Integrated Chemical/Membrane Treatment for Oil Sands Produced Water

by

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Abstract

Over the last decade, the treatment of the produced water streams from steam assisted gravity drainage (SAGD) operation has attracted a significant attention. In this study, an integrated method based on the membrane filtration and chemical treatment was proposed for the treatment of the boiler blow-down (BBD) water. First, the potential application of ion exchange regeneration wastewater (IERW), containing high concentration of magnesium ions, to act as a coagulant for the treatment of BBD water was investigated. Conventional techniques for the treatment of BBD water require significant operational costs as they rely on the extensive use of chemical coagulants. Since the proposed process design in this study uses another wastewater stream of a SAGD plant, operational costs and energy consumption are predicted to be minimized. The effects of temperature, the mixing ratio of BBD water and the IERW, and the stirring intensity on the removal of organic matter and dissolved minerals were investigated. Utilizing IERW as a coagulant enhanced the removal of impurities; removal efficiency of 81.1% and 98.6% were obtained for organic matter and silica, respectively. The treatment of BBD water by IERW, however, has led to an increase in the concentration of calcium in the effluent, which was effectively mitigated by soda ash softening. Furthermore, resource recovery from the coagulated sludge was explored by chemical methods of characterization, and it was revealed that the precipitated compounds were mostly composed of calcium, magnesium, and silica. In conclusion, the IERW water proved to be highly effective in removing contaminants from SAGD produced water. In the next step, different membrane-based hybrid processes were applied to further purify the treated BBD by IERW. The first scenario studied the usage of soda ash softening to reduce the calcium concentration, followed by nanofiltration (NF). It was observed that using soda ash softening as a chemical pre-treatment for the NF can reduce the deposition of calcium on the surface of the membrane. Second scenario involved direct treatment of the BBD water using NF and then purifying the NF retentate using an integrated IERW conditioning and NF process. The filtration of BBD water demonstrated a relatively low total flux decline ratio due to having a low TDS concentration and the treated water resulted from the IERW conditioning of concentrated BBD showed a relatively low concentration of calcium. Third scenario was to investigate the potential of using the IERW as the draw solution of forward osmosis (FO) for the treatment of the BBD. However, the NF of diluted IERW was inefficient in terms of requiring a higher operating pressure to purify this wastewater. The effectiveness of these methods was compared based on flux recovery ratio and contaminants removal efficiency. The direct NF of BBD followed by another cycle of IERW conditioning and NF was found to be the optimum scenario regarding water recovery and water product quality.

Keywords: Oil sands; Produced water treatment; Boiler blowdown; Coagulation/flocculation; SAGD; Process integration; Membrane filtration, Nanofiltartion, Forward osmosis,

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Nomenclature

J_w	Permeate water flux
DR_t	Total flux decline ratio
DR_r	Reversible flux decline ratio
DR_{ir}	Irreversible flux decline ratio
FRR	Flux recovery ratio
J_{w1}	Pure water flux at first
J_{w2}	Pure water flux after hydraulic cleaning
J_p	Permeate water flux of the wastewater
J_s	Reverse solute passage
R	Rejection
C_p	Concentration of permeate
C_t	Concentration of feed water
A	Active surface area of the membrane
Δm	Mass of collected permeate water

List of Abbreviations

SAGD	Steam assisted gravity drainage
BBD	Boiler blow-down
IERW	Ion exchange regeneration waste
OTSG	Once through steam generators
TOC	Total organic carbon
TDS	Total dissolved solids
MF	Microfiltration
UF	Ultrafiltration
RO	Reverse osmosis
NF	Nanofiltration
FO	Forward osmosis
PRO	Pressure retarded osmosis
UV	Ultraviolet
ICP-OES	An inductively coupled plasma optical emission spectroscopy
NTU	Nephelometric turbidity unit
FESEM	Field emission scanning electron microscopy
EDXS	Energy-dispersive X-ray spectroscopy
XPS	X-ray photoelectron spectroscopy
XRD	X-ray powder diffraction
DRIFT	Diffuse reflectance infrared fourier transform
IC	Ion chromatography
UV_{254}	UV absorbance values at 254 nm
SUVA	Specific ultraviolet absorbance
ppm	Parts per million
SS	Sum of square
DOF	Degrees of freedom
CP	Concentration polarization
ICP	Internal concentration polarization

Chapter 1

1 Introduction

1.1 Problem Statement

Water is the lifeline of oil sands industry and much research and development is currently underway to improve the water treatment process in the steam assisted gravity drainage (SAGD) operation . SAGD process is used to extract the bitumen from the oil sand reservoir. The SAGD process involves drilling a pair of parallel horizontal wells deep underground. The steam and production wells are placed above each other in a way that the steam is injected through the upper well to reduce the viscosity of the bitumen and a mixture of the bitumen and water is extracted through the lower well. In the surface facilities, the bitumen is first separated from water, and then the produced water is purified to be reused as the boiler feed water (BFW). In order to achieve a reasonable efficiency for the boilers, the quality of the BFW should be within a standard range, depending on the type of the boiler. Most of the SAGD plants use the once-through steam generators (OTSG) for the bitumen extraction. For the OTSG, the concentration of hardness, silica and total dissolved solids (TDS) should be lower than 1, 50 and 7000 ppm, respectively [1–4].

Hence, water treatment, recycle and reuse is essential for the sustainable production of oil in the SAGD operation. Different water treatment processes are currently being applied in the SAGD plants to remove contaminants, especially silica, calcium, and magnesium as these ions are mainly responsible for fouling and scaling of boiler tubes and other equipment [5–7]. One of the commonly used methods to remove these contaminants is the ion exchanger. This method enables removing almost all magnesium and calcium cations. As demonstrated in Figure 1.1, the regeneration of resin bed in the ion exchanger can produce a saline waste brine named ion exchange regeneration wastewater (IERW), which contains a high concentration of sodium, chloride, calcium and magnesium. The disposal of IERW is challenging because it has an extreme amount of sodium, magnesium and calcium and is considered as a hard water. Therefore, some methods have been explored to handle the IERW to increase the efficiency of this process such as reusing the IERW for the biological denitrification process or recovering some more valuable materials, such as sodium chloride, from this waste stream [8–11]. In the SAGD operation, the IERW is usually being transferred to the disposal wells.

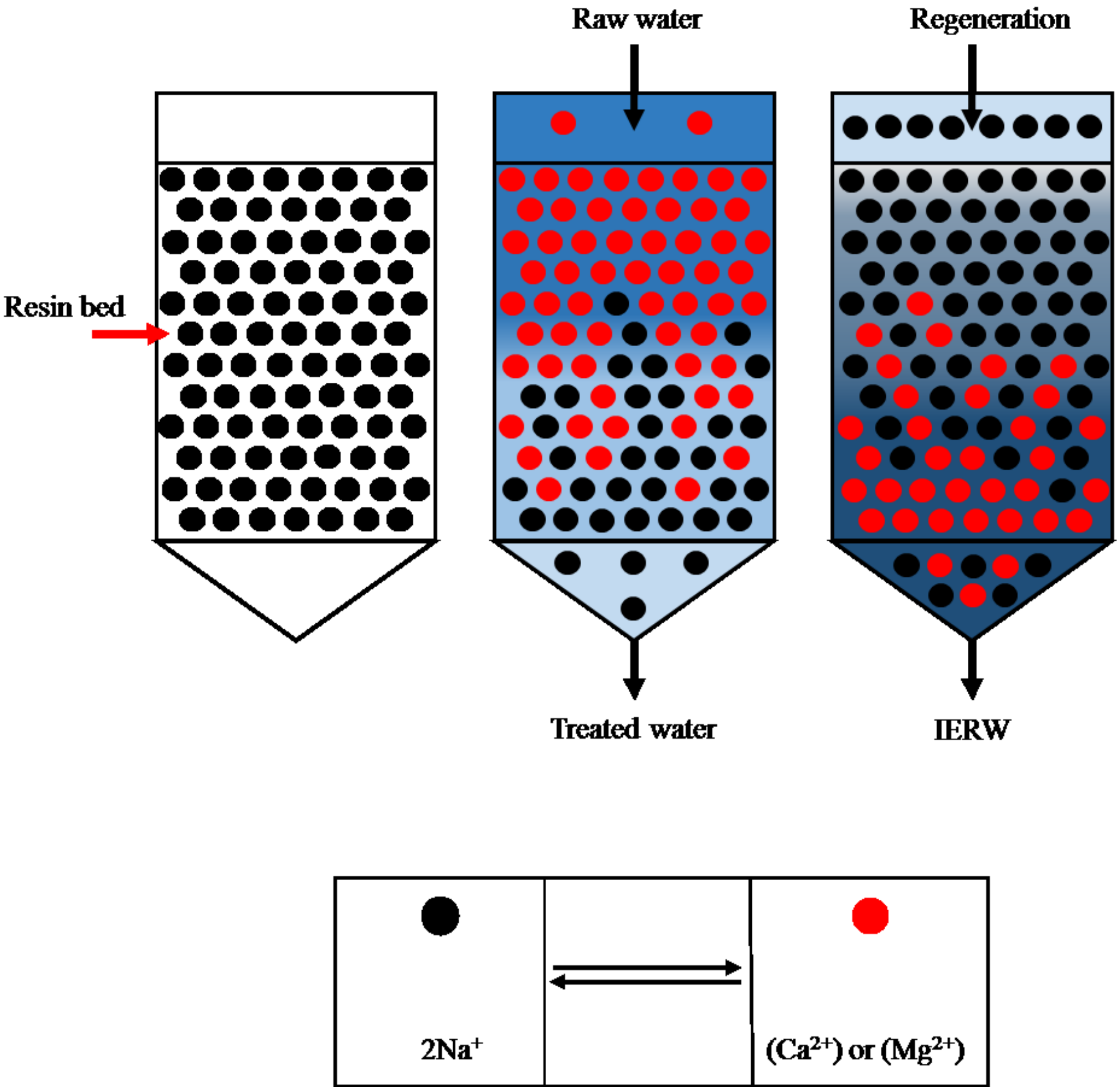


Figure 1.1: Details of the formation of ion exchange regeneration wastewater.

The IERW is not the only wastewater in SAGD operation, which is being sent to the disposal vessel. A portion of the OTSG blowdown, called boiler blowdown (BBD) water, with a high concentration of organic matter, silica and TDS, and is also sent to the disposal wells [2]. In current processes, a portion of the BBD is being recycled and treated to be used as the BFW. The disposal of BBD stream, which is a high alkaline wastewater, not only causes environmental issues but also presents a serious technical issue of well clogging by silica-organic matter co-precipitation [4,12,13]. Therefore, some studies have investigated different water treatment methods such as acidification, coagulation, advanced oxidation, and membrane filtration to treat the BBD and eliminate the improper disposal problem and simultaneously mitigate freshwater withdrawals [4,13–16]. However, most of these treatment methods are not energy- and cost-efficient and usually produce a lot of waste as by-product. Hence, oil sands companies are actively seeking for novel methodologies that can be utilized for the effective treatment of BBD in terms of operational and capital costs.

1.2 Chemical treatment overview

Chemical treatment methods have been widely used for the wastewater treatment applications. These methods usually involve conditioning the wastewaters by coagulation and flocculation to remove the impurities through sedimentation or filtration [14,17]. Coagulation is responsible for destabilizing the contaminants ions by the addition of a coagulant. Generally, the DLVO theory is used to explain that stability of a particle based on the electrostatic repulsion and van der Waals attraction forces. After the addition of the coagulant, the balance between the two opposing forces will shift from the electrostatic repulsion to the attraction forces leading to destabilization and formation of large flocs. Flocculation, which is the aggregation of the destabilized particles, plays an important role in the coagulation process [18]. In the case of presence of negatively charged impurities in the wastewater, positive counterions will be accumulated near their surface to maintain the electroneutrality. This positive ions adsorbed layer near the particle surface is known as stern layer. The stern layer ions are not moving due to shear forces. A layer above the stern layer, which again has a more concentration of positive ions, but the ions, can freely move, is called the diffuse layer. The thickness of these two layers together is called electric double layer (EDL). These negatively charged particles rapidly move and contact each other in water due to the Brownian motion. Thus, their EDL overlaps and since they have similar surface charge, they repel each other due to the electrostatic repulsion. However, the thickness of the EDL depends on the ionic strength of the solution. The EDL can be compressed by increasing the ionic strength. This is typically done by the addition of coagulants. After the addition of high valency cations such as aluminum and iron ($z=3$) salts, the ionic strength increases, the thickness of EDL decreases, and thus the attraction forces will become more dominate leading to the formation of the larger flocs [17,19–25].

