for parametric removals vs. pH and temperature, with their interaction

Water Type	Parameter	Regression Equation	R ²	R ² _{adj}	P-value
BW	Ca	-345.6122 - 6.0927 T + 34.5645 pH + 0.7128 T*pH	0.8736	0.8675	2.2e-16
	Mg	-514.867 - 4.138 T + 46.651 pH + 0.579 T*pH	0.646	0.6279	2.507e-13
	SiO ₂	-1506.599 + 63.272 T + 141.383 pH - 5.663 T*pH	0.3487	0.3172	6.51e-06
	H ₃ BO ₃	-1935.825 + 89.493 T + 190.987 pH - 8.496 T*pH	0.6789	0.6253	0.0001079
	Sr	176.922 - 26.180 T - 10.456 pH + 2.322 T*pH	0.8391	0.815	3.968e-08
BW B	Ca	-470.5031 - 0.6649 T + 45.8506 pH + 0.2240 T*pH	0.8625	0.8559	2.2e-16
	Mg	-728.0996 + 4.7245 T + 66.5086 pH - 0.2203 T*pH	0.7216	0.7071	4.156e-16
	SiO ₂	-1380.5522 + 59.6143 T + 130.6731 pH - 5.3278 T*pH	0.5394	0.5175	1.181e-10
	H ₃ BO ₃	-1175.719 + 67.124 T + 120.167 pH - 6.395 T*pH	0.7646	0.7253	6.956e-06
	Sr	-256.4410 - 9.0142 T + 28.4836 pH + 0.7897 T*pH	0.8514	0.8291	1.811e-08

4.2.4. Spiked Experiments

Since the water used in this study did not contain sufficient concentrations of bacteria (fecal and total coliforms), iron, and barium to cause effective fouling in an RO element, it was necessary to boost these concentrations so as to more confidently evaluate their removal efficiencies. In order to simulate the possible occurrence of microorganisms like bacteria and viruses as well as iron and barium, which are quite common in BW, samples were spiked with specific quantities of the foulant of interest. Experiments were conducted at the four experimental pH values (10.5, 11, 11.2, and 11.5) and room temperature ($\approx 25 \pm 2^\circ\text{C}$) for the three spiking categories, and 30°C for bacteria spiking and Fe spiking, based on the results from previous experimental runs

and the resulting optimal removal efficiencies accomplished for Ca and Mg, which are the chief inorganic foulants in BWRO.

4.2.4.1. Addition of Wastewater

Microorganisms can pose a serious threat on RO membranes, so disinfection is always practiced to prevent biological fouling of these membranes. To assess the efficiency of the suggested precipitation process on the inactivation of bacteria and viruses, municipal wastewater was added to the water samples (BW: 0.005-0.0075% by volume; BWB: 0.0065-0.01% by volume) and jar tests were conducted under different pH and temperature conditions, since elevated pH has been proven to successfully destroy bacteria (Rincón & Pulgarin, 2004; Ayoub et al., 2013). It is important to mention that the spiking of wastewater had negligible effects on the sample water constituents, whereby the initial concentrations of the key contaminants were within one standard deviation of their means. The control samples as well as the treated samples were analyzed for fecal and total coliforms in the same day as the experiments were conducted, as per the requirements of the standard methods for water analysis (APHA et al., 2012). The coliforms in all the initial samples were too numerous to count (TNTC) at both experimental temperatures. The results of the spiking jar tests conducted are presented in Tables 4.11 and 4.12 for $T \approx 23^\circ\text{C}$ and Tables 4.13 and 4.14 for $T = 30^\circ\text{C}$.

Table 4.11 Results of Treatment of BW Spiked with wastewater at experimental pH values and temperature $T = 23^\circ\text{C}$

Parameter	Unit	Initial Spiked BW Mean \pm sd	Treated Water at pH \approx 10.5 Mean \pm sd	Treated Water at pH \approx 11 Mean \pm sd	Treated Water at pH \approx 11.2 Mean \pm sd	Treated Water at pH \approx 11.5 Mean \pm sd
Experimental pH	pH units	7.54 \pm 0.1	10.5 \pm 0	10.97 \pm 0	11.18 \pm 0	11.49 \pm 0
Temperature	$^\circ\text{C}$	25.3 \pm 1.7	23.2 \pm 0.14	23.2 \pm 0.14	23.2 \pm 0.14	23.2 \pm 0.14

Fecal Coliforms	CFU/ 100 mL After 24 hrs	TNTC	0 ± 0	0 ± 0	0 ± 0	0 ± 0
	CFU/ 100 mL After 48 hrs	TNTC	0 ± 0	0 ± 0	0 ± 0	0 ± 0
Fecal Coliforms Removal	%	N/A	100 ± 0	100 ± 0	100 ± 0	100 ± 0
	%	N/A	100 ± 0	100 ± 0	100 ± 0	100 ± 0
Total Coliforms	CFU/ 100 mL After 24 hrs	TNTC	0 ± 0	0 ± 0	0 ± 0	0 ± 0
	CFU/ 100 mL After 48 hrs	TNTC	19 ± 0	4 ± 0	1 ± 0	7 ± 0
Total Coliforms Removal	%	N/A	100 ± 0	100 ± 0	100 ± 0	100 ± 0
	%	N/A	99.988 ± 0	99.998 ± 0	99.999 ± 0	99.996 ± 0

Table 4.12 Results of Treatment of BWB Spiked with wastewater at experimental pH values and temperature T=23°C

Parameter	Unit	Initial Spiked BWB Mean ± sd	Treated Water at pH≈ 10.5 Mean ± sd	Treated Water at pH≈ 11 Mean ± sd	Treated Water at pH≈ 11.2 Mean ± sd	Treated Water at pH≈ 11.5 Mean ± sd
Experimental pH	pH units	7.4 ± 0.1	10.49 ± 0	10.91 ± 0	11.21 ± 0	11.43 ± 0
Temperature	°C	25.5 ± 1.9	23.3 ± 0.1	23.2 ± 0.1	23.2 ± 0.1	23.2 ± 0.1
Fecal Coliforms	CFU/ 100 mL After 24 hrs	TNTC	0 ± 0	0 ± 0	0 ± 0	0 ± 0
	CFU/ 100 mL After 48 hrs	TNTC	0 ± 0	0 ± 0	0 ± 0	0 ± 0
Fecal Coliforms Removal	%	N/A	100 ± 0	100 ± 0	100 ± 0	100 ± 0
	%	N/A	100 ± 0	100 ± 0	100 ± 0	100 ± 0
Total Coliforms	CFU/ 100 mL After 24 hrs	TNTC	0 ± 0	0 ± 0	0 ± 0	0 ± 0
	CFU/ 100 mL After 48 hrs	TNTC	16 ± 0	3 ± 0	2 ± 0	1 ± 0
Total Coliforms Removal	%	N/A	100 ± 0	100 ± 0	100 ± 0	100 ± 0
	%	N/A	99.997 ± 0	99.999 ± 0	100 ± 0	100 ± 0

**Table 4.13 Results of Treatment of BW Spiked with wastewater at experimental pH values and temperature
T=30°C**

Parameter	Unit	Initial Spiked BW Mean ± sd	Treated Water at pH≈ 10.5 Mean ± sd	Treated Water at pH≈ 11 Mean ± sd	Treated Water at pH≈ 11.2 Mean ± sd	Treated Water at pH≈ 11.5 Mean ± sd
Experimental pH	pH units	7.54 ± 0.1	10.4 ± 0.2	10.9 ± 0.2	11.2 ± 0.0	11.4 ± 0.1
Temperature	°C	25.3 ± 1.7	30.0 ± 0.8	29.6 ± 0.4	29.9 ± 0.5	29.9 ± 0.4
Fecal Coliforms	CFU/ 100 mL After 24 hrs	TNTC	0 ± 0	0 ± 0	0 ± 0	0 ± 0
	CFU/ 100 mL After 48 hrs	TNTC	0 ± 0	0 ± 0	0 ± 0	0 ± 0
Fecal Coliforms Removal	%	N/A	100 ± 0	100 ± 0	100 ± 0	100 ± 0
	%	N/A	100 ± 0	100 ± 0	100 ± 0	100 ± 0
Total Coliforms	CFU/ 100 mL After 24 hrs	TNTC	0 ± 0	0 ± 0	0 ± 0	0 ± 0
	CFU/ 100 mL After 48 hrs	TNTC	21.5 ± 30.4	0.5 ± 0.7	0 ± 0	0 ± 0
Total Coliforms Removal	%	N/A	100 ± 0	100 ± 0	100 ± 0	100 ± 0
	%	N/A	100 ± 0	100 ± 0	100 ± 0	100 ± 0