Magnesium oxide (Magox) has also been proven to be effective as a coagulating agent at high pH. It is mainly used for the removal of silica through adsorption and partial reaction mechanisms. Magnesium precipitates as magnesium hydroxide ($Mg(OH)_2$) by increasing the pH and silica and organic matter co-precipitate with Magnesium oxide/hydroxide. It was reported that the magnesium hydroxide could successfully remove 80% of algae from seawater at a pH of 10.5 [21]. Moreover, it was demonstrated that the precipitation of the magnesium hydroxide could improve the removal of organic matter [20].

Another common chemical treatment method is softening which is applied to lower the concentration of water hardness (magnesium and calcium ions). In the softening process, the soluble calcium and magnesium ions are converted to the insoluble ions by adding the coagulant.

For the carbonate hardness, lime ($Ca(OH)_2$) and caustic ($NaOH$) reduce hardness by the following reactions [26–28]:

$$Ca(HCO_3)_2 + Ca(OH)_2 \leftrightarrows 2CaCO_3 \downarrow + 2H_2O \tag{1}$$

$$Ca(HCO_3)_2 + 2NaOH + Ca^{2+} \leftrightarrows 2CaCO_3 \downarrow + 2H_2O + 2Na^+ \tag{2}$$

$$Mg(HCO_3)_2 + Ca(OH)_2 \leftrightarrows CaCO_3 \downarrow + MgCO_3 + 2H_2O \tag{3}$$

$$MgCO_3 + Ca(OH)_2 \leftrightarrows CaCO_3 \downarrow + Mg(OH)_2 \downarrow \tag{4}$$

For the removal of the non-carbonate calcium, soda ash (Na_2CO_3) can be used according to the following reactions:

$$CaSO_4 + Na_2CO_3 \leftrightarrows CaCO_3 \downarrow + Na_2SO_4 \tag{5}$$

$$CaCl_2 + Na_2CO_3 \leftrightarrows CaCO_3 \downarrow + 2\mathrm{Na}Cl \tag{6}$$

Moreover, the non-carbonate magnesium can be removed by $Ca(OH)_2$ and Na_2CO_3 as follows:

$$MgCl_2 + Ca(OH)_2 \leftrightarrows Mg(OH)_2 \downarrow + CaCl_2 \tag{7}$$

$$CaCl_2 + Na_2CO_3 \leftrightarrows CaCO_3 \downarrow + 2\mathrm{Na}Cl \tag{8}$$

$$MgSO_4 + Ca(OH)_2 \leftrightarrows Mg(OH)_2 \downarrow + CaSO_4 \tag{9}$$

$$CaSO_4 + Na_2CO_3 \leftrightarrows CaCO_3 \downarrow + Na_2SO_4 \tag{10}$$

1.3 Membrane purification overview

Recently, membrane technology has proven to be a promising technology for the treatment of oil sand produced water owing to its compact design and lower operating costs and energy consumption. The pressure-driven membrane processes for water treatment are generally classified as microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), and reverse osmosis (RO). This classification is based on the pore size of the membrane with the MF being the most porous membrane and RO being the densest one (Figure 1.2). As the pore size gets smaller, a higher operating pressure is required for the filtration. NF membranes have a bigger pore size as compare to RO membranes, However, NF and RO are often categorized as the high-pressure filtration processes. UF membranes have a smaller pore size than MF membranes, both considered as a low-pressure filtration processes [29,30].

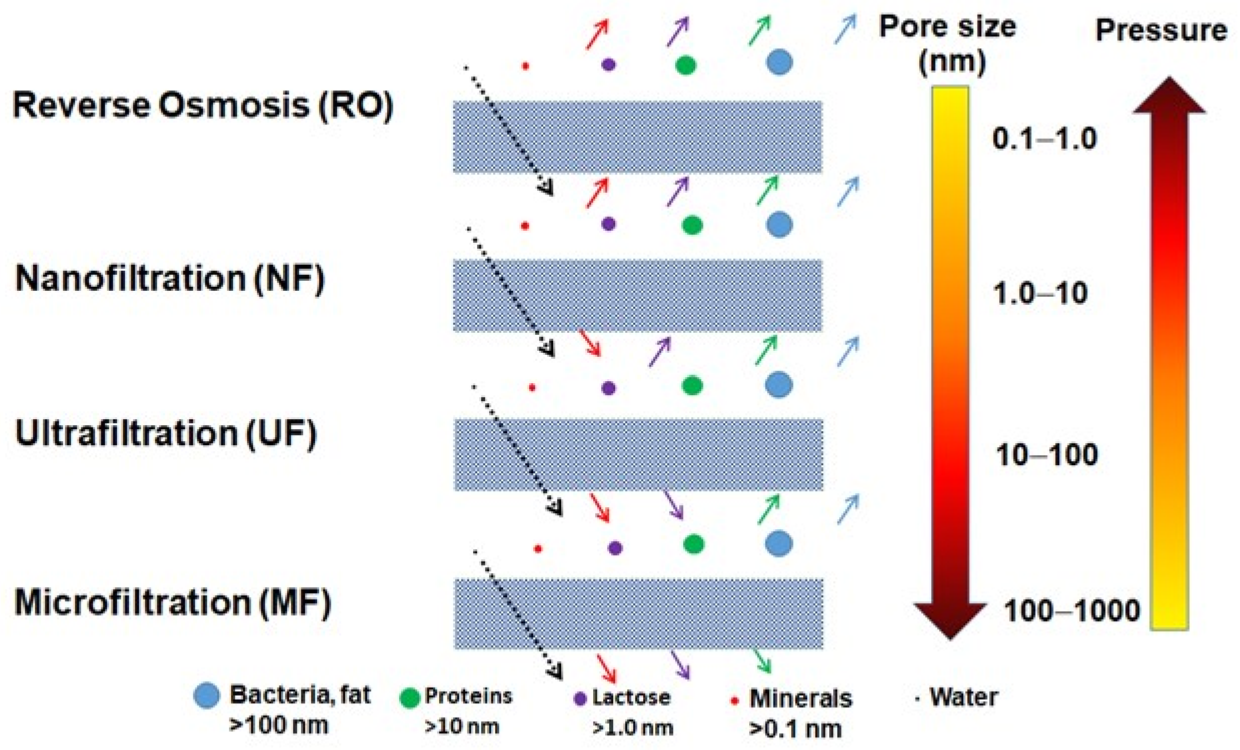


Figure 1.2: Classification of pressure-driven water treatment processes.

NF and RO have been widely applied to provide a higher quality BFW for the OTSG because of their high capability to remove silica, total organic carbon (TOC) and total dissolved solids (TDS) [13,31]. Forward osmosis (FO), as a concentration-driven membrane process, has also been utilized for the treatment of SAGD produced water due its low fouling potential as compared to pressure-driven membrane processes [13,32]. FO uses the high osmotic pressure difference between the wastewater, which is referred to as the feed solution, and a highly concentrated draw by placing a semi-permeable membrane between them. In the FO process, the membrane allows the passage of water molecule from the wastewater to the draw side and prevents the passage of the ions from the one sides of the semi-permeable membrane to the other side [15]. The difference between RO and FO process is shown in Figure 1.3. As can be observed, in the RO process a minimum transmembrane pressure more than osmotic pressure difference is required to filter the wastewater. Hence, MF, UF, NF, and RO are more energy intensive than FO.

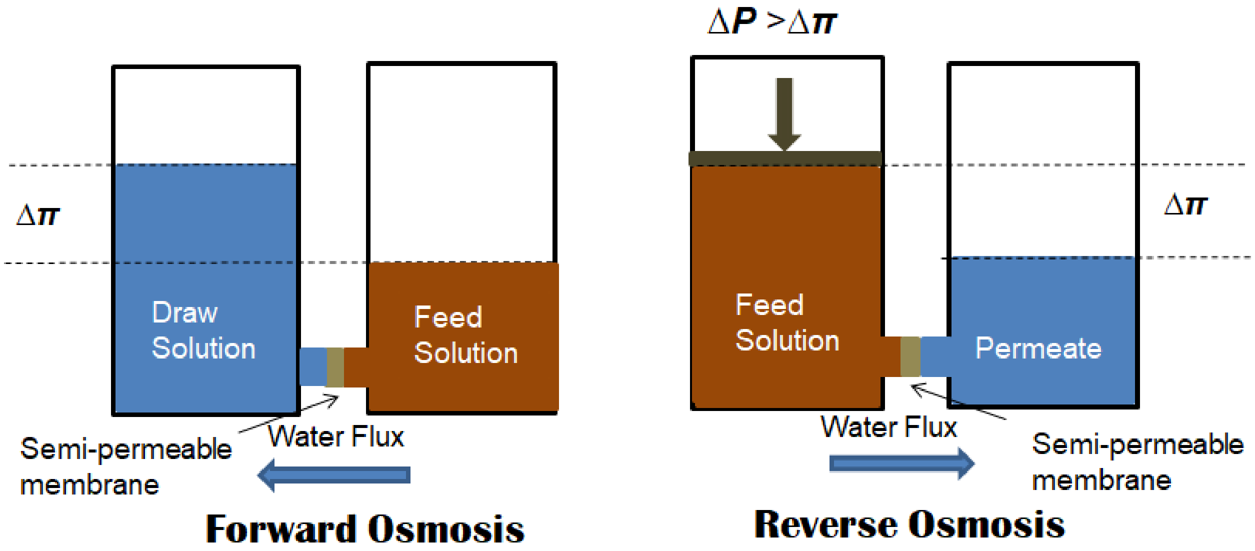


Figure 1.3: FO and RO processes [33].

1.4 Membrane purification in a SAGD plant

Process flow diagram of a typical SAGD operation is shown in Figure 1.4. Silica and hardness are removed by warm lime softener (WLS) and ion exchanger (IX), however, the current treatment scheme do not provide any treatment for organic matter and it even increases the TDS concentration. The current WLS/IX process can be replaced with a single-through membrane process to remove more than 90% of silica, hardness, organic matter, and salt. However, high concentration of salt and foulant materials in SAGD produced water results in a concentration polarization phenomenon and fouling, respectively, that consequently reduces the water flux and rejection of contaminants.