**Table 4.14 Results of Treatment of BWB Spiked with wastewater at experimental pH values and temperature
T=30°C**

Parameter	Unit	Initial Spiked BWB Mean ± sd	Treated Water at pH≈ 10.5 Mean ± sd	Treated Water at pH≈ 11 Mean ± sd	Treated Water at pH≈ 11.2 Mean ± sd	Treated Water at pH≈ 11.5 Mean ± sd
Experimental pH	pH units	7.4 ± 0.1	10.4 ± 0.1	10.9 ± 0.1	11.2 ± 0.1	11.5 ± 0.1
Temperature	°C	25.5 ± 1.9	30.5 ± 0.6	30.7 ± 0.8	30.2 ± 0.5	29.9 ± 0.8
Fecal Coliforms	CFU/ 100 mL After 24 hrs	TNTC	0 ± 0	0 ± 0	0 ± 0	0 ± 0
	CFU/ 100 mL After 48 hrs	TNTC	0 ± 0	0 ± 0	0 ± 0	0 ± 0
Fecal Coliforms Removal	%	N/A	100 ± 0	100 ± 0	100 ± 0	100 ± 0
	%	N/A	100 ± 0	100 ± 0	100 ± 0	100 ± 0
Total Coliforms	CFU/ 100 mL After 24 hrs	TNTC	0 ± 0	0 ± 0	0 ± 0	0 ± 0
	CFU/ 100 mL After 48 hrs	TNTC	0 ± 0	0 ± 0	0.5 ± 0.7	0 ± 0

	hrs					
Total Coliforms Removal	%	N/A	100 ± 0	100 ± 0	100 ± 0	100 ± 0
	%	N/A	100 ± 0	100 ± 0	100 ± 0	100 ± 0

The results prove that the precipitation softening process performed in this research almost completely inactivated the total and fecal coliforms under all pH and temperature conditions. Additionally, the removal efficiencies of Ca, Mg, Si, Sr, and B were calculated and occurred within one standard deviation of their average removal percentages during the non-spiking runs at both temperatures.

4.2.4.2. Addition of Iron

Since the water obtained for the research at hand had negligible amounts of iron, the water samples were spiked using ferrous sulfate (FeSO₄) to produce average concentrations of 3.16- 3.42 mg/L for BW and 5.55- 5.86 mg/L for BWB. Control samples were prepared and used for Fe analysis, and 10 mL aliquots were also taken from every experimental jar prior to the jar tests and were used to measure the initial concentrations of Fe. The experimental results in terms of Fe removal, along with other parametric removals, are shown in Tables 4.15 and 4.16 for T≈23°C and Tables 4.17 and 4.18 for T=30°C.

Table 4.15 Results of Treatment BW Spiked with Iron at experimental pH values and temperature T≈23°C

Parameter	Unit	Initial Spiked BW Mean ± sd	Treated Water at pH≈ 10.5 Mean ± sd	Treated Water at pH≈ 11 Mean ± sd	Treated Water at pH≈ 11.2 Mean ± sd	Treated Water at pH≈ 11.5 Mean ± sd
Experimental pH	pH units	7.54 ± 0.1	10.44 ± 0.15	10.92 ± 0.07	11.11 ± 0.12	11.46 ± 0.03
Temperature	°C	25.30 ± 1.7	23 ± 0.3	23.07 ± 0.35	23.47 ± 1.05	23.37 ± 0.88
Ca Hardness	mg/L as CaCO₃	920.56 ± 115	543.3 ± 72.34	150 ± 20	10 ± 10	0 ± 0
Ca Removal	%	N/A	40.98 ± 7.86	83.71 ± 2.17	98.91 ± 1.09	100 ± 0

Mg Hardness	mg/L as CaCO₃	1625.6 ± 353.3	1475 ± 35.36	976.7 ± 158.2	870 ± 100	666.67 ± 15.28
Mg Removal	%	N/A	9.26 ± 2.17	39.92 ± 9.73	46.48 ± 6.15	58.99 ± 0.94
Silica	mg/L as Si	4.17 ± 1.6	2.13 ± 0.46	0.37 ± 0.32	0.83 ± 0.4	0.93 ± 0.15
	mg/L as SiO₂	9.02 ± 3.2	4.5 ± 0.95	0.73 ± 0.64	1.73 ± 0.86	2.00 ± 0.36
Silica Removal	% as Si	N/A	48.85 ± 11.07	91.21 ± 7.71	80.02 ± 9.69	77.62 ± 3.66
	% as SiO₂	N/A	50.13 ± 10.57	91.87 ± 7.12	80.79 ± 9.55	77.84 ± 4
Fe	mg/L	5.47 ± 1.28	0.05 ± 0.01	0.04 ± 0.04	0.08 ± 0.07	0.08 ± 0.08
Fe Removal	%	N/A	99.08 ± 0.15	99.21 ± 0.68	98.49 ± 1.33	98.54 ± 1.51

Table 4.16 Results of Treatment of BWB Spiked with Iron at experimental pH values and temperature T=23°C

Parameter	Unit	Initial Spiked BWB Mean ± sd	Treated Water at pH≈ 10.5 Mean ± sd	Treated Water at pH≈ 11 Mean ± sd	Treated Water at pH≈ 11.2 Mean ± sd	Treated Water at pH≈ 11.5 Mean ± sd
Experimental pH	pH units	7.4 ± 0.1	10 ± 0.16	10.91 ± 0.08	11.09 ± 0.13	11.43 ± 0.05
Temperature	°C	25.5 ± 1.9	23.06 ± 0.29	23.16 ± 0.32	23.03 ± 0.23	23.07 ± 0.29
Ca Hardness	mg/L as CaCO₃	1197.2 ± 130.7	706.67 ± 110.15	206.67 ± 20.82	26.67 ± 15.28	0 ± 0
Ca Removal	%	N/A	40.97 ± 9.2	82.74 ± 1.74	97.77 ± 1.28	100 ± 0
Mg Hardness	mg/L as CaCO₃	2110.6 ± 417.8	1830 ± 98.99	1020 ± 95.39	856.67 ± 30.55	630 ± 55.68
Mg Removal	%	N/A	13.29 ± 4.69	51.67 ± 4.52	59.41 ± 1.45	70.15 ± 2.64
Silica	mg/L as Si	6.12 ± 2.1	1.73 ± 0.51	0.33 ± 0.29	0.93 ± 0.12	0.57 ± 0.55
	mg/L as SiO₂	13.1 ± 4.6	3.8 ± 1.08	0.8 ± 0.61	1.97 ± 0.25	1.17 ± 1.15
Silica Removal	% as Si	N/A	71.69 ± 8.38	94.56 ± 4.71	84.76 ± 1.89	90.75 ± 8.99
	% as SiO₂	N/A	70.99 ± 8.26	93.89 ± 4.64	84.99 ± 1.92	91.09 ± 8.78
Fe	mg/L	9.91 ± 3.39	0.07 ± 0.03	0.07 ± 0.07	0.08 ± 0.08	0.11 ± 0.06
Fe Removal	%	N/A	99.26 ± 0.31	99.32 ± 0.69	99.20 ± 0.76	98.88 ± 0.63

Table 4.17 Results of Treatment of BW Spiked with Iron at experimental pH values and temperature T=30°C

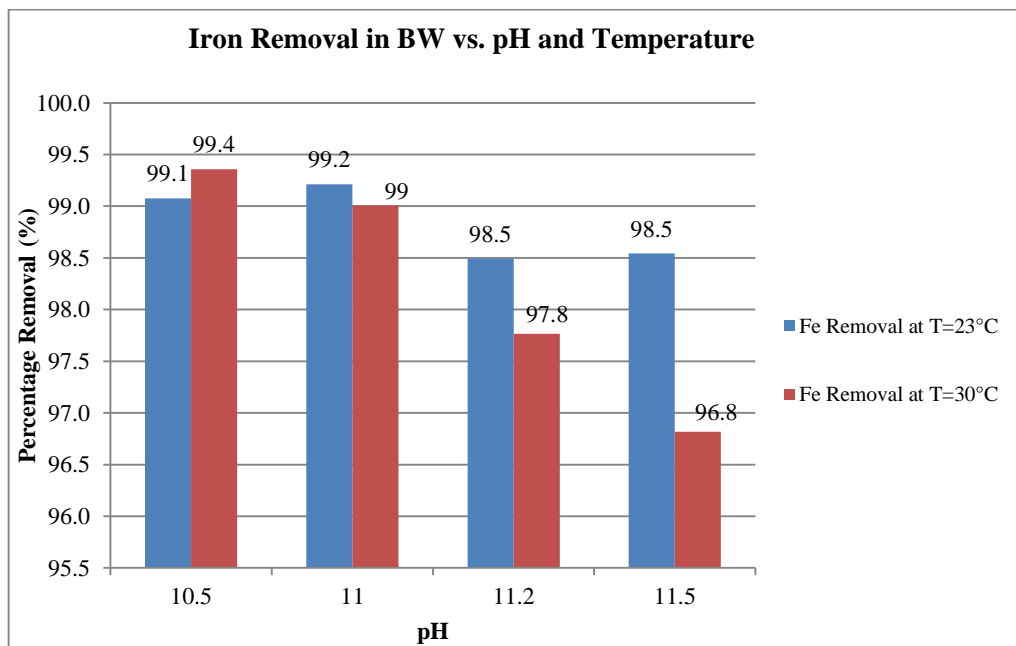
Parameter	Unit	Initial Spiked BW Mean ± sd	Treated Water at pH≈ 10.5 Mean ± sd	Treated Water at pH≈ 11 Mean ± sd	Treated Water at pH≈ 11.2 Mean ± sd	Treated Water at pH≈ 11.5 Mean ± sd
Experimental pH	pH units	7.54 ± 0.1	10.4 ± 0.2	10.9 ± 0.2	11.2 ± 0	11.4 ± 0.08
Temperature	°C	25.30 ± 1.7	30 ± 0.8	29.6 ± 0.4	29.9 ± 1	29.9 ± 0.4

Ca Hardness	mg/L as CaCO₃	920.6 ± 115	445 ± 21.21	50 ± 56.57	0 ± 0	0 ± 0
Ca Removal	%	N/A	51.7 ± 2.3	94.6 ± 6.1	100 ± 0	100 ± 0
Mg Hardness	mg/L as CaCO₃	1625.6 ± 353.3	1175 ± 91.92	675 ± 7.07	610 ± 127.28	635 ± 134.35
Mg Removal	%	N/A	27.7 ± 5.7	58.5 ± 0.4	62.5 ± 7.8	60.9 ± 8.3
Silica	mg/L as Si	4.17 ± 1.6	0.6 ± 0.5	0.7 ± 0.4	2.0 ± 0.1	3.2 ± 0.1
	mg/L as SiO₂	9.02 ± 3.2	1.1 ± 1.1	1.4 ± 0.8	4.3 ± 0.4	6.8 ± 0.2
Silica Removal	% as Si	N/A	86.8 ± 11.9	84.4 ± 8.5	52 ± 3.4	24.5 ± 1.7
	% as SiO₂	N/A	87.8 ± 12.5	84.5 ± 9.4	52.3 ± 4.7	25.2 ± 2.4
Fe	mg/L	3.844 ± 1.91	0.02 ± 0.03	0.04 ± 0.05	0.09 ± 0.03	0.12 ± 0.15
Fe Removal	%	N/A	99.36 ± 0.81	99.01 ± 1.18	97.76 ± 0.69	96.82 ± 3.79

Table 4.18 Results of Treatment of BWB Spiked with Iron at experimental pH values and temperature T=30°C

Parameter	Unit	Initial Spiked BWB Mean ± sd	Treated Water at pH≈ 10.5 Mean ± sd	Treated Water at pH≈ 11 Mean ± sd	Treated Water at pH≈ 11.2 Mean ± sd	Treated Water at pH≈ 11.5 Mean ± sd
Experimental pH	pH units	7.4 ± 0.1	10.4 ± 0.1	10.9 ± 0.1	11.2 ± 0.1	11.5 ± 0.1
Temperature	°C	25.5 ± 1.9	30.5 ± 0.6	30.7 ± 0.8	30.2 ± 0.5	29.9 ± 0.8
Ca Hardness	mg/L as CaCO₃	1197.2 ± 130.7	520 ± 56.57	5 ± 7.07	0 ± 0	0 ± 0
Ca Removal	%	N/A	56.6 ± 4.7	99.6 ± 0.6	100 ± 0	100 ± 0
Mg Hardness	mg/L as CaCO₃	2110.6 ± 417.8	1340 ± 113.14	790 ± 42.43	655 ± 49.5	260 ± 368
Mg Removal	%	N/A	36.5 ± 5.4	62.6 ± 2	69 ± 2.3	87.7 ± 17.4
Silica	mg/L as Si	6.12 ± 2.1	0.3 ± 0.4	0.3 ± 0.4	2.1 ± 1.4	3.4 ± 0.1
	mg/L as SiO₂	13.1 ± 4.6	0.7 ± 0.8	0.7 ± 0.8	4.5 ± 3	7.2 ± 0.1
Silica Removal	% as Si	N/A	95.1 ± 6.9	95.1 ± 6.9	65.7 ± 23.1	45.3 ± 1.2
	% as SiO₂	N/A	94.7 ± 6.5	94.7 ± 6.5	65.6 ± 22.7	45 ± 1.1
Fe	mg/L	9.57 ± 7.31	0.05 ± 0.01	0.02 ± 0.02	0.04 ± 0.04	0.07 ± 0.05
Fe Removal	%	N/A	99.51 ± 0.15	99.79 ± 0.23	99.57 ± 0.4	99.27 ± 0.56

The maximum removal percentages of Fe occurred at pH between 10.5 and 11 for both temperatures, while Fe removals at higher pH values were slightly lower, at a minimum of $96.82 \pm 3.79\%$. One-way ANOVA tests were performed on Fe removal versus pH and temperature separately, showing no statistically significant difference in removal between operating conditions. A comparative bar chart of the percentage removals of Fe at the two temperatures is presented in each of Figures 4.14 and 4.15 for BW and BWB respectively. Furthermore, a two-way ANOVA test showed that the interaction between pH and temperature did not significantly affect Fe removal (p-value: for 0.256 BW and 0.832 for BWB). Though pH did not significantly affect Fe removal, single linear regressions were performed for Fe removal versus pH at the different operating temperatures, as presented in Table 4.19.



Error! Use the Home tab to apply 0 to the text that you want to appear here. **Figure 4.14 Average Percentage Removals of Fe in BW at different experimental pH values and temperatures**

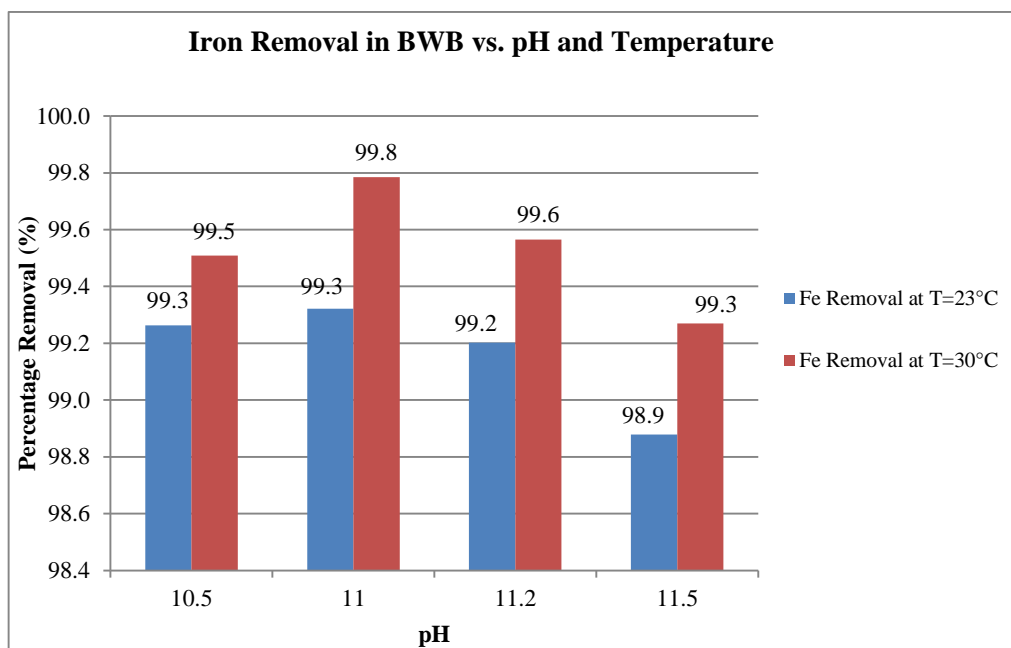


Figure 4.15 Average Percentage Removals of Fe in BWB at different experimental pH values and temperatures

Table 4.19 Single Linear Regression Analysis of Fe removal vs. pH and Temperature

Water Type	Parameter % Removal	Regression Equation	R ²	R ² _{adj}	P-value
BW	Fe (T=25°C)	105.7979 - 0.6305 pH	0.06145	-0.03241	0.4373
	Fe (T=30°C)	126.680 - 2.574 pH	0.2797	0.1596	0.1778
BWB	Fe (T=25°C)	103.0098 - 0.3478 pH	0.05615	-0.03823	0.4584
	Fe(T=30°C)	101.8845 - 0.2127 pH	0.05818	-0.09879	0.565

It is observable from the iron spiking runs that Mg removal efficiency decreases at each pH for both tested temperatures, as compared to the runs where no spiking was carried out. The difference in Mg removal between Fe spiking and non-spiking experiments is statistically significant at 23°C (p-value: 0.0108 for BW and 0.0161 for BWB) but not at 30°C. The decline in Mg removal is probably due to the competitive uptake of hydroxyl ions by the abundant Fe³⁺, in order to form insoluble iron hydroxide, which in turn lowers the pH further preventing Mg precipitation (Chao

& Westerhoff, 2002). Graphical representations are shown in Figures 4.16 and 4.17 for $T \approx 23^\circ\text{C}$ and Figures 4.18 and 4.19 for $T = 30^\circ\text{C}$.