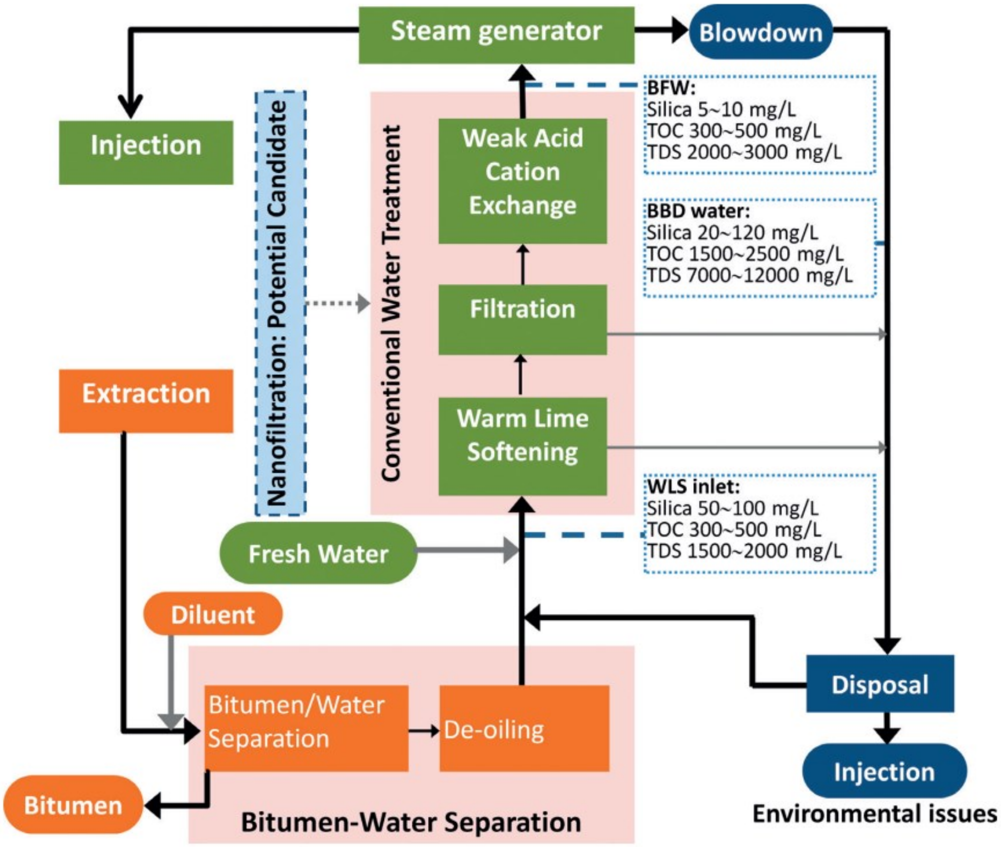


Figure 1.4: Flow diagram of the water treatment section in a SAGD plant [34].

In the membrane filtration, high salinity of feed solution (e.g., BBD water in SAGD) can increase the osmotic pressure difference between the feed and permeate side leading to a decrease in the flux due to the effect of concentration polarization [35,36]. Furthermore, the BBD water contains a high concentration of dissolved solids making the treatment of this water with the membrane very challenging due to the fouling and scaling by silica and organic matter [12–16,26,37].

Membrane fouling occurs by the attachment of water contaminants on the surface and within the pores of the membrane, which can lower the efficiency of the membrane filtration by decreasing the permeate flux and separation performance. Membrane fouling is generally categorized as the colloidal, organic, biofouling and inorganic fouling. Colloidal fouling lowers the water transport through the membranes by the deposition of the large particles on their surface and forming a cake layer. The presence of oil or humic acid in the wastewater can lead to organic fouling. Biofouling occurs due to the accumulation of the microbiological and microorganism on the membrane surface. Inorganic fouling or scaling happens due to the precipitation of the inorganic salts such as calcium, magnesium and silica compounds on the membrane surface. Given the adverse effect of all these types of fouling, many efforts have been made to mitigate fouling before the filtration process (e.g., improving membrane properties and pre-treatment of feed water), during the filtration process (e.g., optimization of operating condition and pulsation techniques), and after the filtration process (physical and chemical cleaning methods). The focus of this thesis is on the pre-treatment of SAGD produced water by chemical methods to reduce the concentration of foulants down to a reasonable level and thus decrease the fouling propensity of membranes.

Among all membrane processes, NF has attracted significant attention for the treatment of SAGD produced water. The main reason is that the NF process is capable of achieving a high removal of organic matter and divalent ions, such as calcium and magnesium ions, by consuming less energy compared to the RO process [38,39]. BBD treatment using NF has demonstrated up to 75% organic and TDS rejection with 10 - 15% flux decline [1]. Hayatbakhsh et al. [31] showed that using a tight NF for the treatment of a SAGD produced water (WLS feed water) provides a high silica, TDS and organic removal (>90%). They used pH adjustment to mitigate the fouling during operation and reported a significant effect of pH swinging on the flux recovery. Furthermore, Sadrzadeh et al. [13] proved the successful application of the NF in the treatment of another stream of a SAGD plant (BFW) and explored the fouling behaviour of membranes by characterizing the fouled membranes. Al-Shammiri studied the removal of $CaSO_4$ and $CaCO_3$ using NF at different experimental conditions. It was proved that a higher flux could be achieved by lowering the pH of the feed stream for the NF process. It has also been proved that applying a higher transmembrane pressure could increase the scaling of membranes [40]. Given that, in the present study, we mainly focus on NF for the integration of a chemical treatment method with a membrane process.

1.5 Membrane filtration with chemical pre-treatment

In the membrane purification processes, chemical pre-treatment can be applied to increase the efficiency of the membrane filtration. The purpose of the chemical pre-treatment is to reduce the concentration of contaminants in the wastewater that are responsible for membrane fouling. Coagulation-flocculation has proven to be an effective chemical pre-treatment for the membrane separation processes. The effect of coagulation on the membrane process performance by removing the colloidal particle, organic matter, and suspended solids before membrane filtration was studied [41]. Organic salts can cause severe scaling on the membrane surface. To resolve this issue, soda ash, lime and caustic can be used as the coagulant to remove these salts from the wastewater. According to chemical reactions 1-10, using lime and caustic, calcium and magnesium ions are removed, but this results in an increase in the sodium concentration in the water. Gilron et al. [42] studied the effect of softening prior to the RO treatment. It was observed that the chemical softening combined with the RO resulted in a higher water recovery as compared to a single RO process. Overall, the chemical pre-treatment of wastewater has been demonstrated to be advantageous for the integrated membrane process regarding an improvement in water flux and fouling mitigation.

1.6 Research objectives

The main objective of this thesis is to develop an efficient method for the treatment of the BBD water of a SAGD plant. These objectives are accomplished through the following activities:

(i) Examining the utilization of the IERW as a coagulant for the treatment of BBD water. The IERW waste was added to BBD water at different ratios, stirring speed and temperatures to obtain the optimum condition for the coagulation process. The treated water using IERW conditioning was analyzed to find out the advantageous and disadvantageous of this treatment method. The produced sludge was characterized using different techniques to asses its potential to be reused as an industrial by-product. The application of IERW for treatment of BBD streams of other plants, with a relatively higher concentration of organic matter and silica, was also investigated.

(ii) Proposing different membrane-based separation methods for the treatment of the BBD water. Based on the features of the IERW conditioning, membrane filtration was applied with different combinations to treat the BBD. One of the approaches was using the IERW for the pre-treatment of BBD and reduce the silica and organic concentrations, followed by an NF process to reduce the TDS of the solution. The other method involved direct treatment of the BBD water with an NF process to remove silica, organic matter and other dissolved solids. This filtration was conducted at 50% water recovery ratio followed by conditioning the concentrated retentate with IERW and then using another NF as the final treatment. The possibility of using IERW as the draw solution of an FO process was evaluated by using the BBD water as the feed solution. FO process was then integrated with an NF process to treat the diluted draw. Finally, the flux and fouling behaviour of all these scenarios were compared to recommend the best alternative to the conventional WLS/IX method for the treatment of the BBD water.

1.7 Overview of the thesis

This thesis includes four chapters and it is written in a paper-based format. In the first chapter, the problem has been stated, different potential pre-treatment methods of SAGD produced water are explained, and the main pressure-driven membrane processes (MF, UF, NF, and RO), as well as concentration-driven FO are provide. Finally, the objective of this thesis is provided.

The second chapter describes the application of using the IERW as a coagulant for the treatment of the BBD water. Different experimental parameters were studied to propose an optimized condition for the treatment of BBD water. The possibility of using the produced sludge from the coagulation-flocculation process as an industrial by-product was studied. Finally, the IERW was used for the treatment of another produced water in a SAGD operation to prove its applicability for other streams.

The third chapter comprises of different membrane-based processes for the purification of the BBD water. In this section, different filtration methods are compared considering the permeate flux and the fouling characteristic. Finally, the most efficient method is recommended based on the flux recovery and total flux decline during filtration.

In the last chapter, major findings of this research have been summarized. In addition, based on the outcome of this work, recommendations are provided for the further trend in SAGD produced water treatment,

Chapter 2

2 Efficient Treatment of Oil Sands Produced Water: Process Integration Using Ion Exchange Regeneration Waste as a Chemical Coagulant*

* This chapter is submitted for publication to "Separation and Purification Technology", November 2018.

2.1 Introduction

SAGD technology is considered a practical process to recover bitumen from oil sands reservoirs [1–4]. The SAGD process uses two parallel horizontal wells, which are drilled above each other deep underground into the oil sand reservoir. To increase the temperature and thus reduce the viscosity of the bitumen, steam is injected through the upper well and the low viscous drained bitumen collected into the lower well as a mixture to be pumped to the surface for bitumen extraction. This process requires a high volume of fresh water, and currently about 80% of the BFW is coming from the recycled oil sands affected water.

Recently, significant attention has been given to water treatment methods of SAGD plants since a poor quality feed for the steam generator will lower the efficiency of the boiler, BFW purity should be at an acceptable level. In SAGD industry, OTSG are widely used to generate steam. To provide feed water for OTSG, water treatment processes should reduce silica and hardness concentration to <50 mg/L and <1 mg/L, respectively. Also, the BFW should have TDS and oil content, lower than 7000 mg/L and 0.5 mg/L [1,5,6]. Ion exchange regeneration treatment is a commonly used method to remove hardness from the BFW by replacing the calcium and magnesium ions with sodium ions [43]. In this process, a concentrated sodium chloride solution regenerates the ion exchanger. The purpose of the regeneration is to replace the calcium and magnesium ions, which were removed from the wastewater and retained in the ion exchanger, with sodium ions and return the resin to its original state. Therefore this process results in wastewater with a high concentration of sodium, calcium, and magnesium (which is called the IERW) [44,45]. After removing hardness, the treated water is guided to the boiler, and the IERW is moved to the disposal system. The OTSG steam generation process typically produces 80% steam quality resulting in a concentrated solution, which is known as boiler blowdown (BBD). The impurity concentration of BBD water is much higher than the BFW. In a typical SAGD plant, an amount of the BBD water is recycled back to the water treatment section, and the rest is partially directed to the system [2]. In conventional approaches, BBD water can be treated for reuse with the help of membrane filtrations, evaporation, chemical and biological treatment techniques. Previous research has shown that the concentration of contaminants in the BBD is higher than in other types of wastewater in a SAGD plant. Membrane filtration is an effective method to treat the BBD water due to its high TDS, organic matter and silica removal efficiency [1,13,14] and Fenton's oxidation and acidification are effective for the removal of silica and organic matter from this wastewater [3]. However, these methods increase the capital cost and energy consumption of the SAGD plant and can result in significant waste [1]. What's more, the use of water treatment applications for the reuse of BBD demands specialized and expensive equipment. Therefore, it is highly beneficial to use inexpensive but efficient technology to treat the BBD water.

In conventional water treatment plants, flocculation is an essential technique to separate impurities from contaminated water solutions [14,17]. In this process, colloidal particles are destabilized and adsorbed by a coagulant. These particles then form large flocs that can be removed via sedimentation and filtration [18]. At present, various types of coagulants (such as lime, soda ash, caustic) are used in wastewater plants to improve the efficiency of the chemical process [24]. Previous studies reported the successful use of magnesium at high pH for achieving a high removal efficiency of unwanted contaminants from wastewater [17,19–25]. Magnesium appeared to be an effective coagulant in the reduction of silica from the heavy oil wastewater [46]. Silica removal using magnesium substances also proved to be useful as a pre-treatment for filtration processes [22]. The usage of magnesium and calcium for production of Chlorella vulgaris was also studied. One of the low cost techniques to remove and harvest microalgae is flocculation [47]. It was seen that microalgae could be concentrated through flocculation at high pH due to precipitation of magnesium [19]. The influence of magnesium hydroxide in the separation of organic matter from wastewater was also investigated. It was demonstrated that organic matter removal of wastewater could be improved by increasing the concentration of magnesium hydroxide [20]. In the oxidation pond effluents, it was observed the removal of algae with coagulant using magnesium ions was more effective by increasing the pH [21].