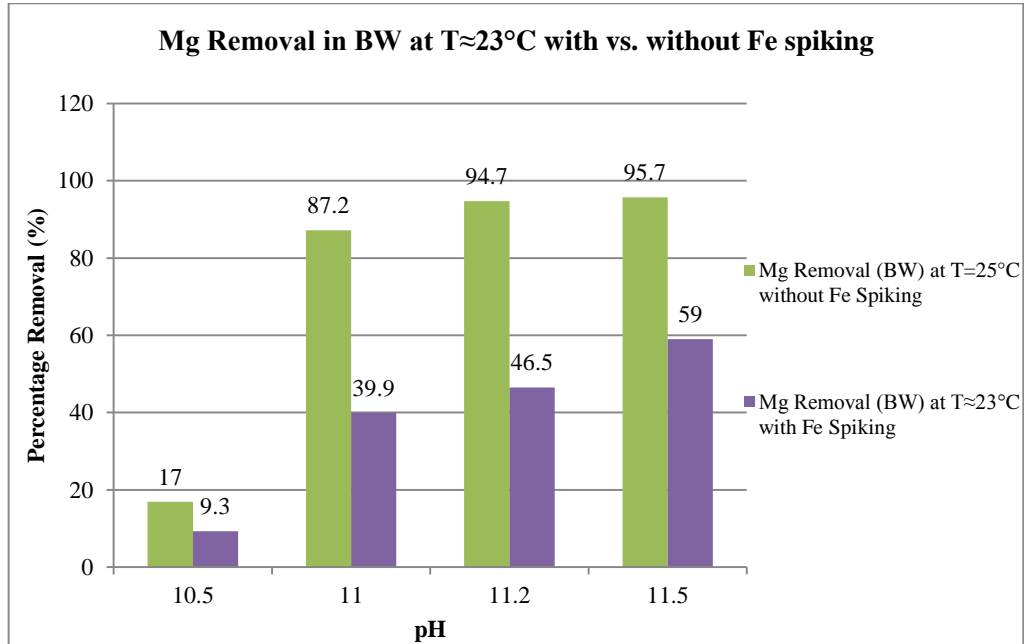


Figure 4.16 Average Percentage Removals of Mg in BW with and without Fe Spiking at $T \approx 23^\circ\text{C}$ and different experimental pH values

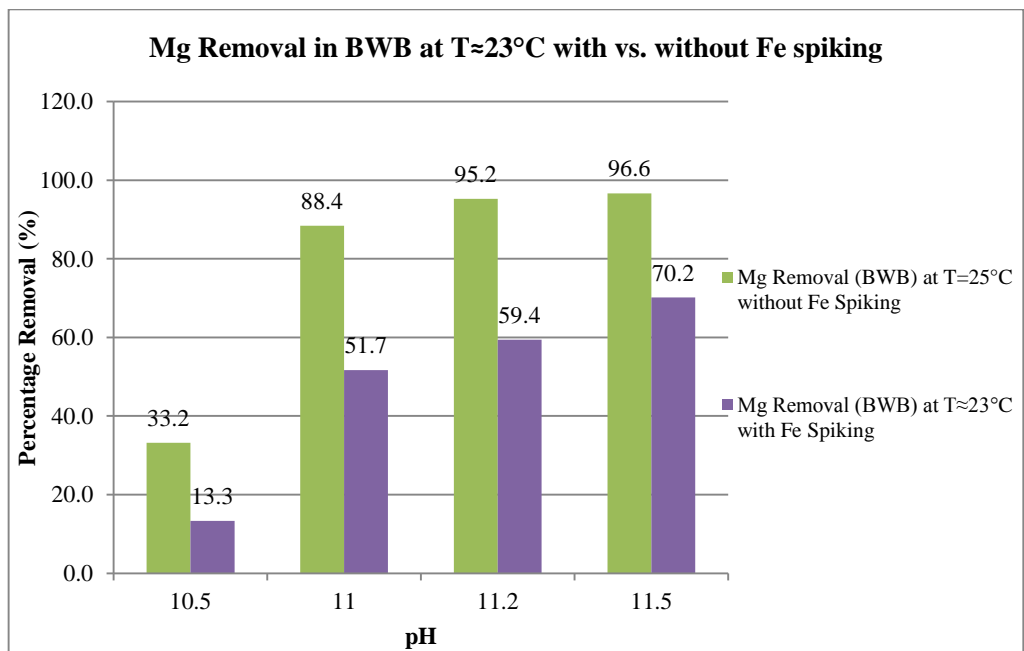


Figure 4.17 Average Percentage Removals of Mg in BWB with and without Fe Spiking at $T \approx 23^\circ\text{C}$ and different experimental pH values

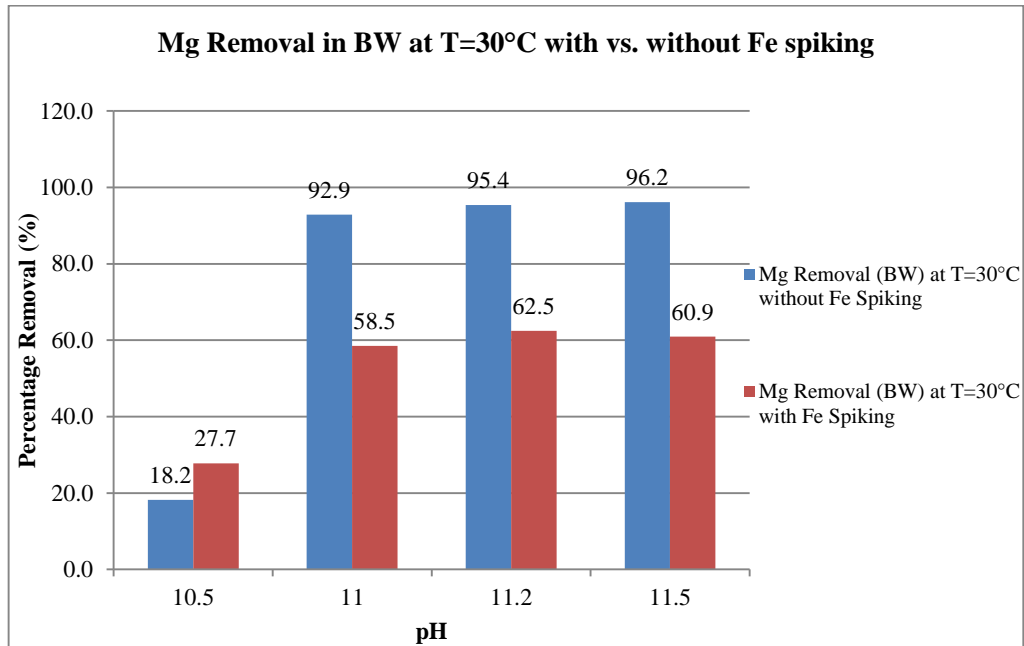


Figure 4.18 Average Percentage Removals of Mg in BW with and without Fe Spiking at T=30°C and different experimental pH values

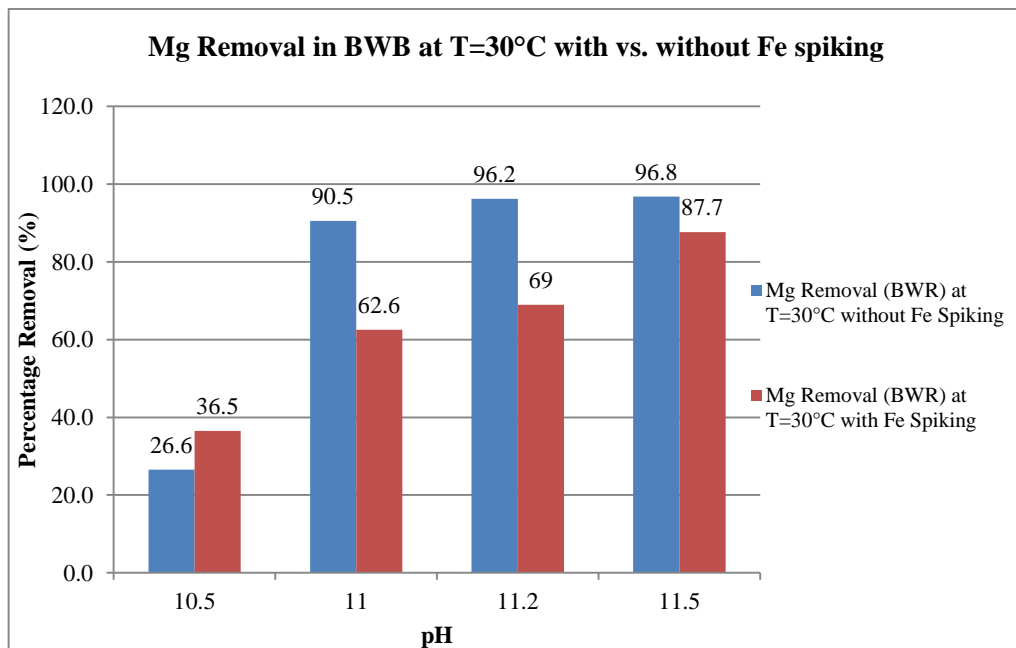


Figure 4.19 Average Percentage Removals of Mg in BWB with and without Fe Spiking at T=30°C and different experimental pH values

At 23°C and pH 11 and 11.5, higher SiO₂ removal efficiencies were noticed in the presence of elevated Fe concentration, but the differences in SiO₂ removal were not statistically significant (p-value: 0.826 for BW and 0.684 for BWB). This increased silica removal seen under Fe spiking conditions could be the effect of increased pH on promoting the abundance of hydroxyl ions and the formation of ferric hydroxide flocs that, in turn, enhance silica adsorption and removal (Teunissen et al., 2008).