At a high pH, magnesium precipitates as magnesium hydroxide according to the following reaction [24]:

$$Mg^{2+} + 2OH^{-} \leftrightarrows Mg(OH)_2 \downarrow \tag{2.1}$$

The resulting magnesium hydroxide that carries positive charges acts as an effective coagulant by charge neutralization; and, according to DLVO theory, this substance can remove negatively charged organic matters and silica particles [48]. The DLVO theory explains the stability of colloidal particles as a balance between the electrostatic repulsion due to the surface charges and van der Waal's interaction of the colloids in the suspension. [49]. Coagulation can happen when the mean of the electrostatic repulsion is weaker than the attraction forces and the balance shifts in favor of attraction [19]. In the water treatment, adsorption occurs when the attraction force between the solid and the impurity ion is stronger than the attraction force of the water and the unwanted solute [50,51]. What's more, calcium carbonate can be removed by adsorption to the magnesium hydroxide floc [19,24]. Thus, the active surface of the magnesium hydroxide can attract organic matter, calcium carbonate, and silicate through adsorption [46].

Rapid-settling floc particles can be optimized by controlling different parameters such as temperature, mixing intensity and dose of coagulant, to increase the stability and particle size of the formed flocs [25,52–54]. It was observed that between two flocs with the same density, the smaller floc is less likely to settle down [53]. Based on this differential settling, the large and dense aggregate particle can grow when they move past the smaller particles [55,56]. Moreover, it has been shown that forming a compact aggregate will be useful in the water treatment applications involving sedimentation [52].

Although extensive research has been carried out using chemical coagulants to treat the BBD water, the majority of those coagulants are not environmentally friendly and require a high dosage of coagulants. Furthermore, usage of chemical additives may overload the water treatment system and increase the operating resources and costs. Therefore, if a waste stream in the SAGD plant can be used as a coagulant, this will lead to a more cost and energy effective process for BBD treatment. Therefore, the major objective of this study is to investigate the feasibility of using the currently unusable IERW as the coagulant to treat the BBD water under different treatment conditions. This waste contains a high concentration of magnesium and calcium that can act as an effective coagulant. A full factorial design was applied to study the contribution of temperature, the ratio of IERW to BBD and mixing intensity on the outcome of the treatment; the level of these control factors was selected based on the feasibility of these conditions in a SAGD plant. Another important aspect of using IERW as the coagulant is that by applying this method of treatment, the extra cost and energy for the disposal of both IERW and BBD water can be reduced. Finally, the chemical composition of the resulting sludge from this water treatment process was analyzed to explore the feasibility of resource recovery.

2.2 Materials and methods

BBD water and IERW samples were provided by EXEN Pro Ltd. through collection and delivery by Black Pearl Resources Inc., located in Calgary. The IERW was used as a coagulant to treat the BBD. The characteristics of BBD water and IERW are presented in Table 2.1.

Table 2.1: The properties of BBD water and IERW at room temperature.

Parameter	**Unit**	**IERW**	**BBD**	**BBD reported in literature** [1,2]
TDS	ppm	66625±375	6525±25	4026-17200
pH	-	6.20±0.11	11.66±0.01	10.5-12.33
Turbidity	NTU	0.25±0.05	0.86±0.06	0.2-53
UV absorbance at 254 nm	-	0.07±0.01	0.72±0.04	0.55-0.87
$SUVA_{254}$	-	1.04±0.15	0.77±0.08	2.75-5.21
TOC	ppm	6.71±0.07	92.12±0.11	695-2482
Silica	ppm	5.22±0.48	77.6±1.5	65-238
Magnesium	ppm	2201±351	0.24±0.03	0.68-0.08
Calcium	ppm	9455±1059	2.97±2.59	4.25-4.8
Sodium	ppm	22165±3244	1806±130	819-5199
Chloride	ppm	80650± 4203	40±6	494-6715

2.2.1 Design of experiments

A full factorial design was employed in this process to analyze the treatment of BBD water by varying three control factors. STATISTICA software was used for the experimental design and data analysis. This design consists of three dependent variables and two levels. In addition, one replication was done to minimize variability in the experimental results. The control factors and the selected levels for this design are provided in Table 2.2. These control factors were chosen based on the common industrial practices to treat the wastewaters using chemical coagulant. For all of the experiments, the mixing (coagulation) and precipitation time were 30 minutes.

Table 2.2: Full factorial design factors and levels.

Factors	Unit	Levels	
		-1	1
IERW to BBD ratio	Volumetric ratio (IERW:BBD)	1:12	2:12
Temperature	°C	40	80
The speed of the stirring	rpm	0	60

According to the experimental design, the total number of runs was 16 experiments with one replication. This approach is useful to understand the significant factors and the interaction effects between the variables. For all of the experiment, the response variables considered were turbidity, ultraviolet (UV) absorbance at 254 nm, silica concentration and TOC. The blocking was applied using the same batch of BBD and IERW for all experiments. The different experimental runs based on this design are presented in Table 2.3.

Table 2.3: Different experimental runs based on the design of the experiments.

Run	Level of design factors		
	Temperature	Speed	Dose
1	-1	-1	-1
2	-1	-1	1
3	-1	1	-1
4	-1	1	1
5	1	-1	-1
6	1	-1	1
7	1	1	-1

8	1	1	1

2.2.2 Batch test procedure

Jar tests were performed with a total volume of 1 L for the IERW coagulant and BBD water. The IERW to BBD ratios were adjusted to 1:12 or 2:12, and the solution temperature was set to the 40 °C or 80 °C as stated in Table 2.2. Two mixing methods were used for this treatment, including the 30 minutes of mixing at 60 rpm with a magnetic stirrer and no mixing, which involved simply pouring both solutions into the 1 L beaker. This procedure was followed by emptying the mixture solution into a 1 L graduated cylinder and placing it in an oven to keep the solution at the desired temperature. The solution was then allowed to settle for 30 minutes. Finally, samples were taken from the supernatant and slurry phase for characterization.

2.2.3 Characterization of wastewater and sludge samples

An inductively coupled plasma optical emission spectroscopy (ICP-OES) was used to determine the concentration of silica, calcium, sodium, and magnesium. Dissolved organic matter (DOC) was analyzed as TOC and was measured with the non-purge able organic carbon method using the Shimadzu TOC-VCSH analyzer. UV absorbance was measured using a Hach DR 5000 spectrophotometer. Turbidity and pH were analyzed using a turbidity meter, (expressed in nephelometric turbidity unit (NTU)), and pH meter, respectively. Field emission scanning electron microscopy (FESEM, Zeiss Sigma 300 VP) was used to observe sludge samples after precipitation. The elemental compositions of the precipitated solids were evaluated using energy-dispersive X-ray spectroscopy (EDXS), X-ray photoelectron spectroscopy (XPS, Kratos AXIS ULTRA spectrometer) and X-ray powder diffraction (XRD, Rigaku Ultima IV X-ray diffractometer) methods. The chemical functional groups present in the produced sludge were analyzed by diffuse reflectance infrared Fourier transform (DRIFT) spectroscopy. Ion chromatography (IC, DIONEX

ICS-3000 ion chromatography system) was employed to identify major anions. The Zetasizer Nano Z system was used for the zeta potential measurement.

2.3 Results and discussion

2.3.1 Experimental raw data

Figure 2.1 shows the mixture solutions of the BBD water and IERW after 30 minutes of precipitation for run 1 and 8. As it can be seen in this figure, the water recovery of the run 8 resulted 80% percent, which is higher than 65% water recovery of the run 1. In addition, it is evident that the number of suspended solids in the run number 8 is significantly lower than the first run indicating the formation of larger and more compact flocs in the run 8; this can be attributed to a more efficient separation process.

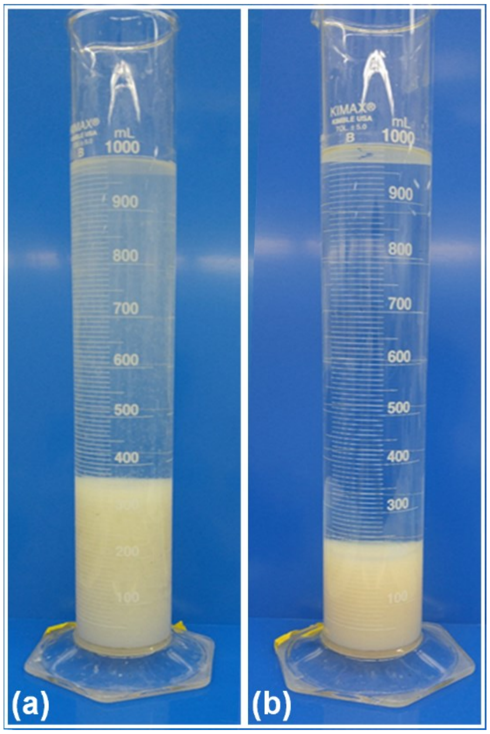


Figure 2.1: Pictures were taken from the one (a) and eight (b) run indicating the effect of control factors based on different water quality and recovery.

Different values of silica concentration and TOC for all of the experimental runs are depicted in Figure 2.2. Based on this figure, the TOC and silica concentration of supernatant phase were reduced significantly after 30 minutes of precipitation. The silica concentration varied from 0.43 to 1.6 ppm under different experimental conditions; thus, silica concentration was at an acceptable range after the treatments. The TOC concertation was in the range of 15.46 to 19.68 ppm. The mean value of all of the experimental runs for silica concentration and TOC was 1.07 ppm (with a standard deviation of 0.47) and 17.20 ppm (with a standard deviation of 1.13), respectively.

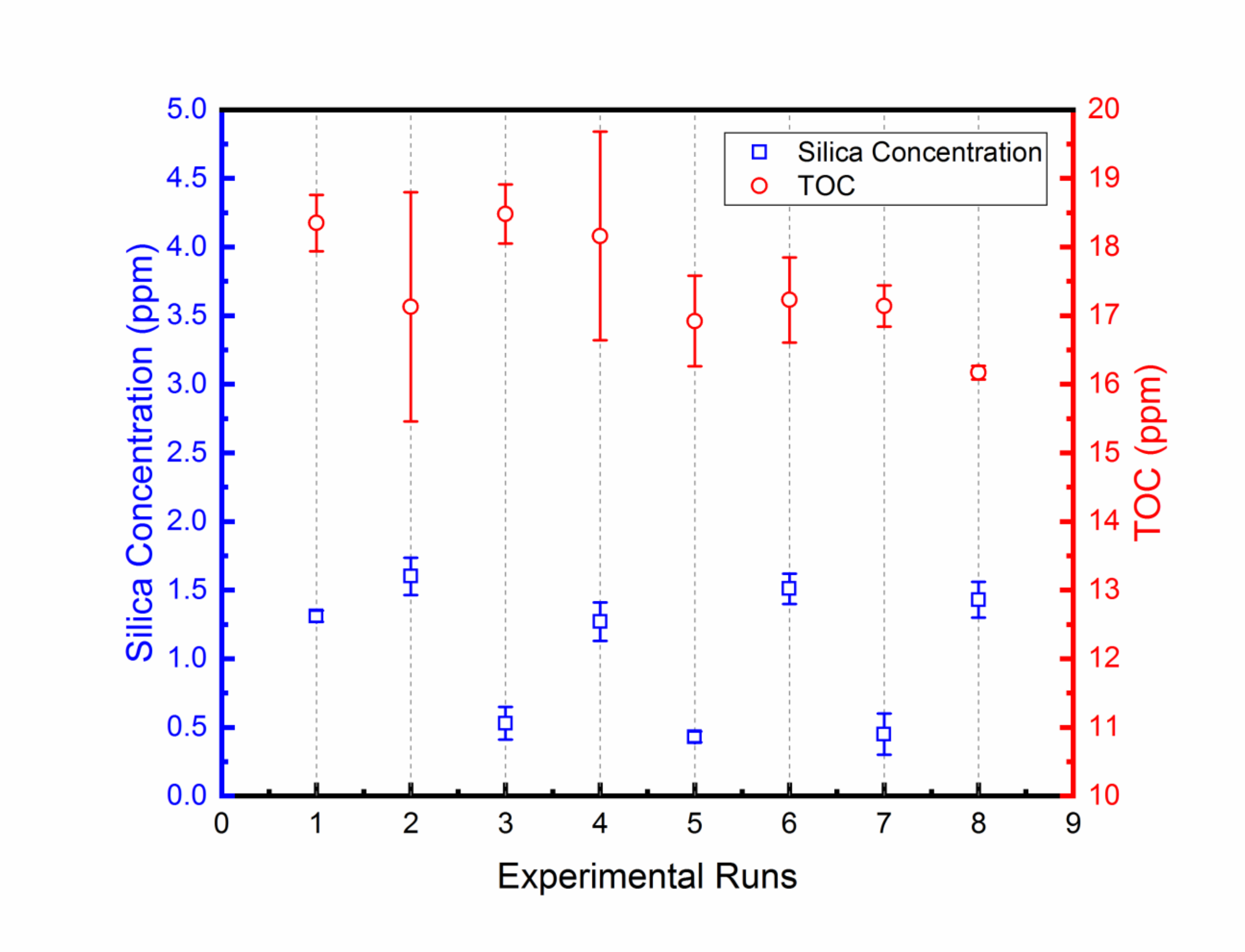


Figure 2.2: Silica concentration and TOC values for all of the experimental trials.