4.2.4.3. Addition of Barium

In order to replicate typical barium concentrations in BW and BWB, barium chloride dehydrate (BaCl₂·2H₂O) was added to the water samples, generating concentrations of 4.53- 7.03 mg/L and 9.33- 13.44 mg/L respectively. Control samples were prepared, and they were analyzed for initial concentrations of barium in BW and BWB. The removal efficiencies of the key inorganic scalants, such as Ca and Mg, remained within the standard deviations of their averages from the non-spiking jar tests. The results of the barium spiking experiments are depicted in Tables 4.20 and 4.21 for BW and BWB respectively.

Table 4.20 Results of Treatment of BW Spiked with Barium at experimental pH values and temperature T=23°C

Parameter	Unit	Initial Spiked BW Mean ± sd	Treated Water at pH≈ 10.5 Mean ± sd	Treated Water at pH≈ 11 Mean ± sd	Treated Water at pH≈ 11.2 Mean ± sd	Treated Water at pH≈ 11.5 Mean ± sd
Experimental pH	pH units	7.54 ± 0.1	10.4 ± 0.2	10.9 ± 0.1	11.1 ± 0.1	11.5 ± 0.1
Temperature	°C	25.3 ± 1.7	23.2 ± 0.4	23.3 ± 0.5	23.0 ± 0.5	22.9 ± 0.5
Barium	mg/L	6.51 ± 0.8	0.46 ± 0.27	0.94 ± 1.16	0.53 ± 0.24	0.65 ± 0.30
Barium Removal	%	N/A	92.89 ± 4.08	85.59 ± 17.86	91.93 ± 3.66	89.95 ± 4.66

Table 4.21 Results of Treatment of BWB Spiked with Barium at experimental pH values and temperature T=23°C

Parameter	Unit	Initial Spiked BWB Mean \pm sd	Treated Water at pH \approx 10.5 Mean \pm sd	Treated Water at pH \approx 11 Mean \pm sd	Treated Water at pH \approx 11.2 Mean \pm sd	Treated Water at pH \approx 11.5 Mean \pm sd
Experimental pH	pH units	7.4 \pm 0.1	10.30 \pm 0.25	10.86 \pm 0.12	11.08 \pm 0.18	11.45 \pm 0.06
Temperature	°C	25.5 \pm 1.9	22.97 \pm 0.15	22.93 \pm 0.21	22.63 \pm 0.06	22.67 \pm 0.06
Barium	mg/L	12.7 \pm 1.1	0.20 \pm 0.06	1.35 \pm 0.03	0.63 \pm 0.84	0.60 \pm 0.51
Barium Removal	%	N/A	98.46 \pm 0.44	89.38 \pm 0.26	95.00 \pm 6.65	95.30 \pm 4.02

The decrease in concentration of barium was a consequence of its precipitation in the form of BaSO₄, and it is possible that it was promoted by improved Ca precipitation. However, the differences in Ba removal efficiency between the varying pH values were not significant (p-value: 0.809 for BW and 0.569 for BWB). The best removals were noticed at pH= 10.5, with pH values of 11.2 and 11.5 yielding slightly lower but significant removal percentages, further supporting evidence that Ba²⁺ removal is expected to parallel Ca removal. These results are comparable to the ones reported in the literature showing significant removals above pH of 10 (Ba²⁺ removal of 97–98%) (Gabelich et al., 2007). Other findings presented up to 90% barium removal at pH=11, possibly as BaCO₃ due to its low solubility, by softening in water that has relatively high carbonate alkalinity or with the addition of Na₂CO₃ as a carbonate source (Parks & Edwards, 2006).

4.3. Settling Rate and Sludge Considerations

4.3.1. *Settling Observation*

As the proposed process is a coagulation-flocculation process, a major factor to be assessed is the resulting sludge mass. Since the combination of NaOH and Na₂CO₃

contributes hydroxyl and carbonate ions to the sample water, these ions are used in the formation of $Mg(OH)_2$ and $CaCO_3$ flocs that end up settling. It is noteworthy that these flocs not only settle, but they also carry down other foulants that adhere, adsorb, or even react with them, thus forming a light colored sludge layer.

After the slow mixing period, sludge settling was observed for $T \approx 23^\circ C$ (during spiking runs) and $T \approx 25^\circ C$ (during non-spiking runs) at all pH values over 60 minutes at least, and settling interface height measurements were recorded at different time intervals. The results of settling and compaction are presented in Figures 4.20 and 4.21 at $T \approx 23^\circ C$ and Figures 4.22 and 4.23 at $T \approx 25^\circ C$.

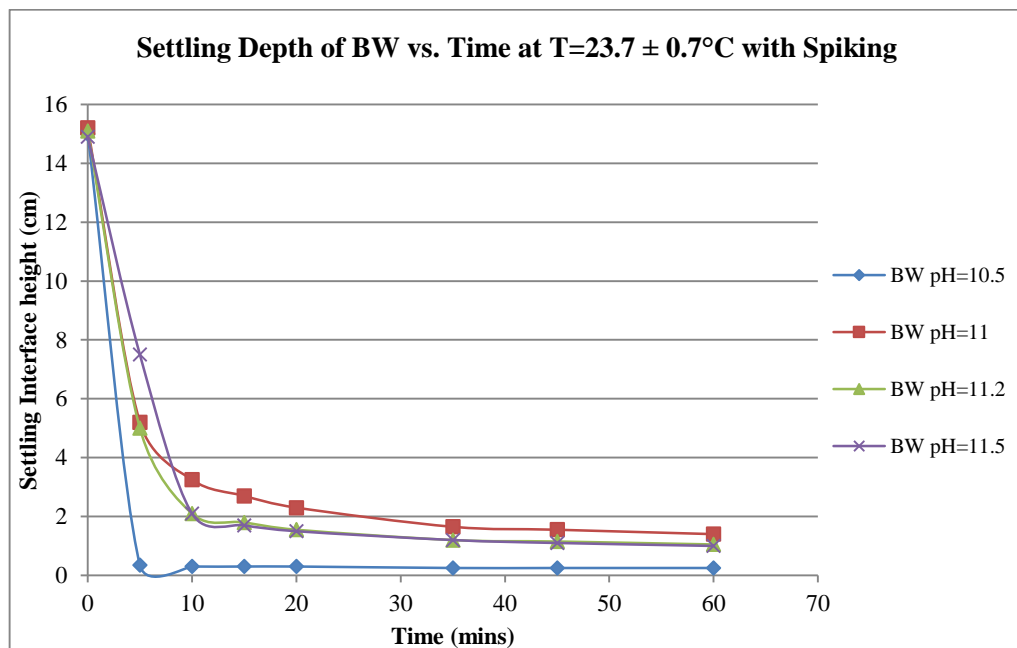


Figure 4.20 Sludge Settling of BW vs. Time at $T \approx 23^\circ C$ with Spiking and different experimental pH values

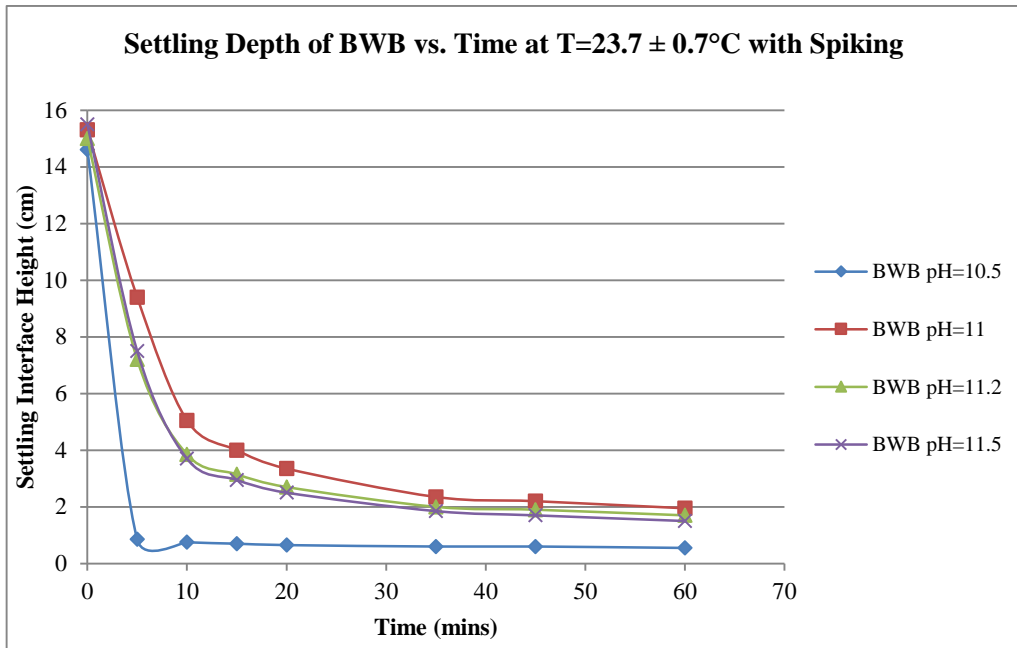


Figure 4.21 Sludge Settling of BWB vs. Time at T≈23°C with Spiking and different experimental pH values