According to Figure 2.2, the silica concentration and TOC values showed a high removal with low variation in the different operating conditions. However, these results demonstrated that all of the experimental trials of this treatment could bring the concentration of silica and organic matter of treated BBD to a standard level minimizing or preventing equipment fouling in the BBD treatment and water recovery process [57].

The UV absorbance of the water solution at 254 nm (UV_{254}) for all eight experiments is presented in Figure 2.3. As can be seen in this figure, the UV absorbance values changed from 0.4 to 0.46. The mean value of all of the experimental runs for UV_{254} was 0.43 (with a standard deviation of 0.02).

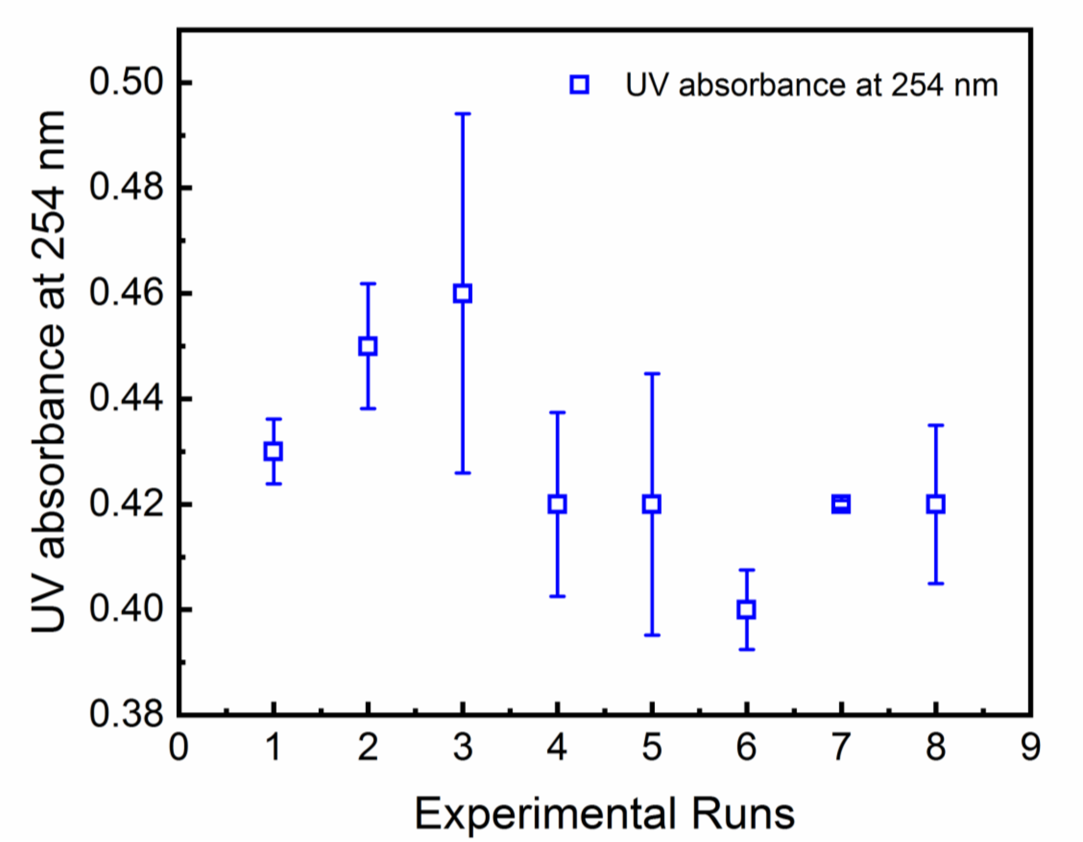


Figure 2.3: UV absorbance value for different experimental runs.

Figure 2.4 presents removal percentage of UV_{254} for different experimental runs after the IERW treatment. As illustrated in Figure 2.4, the removal percentage of UV_{254} varied from 36.38% to 45.83%. In addition, the average UV_{254} for these runs was 0.43, which is lower compared to the UV_{254} of BBD. The reason for the decrease in the UV absorbance value can be attributed to the organic matter removal from BBD. Hence, the UV absorbance results confirm the TOC removal [58].

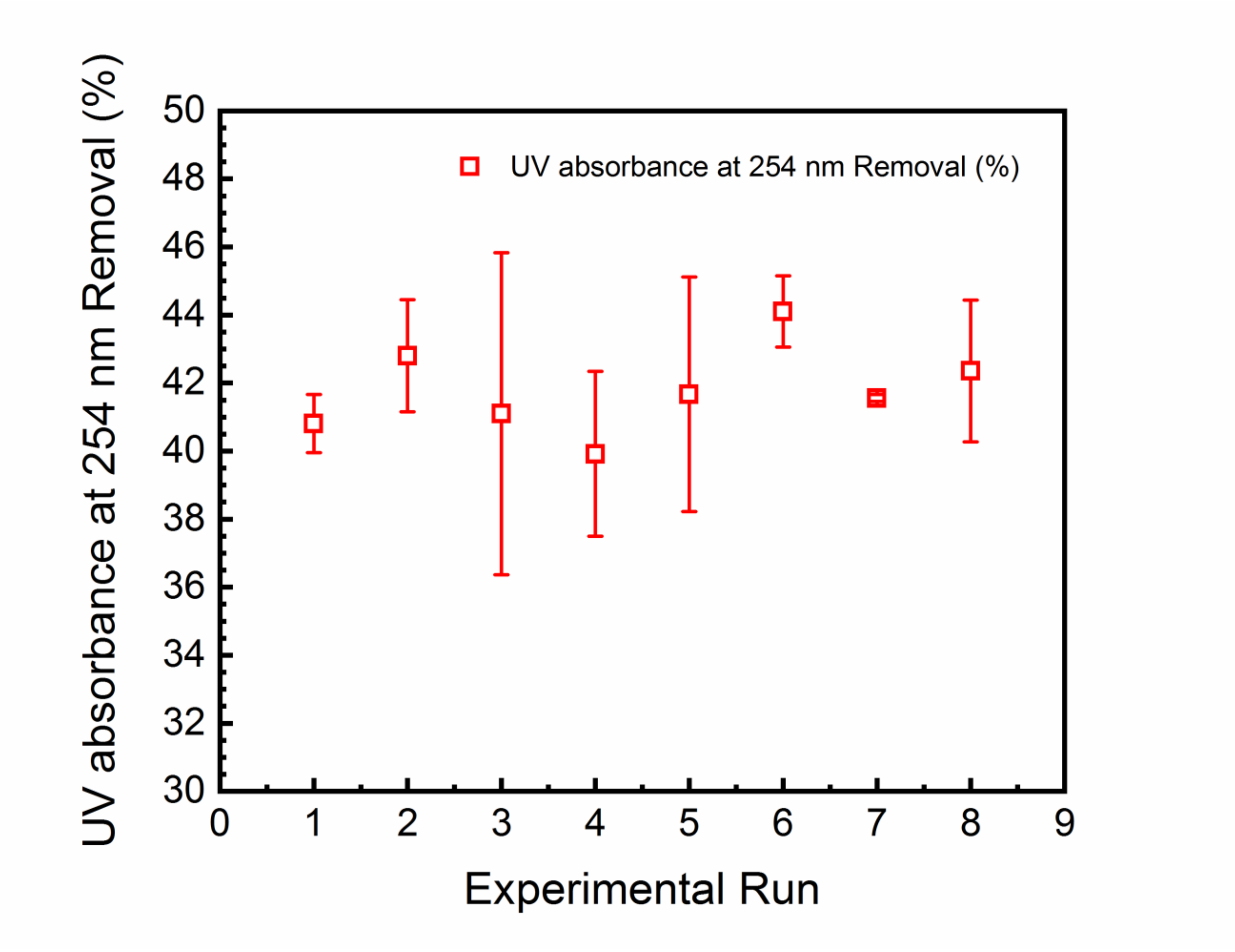


Figure 2.4: Removal percentage of UV absorbance at 254 nm for all of the experimental tests.

2.3.2 Removal efficiency analysis of treated water

Figure 2.5 presents the removal percentage of TOC and silica for different experimental trials after the chemical treatment. Based on this figure, the removal percentage for silica varied from 97.77% to 99.44% and the removal percentage for TOC changed from 78.64% to 83.22%. The removal percentages were obtained by comparing the initial value of the parameters in the BBD to the treated supernatant samples. The mean removal percentage of all eight runs for TOC and silica concentration was 81.06% ± 0.82 and 98.63% ± 0.61, respectively. Therefore, using the IERW for the BBD treatment resulted in a high removal percentage of organic matter and silica concentration for all of the experimental runs. This can be explained by the coagulation-flocculation of silica and organic particles induced by magnesium hydroxide.

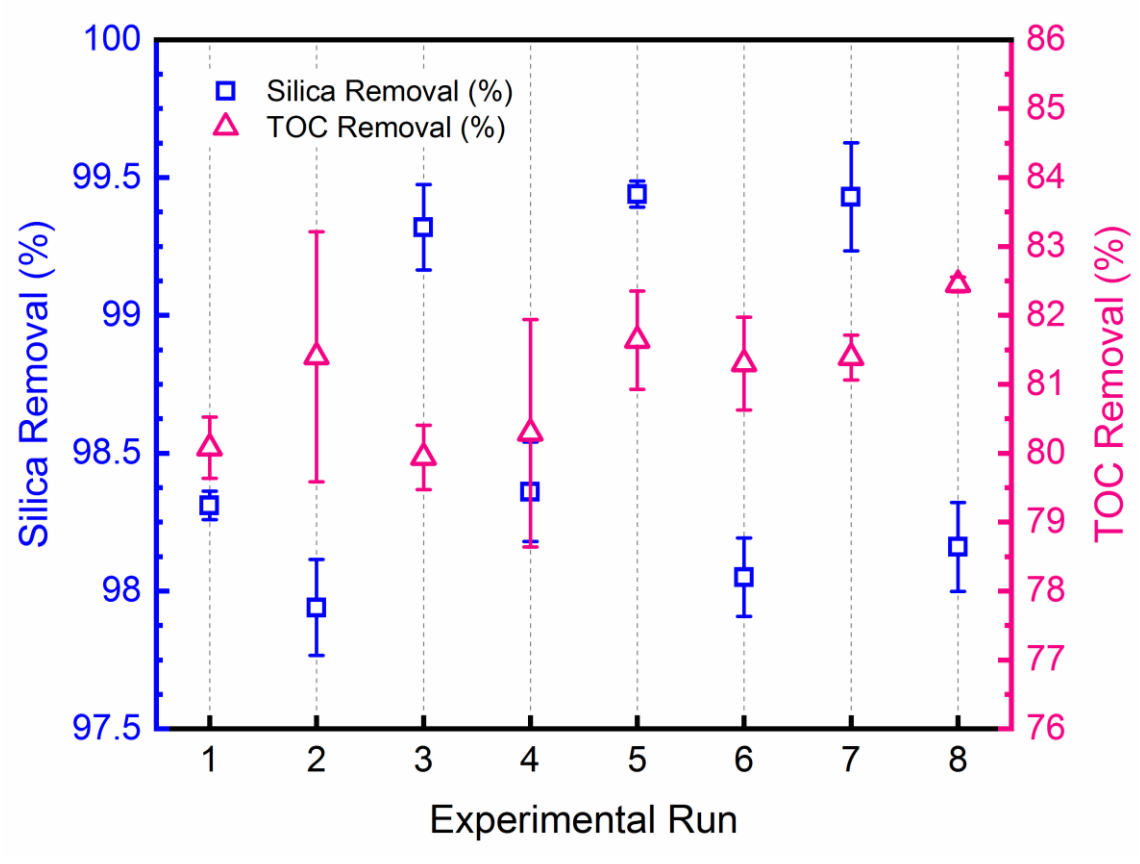


Figure 2.5: Removal percentage of silica and TOC for all of the experimental trials.