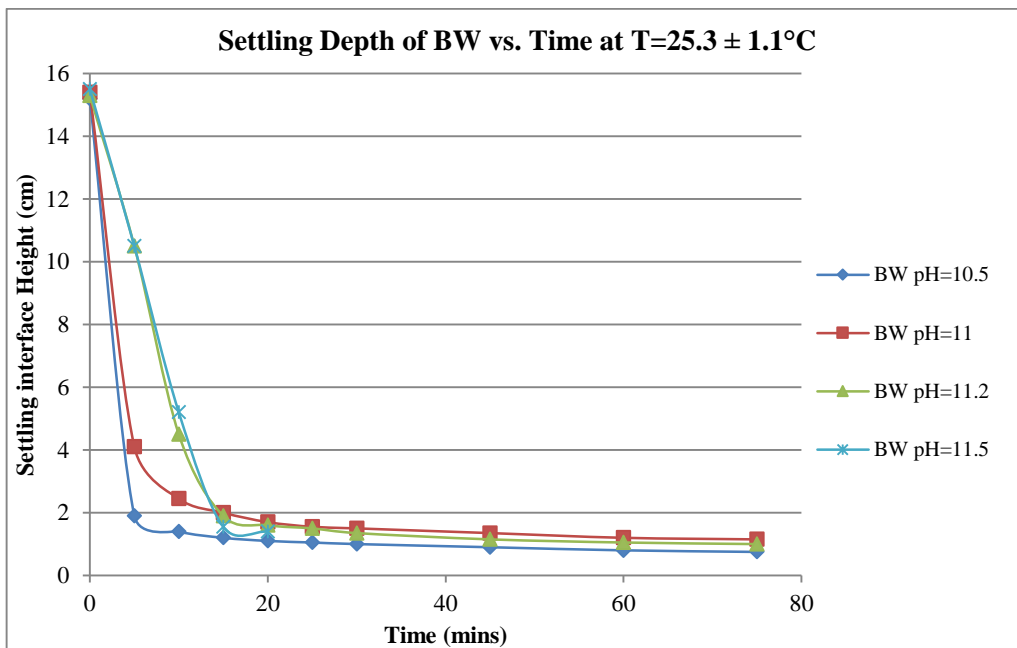


Figure 4.22 Sludge Settling of BW vs. Time at T≈25°C without Spiking and different experimental pH values

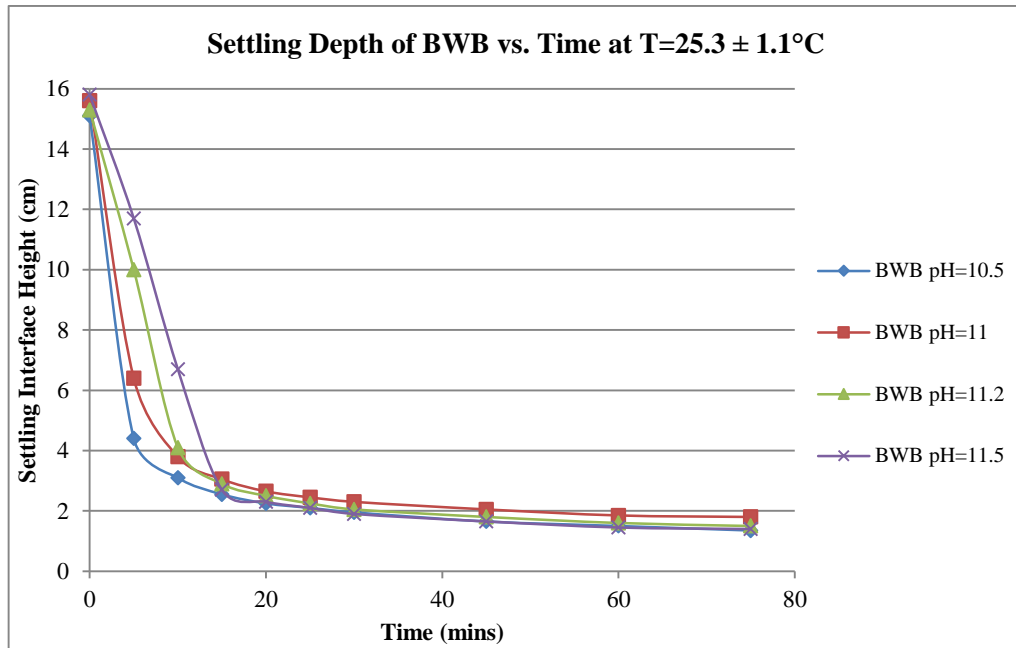


Figure 4.23 Sludge Settling of BWB vs. Time at $T \approx 25^\circ\text{C}$ without Spiking and different experimental pH values

4.3.2. Effect of pH, Temperature, and Spiking on Settling

As seen in the sludge settling graphs, pH has a statistically significant effect on the settling rate of the treated water, whereby both water types showed similar trends under the two experimental conditions (p-value: 0.00306 for BW and 0.0174 for BWB). However, the effect of temperature cannot be asserted since the difference of 2°C between 23°C and 25°C is not significant. Therefore, the possible independent variable that might affect sludge settling is the spiking factor. So the spiking condition was used as a categorical variable in the one-way ANOVA for sludge depth, showing that the final sludge depths during spiking were not significantly different from those during non-spiking runs (p-value: 0.6 for BW and 0.476 for BWB). As well, the two-way ANOVA test demonstrated similar results, while the interaction of pH and spiking was

only significant in the case of BWB (p-value= 0.01012). The final sludge depths at different pH, temperatures, and spiking conditions are shown in Table 4.20.

The highest settling rate was observed at pH=10.5, where the hindered settling interface height for BW and BWB at t= 5 minutes was 1.9 cm and 4.4 cm respectively without spiking and 0.35 cm and 0.85 cm respectively with spiking. As well, the mean sludge depth after 60 minutes compaction achieved at the same pH was 0.73 ± 0.06 cm for BW and 1.48 ± 0.03 cm for BWB at $T \approx 25^\circ\text{C}$ (without spiking), and 0.21 ± 0.05 for BW and 0.43 ± 0.09 for BWB at $T \approx 23^\circ\text{C}$ (with spiking). The observable difference between the BW sludge depths after compaction and those of BWB, which are slightly higher, is in the range of 0.3 to 0.65 cm; this is primarily attributed to the increased concentrations of Ca and Mg in BWB. Though not statistically significant, the lower sludge depths recorded under spiking conditions can be due to adherence and/or interaction of additional contaminants like Fe and Ba with the settling flocs, thus adding to their downward velocity.

The compaction rate was negligible at pH= 10.5, where the sludge depth after hindered settling was practically the same as that after compaction. This is explained by the inferior removal efficiency of Mg at pH=10.5, indicating the dominance of heavier CaCO_3 flocs (molar mass= 100.09 g/mol) compared to Mg(OH)_2 flocs (molar mass= 58.32 g/mol) at this pH value, resulting in the lowest sludge depth after compaction.

The slowest settling rate for both BW and BWB was observed at pH= 11, yet this pH showed the highest compaction rate, whereby the difference in sludge depth after 5 minutes settling as compared to that after 60 minutes compaction was the largest among the experimental pH values.

Furthermore, the slightly higher compaction rate at the higher pH values of 11-11.5 is accompanied with optimal floc formation, whereby better Mg precipitation is known to occur (Ayoub, G. M., 1994; Semerjian & Ayoub, 2003). However, in seawater, the highest compaction was recorded by Ayoub et al. (2013) at 20°C and pH=12, which is attributable to the abundance of Mg ions over Ca ions in seawater. Even though compaction in seawater was at a higher rate, the hindered settling observed in this research had a higher rate than that in seawater, since BW and BWB contain far less Mg concentrations than seawater, thus producing lower floc concentrations as well as sludge depths after 60 minutes compaction. Consistently, the mean sludge depth after compaction is appreciably lower in BW and BWB than in seawater by at least 6 cm, whereby the sludge depth measurements were all below 2 cm for BW and BWB.

Table 4.22 Final Sludge Depth for both water types at different conditions of pH, temperature, and spiking

Water Type	Spiking Status	Experimental Temperature (°C)	pH	Final Sludge Depth (cm) Mean ± sd
Brackish Water	Spiking	23.0	10.5	0.21 ± 0.05
		23.0	11	1.41 ± 0.05
		23.4	11.2	1.08 ± 0.09
		23.2	11.5	1.01 ± 0.07
	No Spiking	25.5	10.5	0.73 ± 0.06
		25.5	11	1.35 ± 0.15
		25.8	11.2	1.08 ± 0.06
		25.8	11.5	0.97 ± 0.03
Brackish Water RO Reject	Spiking	23.1	10.5	0.43 ± 0.09
		23.1	11	1.98 ± 0.07
		23.0	11.2	1.64 ± 0.11
		23.0	11.5	1.48 ± 0.08
	No Spiking	25.8	10.5	1.48 ± 0.03
		25.3	11	1.78 ± 0.16
		25.6	11.2	1.53 ± 0.06
		25.6	11.5	1.38 ± 0.08

A single linear regression was performed to determine the significance of a linear relationship between sludge depth and pH, resulting in the following regression equations:

- For BW: Final sludge depth (cm)= $-4.9037 + 0.5326 \text{ pH}$, $R^2 = 0.2729$, $R^2_{(adj)} = 0.2469$, p-value= 0.003063
- For BWB: Final sludge depth (cm)= $-4.5772 + 0.5466 \text{ pH}$, $R^2 = 0.1858$, $R^2_{(adj)} = 0.1567$, and p-value= 0.01742

4.4. Optimal Process Selection

4.4.1. Optimal Operating Conditions

The removal efficiencies of all the key foulants, Ca, Mg, Si, Sr, and B, were optimal at room temperature ($\approx 25 \pm 2^\circ\text{C}$) and at 30°C , including the spiked contaminants (bacteria, iron, and barium), and temperature was proven not to have a significant effect on removal efficiencies (all p-values > 0.05). Therefore, 25°C can be considered as the optimal operating temperature of the suggested softening process. As previously stated, pH significantly affected the removal efficiencies of the major scaling ions. The pH values above 11 yielded the best removals of potential foulants, with pH=11.2 as an advantageous operating condition, in terms of moderate chemical use and most simultaneous removals of Ca, Mg, Sr, Si, B, and Ba. This is reaffirmed by the negligible decreases in optimal removal efficiencies from 25°C to 30°C compared to the additional chemical volumes needed to achieve the optimal pH at 30°C , as shown in Appendix 3. The removal of foulants such as Ba and Sr under the abovementioned conditions significantly reduced the fouling propensity of the sample water, by decreasing the ionic activity in the solution.