According to the DLVO theory, the stability of the particles in a suspension depends on two opposing forces, namely electrostatic repulsion and van der Waals attraction forces. Generally, the stability of a colloidal particle is described when the individual colloid exists as a separate entity. In the case of BBD water, the zeta potential was -14.65 mv (±0.95) which indicates that the organic matters and silica particles have a negative surface charged. Before adding the coagulant, the negatively charged silica and organic molecules are rapidly making contact with each other due to Brownian motion and are continually being repelled by electrostatic repulsion due to their similar surface charge. The electrostatic repulsion of these particles is caused by the overlap of the interacting electrical double layer. The double layer is generally known as the diffused area of counterions near a charged surface or particle. The double layer interaction can fluctuate based on the ionic strength of the suspension. After adding the IERW to the BBD water, the ionic strength increased which resulted in compression of the double layer thickness of suspended materials like silica and different organic matter ions. At higher ionic strength, the attraction forces between these particles became larger and larger flocs were formed [18,59].

Table 2.4 summarizes the properties of the supernatant for all of the experimental runs. It shows that the treated water for all of the experimental trials had high calcium content. However, in the supernatant samples, the concentration of calcium and sodium increased significantly after the treatment. Since the calcium concentration varied based on the IERW dosage, the average concentration of calcium was presented based on the two different dosages of the IERW, 598 and 1102 ppm for the lower and higher dosages of IERW, respectively. Furthermore, the mean concentration of magnesium for all of the supernatants was about 0.85 ppm. It has been reported that a SUVA value higher than 4 implies the dominant presence of aquatic humic compounds. The presence of these humic substances is the indicator of higher hydrophobicity, which can have an adverse effect such as requiring a higher dosage of coagulant in the chemical treatments and causing severe organic fouling in the membrane filtrations [60]. Table 2.4 also shows the SUVA value calculated from the UV absorbance at 254 nm (UV_{254}). As can be seen, the $SUVA_{254}$ value was between 2.26 to 3.07, which suggests the presence of hydrophobic humic and hydrophilic non-humic acid [61]. Thus, the SUVA values of supernatants for all of the experimental runs were in the acceptable range.

Table 2.4 also shows the turbidity values for all of the experimental trials. Turbidity is a term used to determine water quality; this parameter is determined by optical measurement of light, which scatters due to suspended and dissolved particles [62–64]. The turbidity varied from 1.1 to 17.3 NTU for different runs. This result indicates a noticeable change in the results for different conditions indicating a significant effect of the controllable parameters on the turbidity of the treated water. The significance of the different factors is more evident when comparing run 1 and 8 since all of their factor levels are different. This is because after adding the coagulant, the silica and organic matters were removed from dissolved phase, but the formed flocs were not precipitated in the given time and remained suspended in the supernatant phase; the turbidity measurements confirm this explanation.

Table 2.4: Properties of supernatant for all of the experimental trials.

Run	Turbidity (NTU)	Calcium (ppm)	Magnesium (ppm)	$SUVA_{254}$
1	12.90	569	1.46	2.29
2	8.64	574	0.05	2.39
3	5.31	662	0.51	2.27
4	1.47	586	0.16	2.69
5	10.10	1098	0.76	2.65
6	5.73	1080	1.37	3.07
7	3.44	1147	0.88	2.52
8	1.13	1084	1.63	2.54

2.3.3 Statistical analysis

The efficiency of this chemical process was analyzed to find the significant controllable factors. The performance of this treatment was studied using turbidity since the purpose of this process is to remove the suspended solids through sedimentation and filtration [64–68]. The treated water after the flocculation had high turbidity in all of the experimental runs, however the BBD water had low turbidity. It is worth noting that the reason for the low turbidity value of BBD water is probably due to the relatively high concentration of organic matter and the small amount of suspended solids. The general difference between the means of the turbidity values in different experimental conditions can be determined using the analysis of variation (ANOVA). The results of the ANOVA test considering the turbidity as the response variable is presented in Table 2.5. In this analysis, a probability value (p-value) indicate the significance of the design factors on the response variable (turbidity). This ANOVA table was obtained with a 95% confidence level so in this experiment; a design factor with a p-value lower than 0.05 will have a significant contribution to the outcome of the experiment [69]. In this table, the sum of square (SS) is the variation in the observed result for each factor and the degrees of freedom (DOF) represents the number of values that have the freedom to vary in a statistical study. The mean square can be calculated by the sum of the square over the degree of freedom. The F-value is the mean square of measurements divided by the mean square of the residual. It should be noted that a larger F-value indicates that the factor has a relevant effect on the experiment. For this experiment, the minimum F-value indicating the significant factors is 6.59; this value was found from the F-distribution table. Therefore based on the p-value and F-value, this statistical analysis indicates that all of the controllable factors are significant. Moreover, the p-values and F-values state that the mixing intensity is the most significant factor as it has the lowest p-value and has the highest effect on turbidity. These results also indicated that the temperature had a higher effect on the turbidity compared to the dose of the IERW coagulant [70,71].

Table 2.5: ANOVA table of control factors for turbidity.

Factors (symbol)	ANOVA-Turbidity				
	SS	DOF	Mean square	F-value	P-value
Temperature (A)	27.3060	1	27.3060	37.8161	0.003547
Speed of stirring (B)	84.6001	1	84.6001	117.2040	0.000413
Dose of IERW (C)	7.8408	1	7.8408	10.8587	0.030067
Residual	2.8883	4	0.7221	-	-

The variance of turbidity based on different factor levels can be investigated with mean plot. The effect of temperature on the mean plot of turbidity is illustrated in Figure 2.6. It was found that by increasing the temperature from 40 °C to 80 °C, the turbidity value of supernatant decreased from 7.94 NTU to 4.24 NTU. This behavior can be attributed to the fact that by increasing the temperature, the size of the flocs can become larger which leads to the precipitation of the aggregated particles. In previous studies, a similar trend was observed where it was seen that at higher temperatures, the removal efficiency of silica from heavy oil wastewater was improved [46]. It was also demonstrated that the aggregation in the lower temperature could result in a higher breakage and lower re-growth of the flocs [72,73].

The influence of coagulant dosage on turbidity removal was investigated by using two different levels of dosage; the results are depicted as a mean plot in Figure 2.6. These results indicate that there was a decrease in turbidity value when the dosage increased, resulting in a supernatant with lower turbidity which indicates a more efficient treatment. This trend is expected since increasing the dosage of coagulant will provide more magnesium ions to form insoluble magnesium hydroxide resulting in an improved aggregation process, which can remove more negatively charged ions by neutralization and adsorption improving the flocculation [19–24].

Figure 2.6 also shows the coagulation performance of IERW under different mixing conditions using a mean plot. As can be seen in this figure, the mixing had a significant influence on the supernatant properties. After applying the mixing, the turbidity decreased from 9.34 to 2.84 NTU. This result confirms that mixing intensity can be used to improve the removal percentage of suspended solids by affecting the strength and size of the aggregated particles that are being formed due to flocculation.

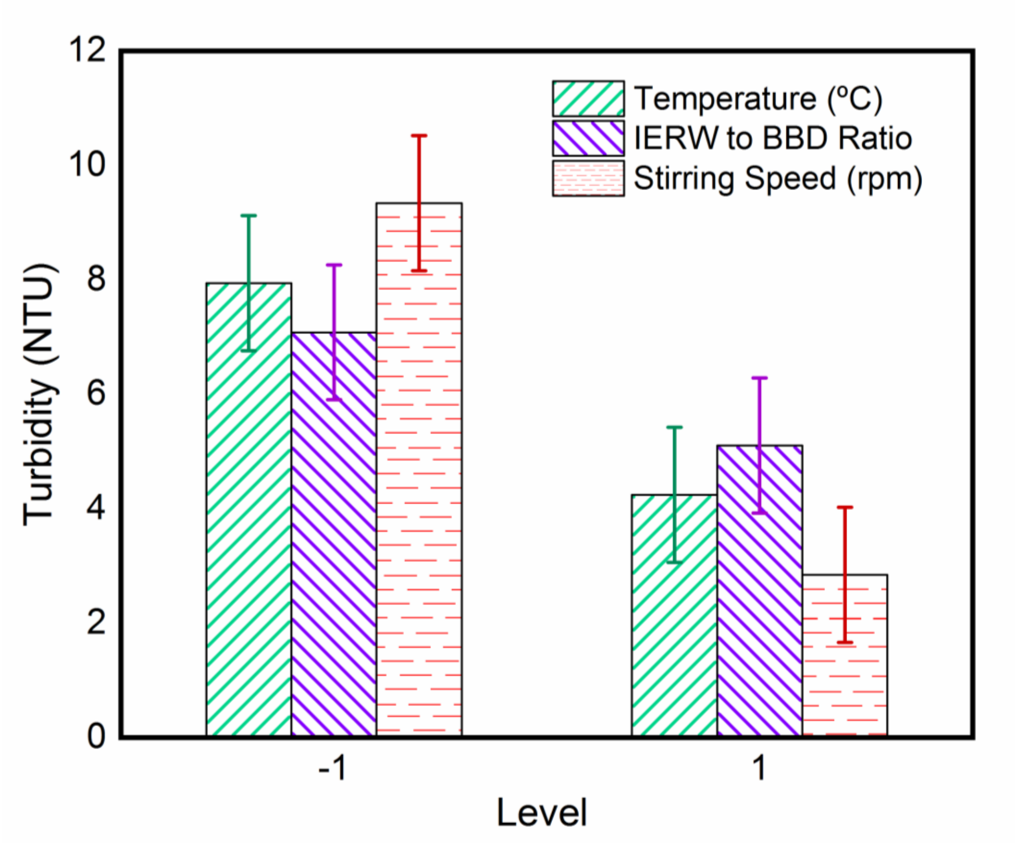


Figure 2.6: The mean plot of temperature, IERW to BBD ratio and mixing intensity for the turbidity.

It can be concluded that mixing can remove more contaminants through sedimentation by allowing larger flocs to be formed [52]. Therefore, mixing the solutions enhanced the adsorption and charge neutralization process. It should be noted that the mixing intensity must be at a proper range. Furthermore, a very high or low stirring speed can have an adverse effect on the flocs properties. For example, a high mixing intensity can result in breakage of the floc into clusters [74].

Based on the variation of the turbidity and the design factors, the optimized level for each parameter can be estimated. For temperature, removal efficiency was highest at 80 °C, and the removal was higher when the IERW and BBD water were mixed for 30 minutes at 60 rpm. Furthermore, increasing the dose improved the flocculation and precipitation so 2:12 volume ratio is recommended coagulant dose to achieve better water quality.