Operating the suggested treatment process at the selected conditions of pH and temperature would not only improve the quality of the BWB but also minimize the fouling concerns for the BWRO system, in terms of inorganic foulants like CaCO_3 , SiO_2 , CaSO_4 , BaSO_4 , SrSO_4 , and CaF_2 , and Mg(OH)_2 .

4.4.2. Mass Balance

As previously noted, the precipitation softening reactions are mostly controlled by the inorganic chemicals, including Ca, Mg, Na, which are also the dominating constituents of the TDS of the BW and BWB. A mass balance was performed on the main parameters involved in the reaction at $T \approx 25^\circ\text{C}$ and experimental pH values of 10.5, 11, 11.2, and 11.5, in order to compare the mass in mg/L of key constituents added, thus increasing the TDS, to the mass of those removed.

To accomplish this, the percent masses of Na in NaOH and Na_2CO_3 were calculated as 57.48% and 43.38%, respectively, using their respective molar ratios, followed by calculating the respective concentration of Na per unit volume of every softening agent (Appendix 6). Then, the added mass of Na was derived from the volume of 2:1 NaOH: Na_2CO_3 used at each pH, as depicted in Table 4.21. As well, the masses in mg/L of removed Ca, Mg, and bicarbonate alkalinity were calculated for every tested pH, and they were subtracted from the added mass of constituents as shown in Table 4.22. Subsequently, Table 4.23 presents the net concentration as compared to the decrease in TDS from the initial BW and BWB measurements.

The assumptions held in these calculations are as follows:

- The Na, carbonate alkalinity, and hydroxide alkalinity concentrations calculated represent the concentrations added to the sample water.

- Bicarbonate alkalinity decreased and is thus subtracted from the added concentrations.

Table 4.23 Calculation of the total Na added to BW and BWB at T=25°C

Water Type	pH	Volume of NaOH (mL)	Mass of Na from NaOH (mg/L)	Volume of Na ₂ CO ₃ (mL)	Mass of Na from Na ₂ CO ₃ (mg/L)	Total Concentration of Na Added (mg/L)
BW	10.5	3.73	85.83	1.87	42.90	128.73
	11	16.94	389.65	8.47	194.78	584.43
	11.2	21.00	482.91	10.50	241.39	724.30
	11.5	24.91	572.93	12.46	286.39	859.32
BWB	10.5	6.04	139.00	3.02	69.48	208.48
	11	25.81	593.55	12.91	296.70	890.24
	11.2	31.61	726.92	15.81	363.37	1090.29
	11.5	35.21	809.71	17.61	404.75	1214.46

Table 4.24 Calculation of the mass balance of constituents in BW and BWB at T=25°C

Water Type	pH	Total Concentration of Na Added (mg/L)	Removed Ca (mg/L)	Removed Mg (mg/L)	Removed Alkalinity (bicarbonate) (mg/L)	Added Alkalinity (hydroxide) (mg/L)	Added Alkalinity (carbonate) (mg/L)	Net concentration (mg/L)
BW	10.5	128.73	468.1	275.6	87.2	0	0	-702.12
	11	584.43	839.8	1417.1	90.8	0	4.8	-1758.48
	11.2	724.30	906.9	1539.2	96.4	16	13.2	-1789.05
	11.5	859.32	916.8	1556.1	96.4	28.8	66.4	-1614.78
BWB	10.5	208.48	659.7	700.6	109.7	0	0	-1261.45
	11	890.24	1094.0	1866.6	112.5	0	5.2	-2177.54
	11.2	1090.29	1182.9	2009.9	116.7	9.4	17.6	-2192.14
	11.5	1214.46	1194.5	2039.1	116.7	46.4	26.8	-2062.52

Table 4.25 Comparison of the mass balance and TDS decrease for BW and BWB at T=25°C

Water Type	pH	Net concentration (mg/L)	TDS Decrease (mg/L)	Difference (mg/L)
BW	10.5	-702.12	1181	479
	11	-1758.48	1168	-591
	11.2	-1789.05	1354	-435
	11.5	-1614.78	1004	-611
BWB	10.5	-1261.45	1777	515
	11	-2177.54	1977	-201
	11.2	-2192.14	1717	-476
	11.5	-2062.52	1473	-589

As Table 4.23 shows, the difference between the net concentration of constituents and TDS decrease ranges between -611 mg/L and 515 mg/L, implying an additional decrease that is not accounted for in the mass balance calculations. Although of moderate magnitudes, these differences can be due to standard error of the experimental data, which can be reduced by increasing the sample size. They can also be due to measurement error, in terms of accuracy and precision of the used instruments.

CHAPTER 5

CONCLUSION AND RECOMMENDATIONS

The purpose of this research is to evaluate the efficiency of a combination of 1N NaOH and 1N Na₂CO₃ in a volumetric ratio of 2:1 in removing foulants typically present in BW and BWB, at different pH values and temperatures. The results and statistical analysis are summarized as follows:

- At T=25 °C: Ca, Mg, and Sr removals were optimal at pH=11.5, followed by pH=11.2. As for silica and boron, their optimal removals were achieved at pH=11, followed by pH=11.2. pH showed a statistically significant effect on Ca, Mg, and Sr removal, but it didn't significantly impact SiO₂, H₃BO₃, and Ba removal.
- At T=10 °C, Ca, Mg, and Si removals were unsatisfactory, compared to the removals achieved under other operating conditions.
- At T=30 °C: Ca and Mg removals were at their absolute maximum levels at 30°C at pH=11.5. Optimal removal of silica was at pH=10.5, while that of boron was recorded at pH=11.5. The optimal removal of Sr was accomplished at pH=11.5, but it was slightly lower than it was at 25°C.
- Wastewater spiking: total and fecal coliforms were almost completely inactivated and removed by the suggested treatment under all pH conditions at 25°C and 30°C.
- Iron spiking: Mg showed lower removal efficiencies during spiking, at each pH for both test temperatures. The difference in Fe removal was not statistically significant under the varying conditions of pH and temperature.

- Ca and Mg removals showed a statistically significant trend of improvement with temperature increase.
- Some inconsistencies were observed with regards to the expected variation of Si removal efficiency versus pH (in parallel to Mg removal) and temperature variation, indicating a possible experimental or instrumental error. Thus, further experiments with a larger sample size are required to increase the statistical power of their relevant results.
- Sludge depth was significantly affected by pH, but spiking did not cause a significant difference in the final sludge depth for both waters.
- In conclusion, the suggested precipitation treatment was successful in achieving optimal parametric removals for the water composition of the BW and BWB samples used.

It is undeniable that RO membrane fouling and reject disposal are the major hurdles in the RO desalination industry. Considering that environmental regulations have become increasingly stringent, brine disposal and treatment can be costly and challenging partly because BWRO plants are often situated inland, where discharge options are limited. To add, the deterioration in water source quantity and quality has contributed to increasing fouling tendency in RO membranes (Hastuti & Wardiha, 2012). Therefore, feed water pretreatment and brine treatment have become necessary to avoid severe membrane fouling, loss of RO performance efficiency, and additional operation costs.

Environmentally and economically effective feed pretreatment and brine treatment would allow RO plants to boost their clean water production without increasing source water extraction, while simultaneously attempting to decrease

chemical and energy consumption (Elimelech & Phillip, 2011; Mogheir et al., 2013). Extensive research has been invested in achieving optimal treatment methods, but these attempts might still be insufficient. Even though membrane surface modification options have been developed, further efforts are recommended to properly characterize RO membrane fouling for a better understanding of this problem (Zhu et al., 2010; Melián-Martel et al., 2012). This would allow an efficient tailoring of the pretreatment process, resulting in decreased expenses and a reduced environmental footprint.

As a BW and BWB treatment option, precipitation softening presents several advantages, including the potential for recycling as well as the ability to remove a wide range of foulants, from calcium and magnesium, to barium and even bacteria (Semerjian & Ayoub, 2003; Ayoub et al., 2013). On the other hand, in the case of excessive chemical use, the process can incur further costs and render the sludge hard to manage. So, it would be interesting to further explore sludge considerations, since the presence of heavy metals like boron, iron, and others, can notably affect the quality of this end product (Mohammadesmaeili et al., 2010a; Mohammadesmaeili et al., 2010b). As well, additional experiments to observe sludge mass and settling rate under variable conditions of spiking and temperature, including 10°C, 20°C, and 30°C, would allow to properly assess the effect of temperature and the combined effect of pH and temperature on settling rate and sludge quality. Moreover, a cost-benefit analysis of the softening process as a BW pretreatment and BWB treatment scheme is crucial in order to assess its effectiveness and feasibility as an alternative to other options.

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APPENDIX 1: STANDARD METHODS USED FOR WATER ANALYSIS

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 Titrimetric Method	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-SO ₄ ²⁻
Chlorides	Argentometric Method	4500-Cl ⁻
Boron	Carminic 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 2: MATRIX OF EXPERIMENTAL CONDITIONS OF THE PROPOSED RESEARCH

	pH			
Temperature (°C)	10.5	11	11.2	11.5
10	✓	✓	✓	✓
25	✓	✓	✓	✓
30	✓	✓	✓	✓

*Three experiments were conducted for each water type, BW and BWB, under every pH-temperature combination

**APPENDIX 3: VOLUMES OF THE OPTIMAL
COMBINATION OF ALKALIZING AGENTS UNDER
DIFFERENT EXPERIMENTAL CONDITIONS OF
TEMPERATURE AND PH**

Optimal Softener		2:1 1N NaOH:1N Na ₂ CO ₃			
Experimental Temperature (°C)	Experimental pH	Optimal Softener Added in 2L of BW		Optimal Softener Added in 2L of BWB	
		Mean Volume (mL)	Standard Deviation	Mean Volume (mL)	Standard Deviation
10	10.5	8.12	0.58	11.42	0
	11	12.61	0	24.07	0.58
	11.2	30	1.15	60	0
	11.5	47.33	0	79.29	1
25 (Room Temperature)	10.5	11.2	3.06	18.13	4.68
	11	50.83	3.39	77.43	3.71
	11.2	63	2.07	94.83	2.04
	11.5	74.74	1.63	105.63	1.17
30	10.5	26.95	1.5	47.58	3.3
	11	63.5	2.58	96.66	1.29
	11.2	70.54	3.3	104.67	2.63
	11.5	80.11	4.79	112.83	3.7

APPENDIX 4: TABLE OF COMPARISON OF BW CHARACTERISTICS

Parameter	Unit	BW From the Literature	BW for Proposed Research	WHO Standards
Alkalinity (carbonate)	mg/L (as CaCO ₃)	292 (Afonso et al., 2004) 43 (Ning & Netwig, 2002)	0	
Alkalinity (bicarbonate)	mg/L (as CaCO ₃)	356 (Afonso et al., 2004) 131 (Shahalam et al., 2002) 94.4 (Ning et al., 2006)	113.2	
Boron	mg/L	0.21 (Alghoul et al., 2009)	1.92	2.4
Barium	mg/L	0.06 (Greenlee et al., 2009) 0.13 (Ning et al., 2006) 0.135 (Rahardianto et al., 2006) 0.014 (Ning & Netwig, 2002)	BDL	0.7
Strontium	mg/L	16 (Shahalam et al., 2002) 2.38 (Ning et al., 2006)	5.56	4
Calcium	mg/L	179 (Greenlee et al., 2009) 207 (Afonso et al., 2004)	368.96	100
Chloride	mg/L	1867 (Greenlee et al., 2009) 987 (Afonso et al., 2004) 1746 (Shahalam et al., 2002) 2052 (Shahalam et al., 2002) 1166 (Turek et al., 2009) 1483 (Alghoul et al., 2009)	3812.9	250
Iron	mg/L	0.1 (Afonso et al., 2004) 0.4 (Shahalam et al., 2002) 9.66 (Stuyfzand & Raat, 2009) 28.87 (Alghoul et al., 2009)	0.04	
Magnesium	mg/L	132 (Greenlee et al., 2009) 98 (Afonso et al., 2004)	395.01	60
Silica	mg/L (as SiO ₂)	18 (Afonso et al., 2004) 30 (Ning et al., 2006) 10.4 (Stuyfzand & Raat, 2009) 20 (Ning & Netwig, 2002)	9.02	
Sodium	mg/L	905 (Greenlee et al., 2009) 470 (Afonso et al., 2004) 1646 (Shahalam et al., 2002) 1125 (Alghoul et al., 2009)	1695.96	200
Potassium	mg/L	14.7 (Ning et al., 2006) 23 (Stuyfzand & Raat, 2009) 19.2 (Alghoul et al., 2009)	18.49	5
Sulphate	mg/L	384 (Greenlee et al., 2009) 276 (Afonso et al., 2004) 2893 (Shahalam et al., 2002) 868.8 (Turek et al., 2009)	500	250
Total hardness	mg/L (as CaCO ₃)	940 (Afonso et al., 2004) 2150 (Shahalam et al., 2002)	2524.4	500

Calcium hardness	mg/L (as CaCO ₃)	660 (Shahalam et al., 2002) 905 (Stuyfzand & Raat, 2009)	920.6	
Magnesium hardness	mg/L (as CaCO ₃)	1485 (Shahalam et al., 2002) 1322 (Stuyfzand & Raat, 2009)	1625.6	
TDS	mg/L	3664 (Greenlee et al., 2009) 2733 (Afonso et al., 2004)	6357.5	1000
pH	pH units	7.3 (Afonso et al., 2004)	7.54	
Conductivity	mS/cm	4.27 (Afonso et al., 2004) 2.7 (Shahalam et al., 2002) 6.35 (Alghoul et al., 2009)	10.62	10

APPENDIX 5: TABLE OF COMPARISON OF BWB CHARACTERISTICS

Parameter	Unit	BWB From the Literature	BWB for Proposed Research
Alkalinity (carbonate)	mg/L (as CaCO ₃)		0
Alkalinity (bicarbonate)	mg/L (as CaCO ₃)	650 (Mohammadesmaeili et al., 2010) 627 (Ning et al., 2006)	117
Boron	mg/L (as H ₃ BO ₃)		11.9
Barium	mg/L	0.9 (Ning et al., 2006)	BDL
Strontium	mg/L	15.9 (Ning et al., 2006)	7.5
Calcium	mg/L		479.8
Chloride	mg/L	1950 (Mohammadesmaeili et al., 2010) 3447 (Ning et al., 2006) 2886 (Turek et al., 2009)	5489
Iron	mg/L		0.041
Magnesium	mg/L		512.9
Silica	mg/L (as SiO ₂)	63 (Mohammadesmaeili et al., 2010) 200 (Ning et al., 2006)	13.1
Sodium	mg/L	1100 (Mohammadesmaeili et al., 2010) 1860 (Ning et al., 2006)	2842.7
Potassium	mg/L	98 (Ning et al., 2006)	35.2
Sulphate	mg/L	1650 (Mohammadesmaeili et al., 2010) 507 (Ning et al., 2006) 2164 (Turek et al., 2009)	666.7
Total hardness	mg/L (as CaCO ₃)		3273
Calcium hardness	mg/L (as CaCO ₃)	550 (Mohammadesmaeili et al., 2010) 497.3 (Ning et al., 2006)	1197
Magnesium hardness	mg/L (as CaCO ₃)	310 (Mohammadesmaeili et al., 2010) 166.7 (Ning et al., 2006)	2111
TDS	mg/L	6500 (Mohammadesmaeili et al., 2010)	9053.3

APPENDIX 6: CALCULATIONS OF MASS PERCENTAGE AND SODIUM CONCENTRATION IN THE OPTIMAL SOFTENING AGENTS

NaOH Calculations:

$$\% \text{ by mass Na of NaOH} = \frac{\text{molar mass of Na } \left(\frac{\text{g}}{\text{mol}}\right)}{\text{molar mass of NaOH } \left(\frac{\text{g}}{\text{mol}}\right)} \times 100\% = \frac{22.99}{39.99} \times 100\% =$$

57.48%

Concentration of NaOH = 1N = 1 mol/L = 40,000 mg/L

$$\text{Concentration of Na in 1N NaOH} = \frac{40,000 \frac{\text{mg}}{\text{L}} \times 57.48}{100} = 22,995.7 \text{ mg Na/L NaOH}$$

Na₂CO₃ Calculations:

$$\% \text{ by mass Na of Na}_2\text{CO}_3 = \frac{2 \times \text{molar mass of Na } \left(\frac{\text{g}}{\text{mol}}\right)}{\text{molar mass of Na}_2\text{CO}_3 \left(\frac{\text{g}}{\text{mol}}\right)} \times 100\% = \frac{2 \times 22.99}{105.99} \times 100\%$$

= 43.38%

Concentration of Na₂CO₃ = 1N = 0.5 mol/L = 52,995 mg/L

$$\text{Concentration of Na in 1N Na}_2\text{CO}_3 = \frac{52,995 \frac{\text{mg}}{\text{L}} \times 43.38}{100} = 22,990 \text{ mg Na/L Na}_2\text{CO}_3$$