From the regression coefficients, the regression model of the process was obtained to study the functional relationship between factors and response variables, and to find the optimized condition for this process. This model can be written as follows:

$$Turbidity = -1.85A - 3.25B - 0.99C \tag{2.2}$$

Where A, B and C represent temperature, mixing intensity, and IERW to BBD ratio, respectively. The relationship and significance of each variable can also be observed in this model. This equation shows more precisely that mixing had the highest effect on the turbidity of the supernatant. Based on the regression model of turbidity, the optimum experimental condition can be achieved by using the higher factor level. Therefore, the supernatant sample of run 8, which was completed at the highest factor levels, showed the most suitable water quality.

2.3.4 Sludge characterization

The treatment of BBD with IERW lead to coagulation followed by sludge formation and water recovery. The physicochemical characterization of the precipitated flocs was further performed to explore resources recovery from the sludge waste. A mass balance was conducted to investigate the removal percentage of different elements in the sedimentation process. The total input and output mass of calcium, magnesium, silica and sodium from run 8 are given in Table 2.6. The samples were prepared by evaporating the slurry phase of the run 8. The water recovery of this run was 80 % and the wet cake sample showed a total dry solid concentration of 9 %. The observed silica removal in Table 2.6 is in agreement with the silica removal observed in Figure 2.5. This table also confirms that the formation of flocs is due to neutralization and adsorption of negative charged particles such as silica and calcium carbonate to the surface charge of the magnesium hydroxide.

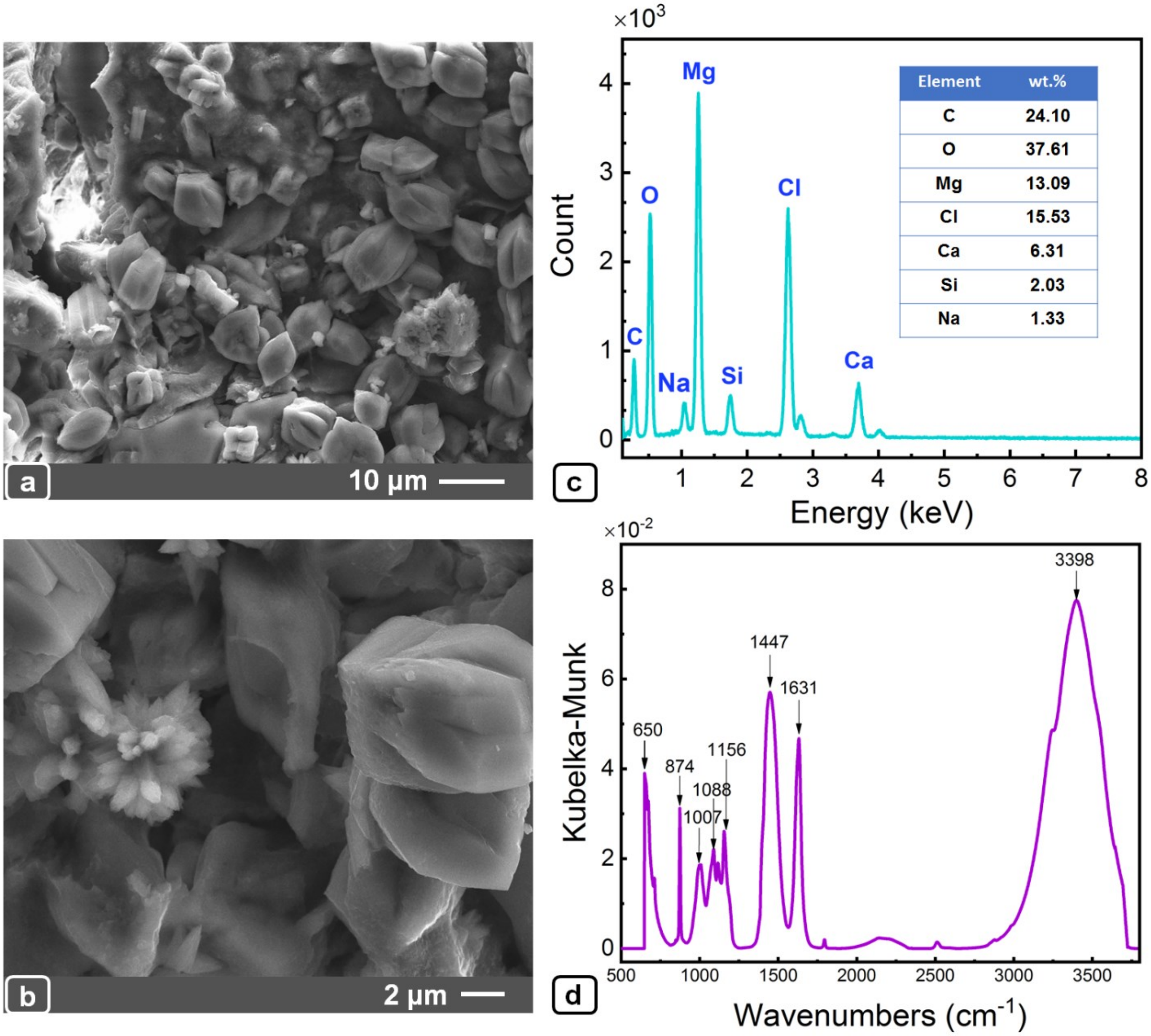
Table 2.6: The input and output concentration of dissolved ions before and after the coagulation-flocculation process from the run 8. The total solid mass of these ions was theoretically calculated by subtracting the total mass of the input (the IERW and BBD) from the output of the treatment (supernatant) and was compared to the total mass of the initial input solutions to obtain the removal percentage (See Appendix A for the Calculations) .

Parameter	Input		Output		Removal percentage (%)
	IERW (ppm)	BBD (ppm)	Supernatant (ppm)	Slurry (ppm)	
Calcium	9455	4.47	1084	1122	19.58
Magnesium	2201	0.24	1.29	6.06	99.34
Silica	4.74	77.60	1	0.14	98.69
Sodium	22165	1806	4397	4057	8.19

The produced sludge after IERW treatment was analyzed using SEM, EDX, FTIR, XPS and XRD techniques. SEM and EDX analyses show the morphology and composition of the sludge residue (Figure 8 (a), (b) and (c)). The SEM micrographs show continuous amorphous phase with the semi-crystalline domain, and an average size of the particles, which was about 5 µm. The elemental composition of the sludge was obtained from the EDX analysis include Ca, Mg, Cl, Si Na, O and C. It was demonstrated that the concentration of Mg and Ca was high in the precipitated solids. This result shows that particles were entrapped by magnesium due to flocculation mechanism, which confirms the silica and organic matter removal by using the IERW as the coagulant [75–78].

In order to identify the major chemical species and functional groups present in the sludge, FTIR analysis of the solid precipitates were performed which is demonstrated in Figure 2.7 (d). The peak at 1007 cm^{-1} can be attributed to the Si-O band and the peaks from 1156-1200 cm^{-1} can be assigned to silica bonding. The 1631 cm^{-1}, 650 cm^{-1} and 3398 cm^{-1} bands can be the characteristics of bending vibration of O-H. The 874 cm^{-1} peak observed at the low-frequency region can represent Mg-O vibration. According to literature, peak at 1447 cm^{-1} with high intensity can be due to the presence of CO_3^{2-} [22,79,80]. Therefore, FTIR data are in agreement with EDX results suggesting the existence of Mg, Ca and Si in the precipitated sludge.

To further investigate the elemental composition of the precipitated sludge and their ionic state, XPS analysis was performed. Figure 2.8 shows the XPS survey spectrum of the precipitated sludge and the high-resolution spectra of Ca 2p and Mg 2p. The peaks in the survey spectrum were assigned to Ca, Mg, Si, Na, Cl, O, S, and C in the solid sample. The peak at 167.3 eV in the survey indicate oxygenated sulfur species, possibly $–SO_4$. These results are in agreement with



Element	wt.%
C	24.10
O	37.61
Mg	13.09
Cl	15.53
Ca	6.31
Si	2.03
Na	1.33

Figure 2.7: SEM, EDX and FTIR analysis of the precipitated sludge obtained after the treatment of BBD water with IERW. Representative SEM images with a magnification of a) 100x, b) 330x, and c) EDX results. (d) Representative FTIR spectra of precipitated sludge obtained after the treatment of BBD water with IERW.

EDX, FTIR and removal percentages mentioned in Table 2.6. Furthermore, different atomic percent of these elements given in Figure 2.8 (a) confirms the precipitation of corresponding compounds after the chemical treatment. Figure 2.8 (c) shows that magnesium was mostly precipitated as magnesium hydroxide, which proves that this coagulant has been generated [81].

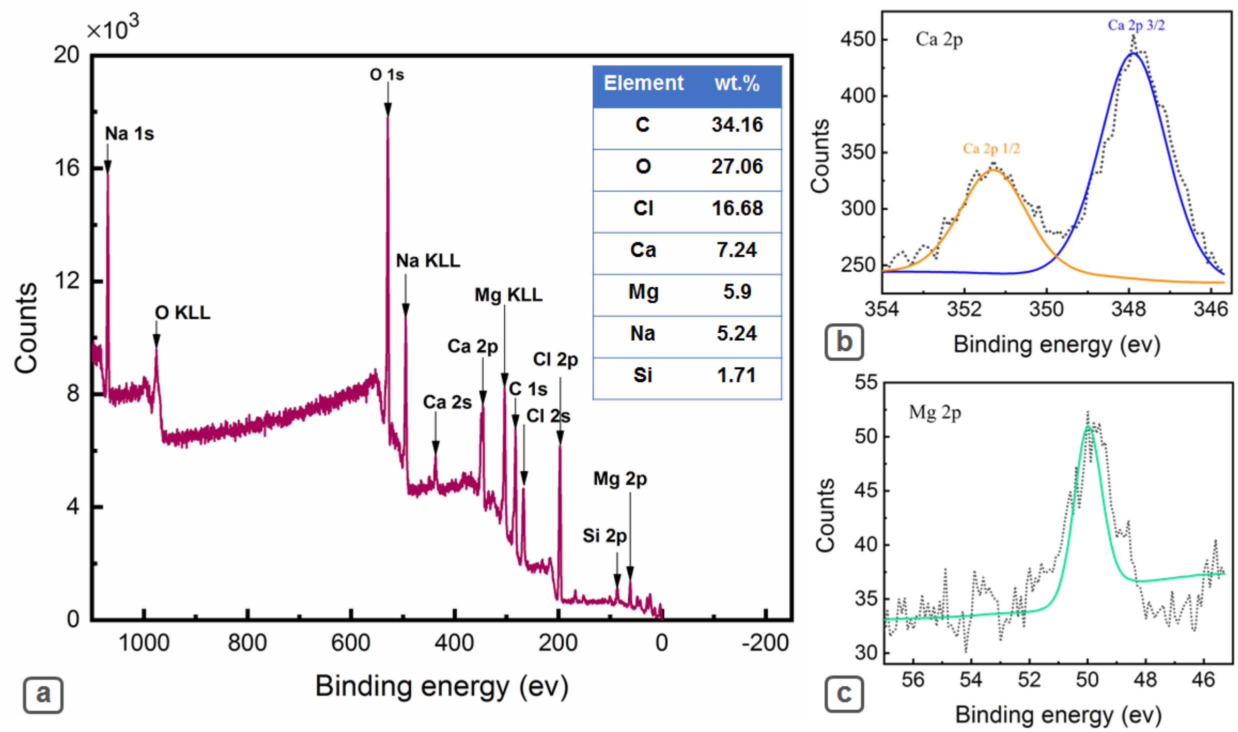


Figure 2.8: XPS analysis of the precipitated sludge. (a) XPS- survey spectrum of the precipitated sludge showing component elemental peaks identified and their relative abundance. The high-resolution XPS spectra for Ca 2p and Mg 2p are shown in (b) and (c), respectively.

The Ca 2p high-resolution spectra clearly shows well-defined peaks at 351.0 eV and 347.5 eV corresponding to 2p 1/2 and 2p 3/2 respectively with a peak area ratio of 1:2. The Ca^{2+} chemical shifts between various compounds (e.g., sulfates and carbonates) fall within a small range (< 1eV), so it is not possible to identify the nature of Ca^{2+} compounds from XPS data alone. Therefore, XRD analysis was performed on the sludge samples as the diffraction data can be used as fingerprints for sample identification.

The XRD pattern of the precipitated sludge collected after the treatment of BBD water with IERW is given in Figure 2.9. The presence of $CaSO_4$, $Mg(OH)_2$, $CaCO_3$ and NaCl were identified after fingerprinting the standard spectra of these compounds with the XRD pattern of the sludge. The XRD results further confirm the EDX, FTIR and XPS results and show successful sedimentation of BBD water in the presence of IERW coagulant. Moreover, based on the presence of calcium sulfate, which is considered as an industrial product, it can be concluded that this sludge has the potential to be used as a by-product through the extraction of calcium sulfate.

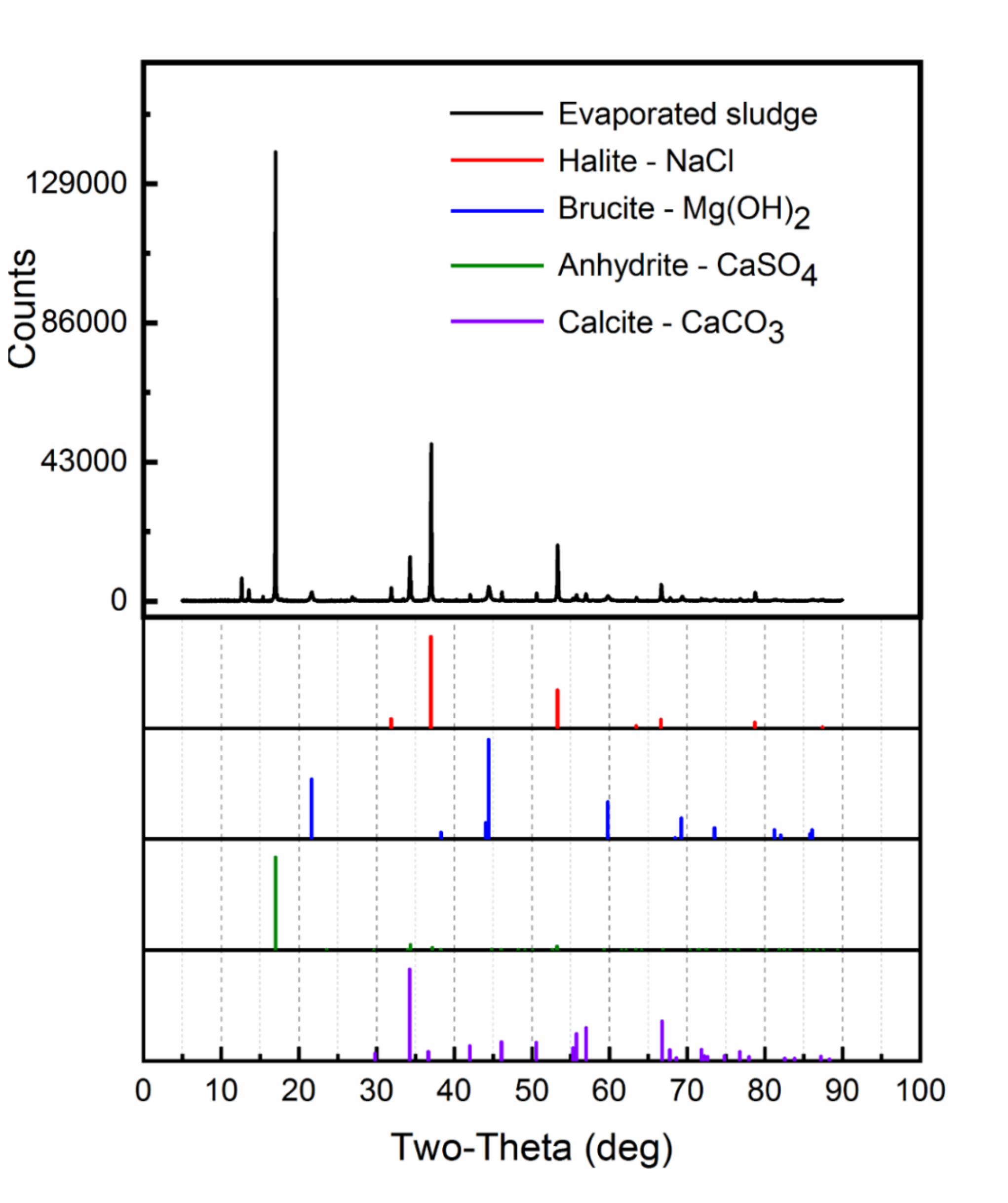


Figure 2.9: XRD Powder pattern of the dried sludge indicating the presence of different crystal patterns in the slurry phase.

2.3.5 Softening of BBD after IERW coagulant treatment

Table 2.4 shows that the concentration of calcium after the coagulation process by the IERW and BBD mixing is high. If the supernatant would be recycled, this hardness can reduce the efficacy of the SAGD plant by causing scaling on the pipes, exchangers and the boilers. Thus, soda softening was applied to remove the abundant calcium ions from the produced supernatant. For this purpose, the supernatant of the most efficient run (run 8) was extracted from the mixture solution. The properties of this supernatant are available in Table 2.7. Based on the IC analysis, the concentration of the chloride and sulfate in this solution was 10990 ppm and 1030 ppm, so presumably, most of the remaining calcium in the solution is in the form of non-carbonate hardness (permanent hardness) such as $CaSO_4$ and $CaCl_2$. Soda ash was chosen to remove calcium ions from the solution because this coagulant has high efficiency in the removal of permanent hardness from water. For this purpose, 5 g of soda ash was added to 1 liter of supernatant with the same experimental method as the run 8. This dosage was selected based on some primary experiments, which analyzed the hardness removal at a different dosage of soda ash. The reactions involved in the removal of calcium are as follow [27,82]:

$$CaSO_4 + \ Na_2CO_3 \leftrightarrows CaCO_3 \downarrow + Na_2SO_4 \tag{2.3}$$

$$CaCl_2 + \ Na_2CO_3 \leftrightarrows CaCO_3 \downarrow + 2\mathrm{Na}Cl \tag{2.4}$$

After the sedimentation, the solution was analyzed for calcium removal. The properties of this solution are provided in Table 2.7. From this table, it can be observed that the concentration of calcium decreased from 1084 ppm to zero ppm, but the sodium concentration increased from 4397 ppm to 6973 ppm. This result shows that after the two treatments, almost all of the hardness was removed. It is worth noting that in a SAGD plant, the volume of BBD is only a portion of the BFW; the volumetric ratio of BBD water used in this study was about 10% of the BFW.

Table 2.7: Comparison of the properties of the supernatant after soda softening.

Parameter	Unit	Supernatant before soda	Supernatant after soda
Calcium	ppm	1084	0
Magnesium	ppm	1.29	0.01
Sodium	ppm	4311	6973
pH		10.75	10.96
TDS	ppm	11350	16665

It can be said that in the industrial practices, the treated BBD water will be mixed with the BFW before entering the boilers. Therefore, the treated BBD water in this study can be diluted almost ten times and then be reused as the BFW. Thus, after dilution, the treated water will have an acceptable concentration range of TDS and sodium too. Figure 2.10 depicts a schematic view of the conventional water treatment process and the proposed new method for the BFW.

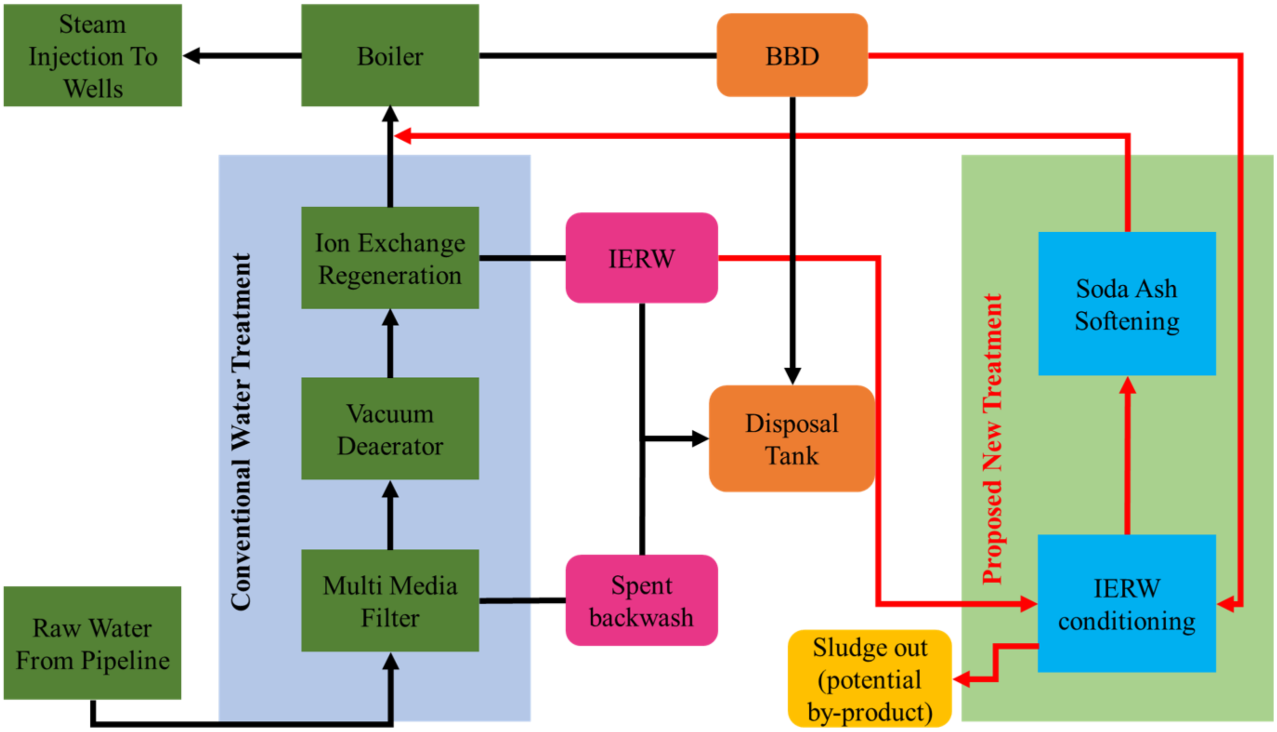


Figure 2.10: Schematic representation of the conventional SAGD water treatment and the proposed new treatment using ion exchange regeneration waste (IERW) water.

2.3.6 Applicability of IERW as a coagulant in the treatment of wastewaters

In order to assess the treatment efficiency of IERW with other types of wastewater, a BBD water sample with a higher concentration of organic matter was treated with the IERW coagulant. The BBD water sample was prepared by increasing the pH and silica concentration (Table 2.8) of the boiler feed water received from a SAGD plant located in the Athabasca oil sands region of Alberta, Canada [13]. Table 2.8 shows that synthesized BBD water contained a high concentration of hardness, silica and organic matter. This wastewater should be treated before reusing it for the boiler since the presented ions can reduce the efficiency of the boiler by scaling and fouling.

Table 2.8: The properties of synthesized BBD water.

Parameter	unit	BBD
Na	ppm	1830
Ca	ppm	310
Mg	ppm	57.3
Si	ppm	165
TOC	ppm	274
pH		11.6

IERW water was added to the BBD sample with the same experimental conditions as run 8. In this experiment, three different dosages of IERW was used for the treatment of BBD water, and the precipitation of the mixture solution was observed for 1 hour. Figure 2.11 shows the effect of using different dosages of IERW for the treatment of the Athabasca BBD water. It can be seen that high silica and organic matter removal were achieved and the color of BBD water became lighter after the treatment with IERW due to the removal of organic matter. An increase in the IERW dosage shows higher removal of TOC and silica, possibly due to the presence of more magnesium ions.

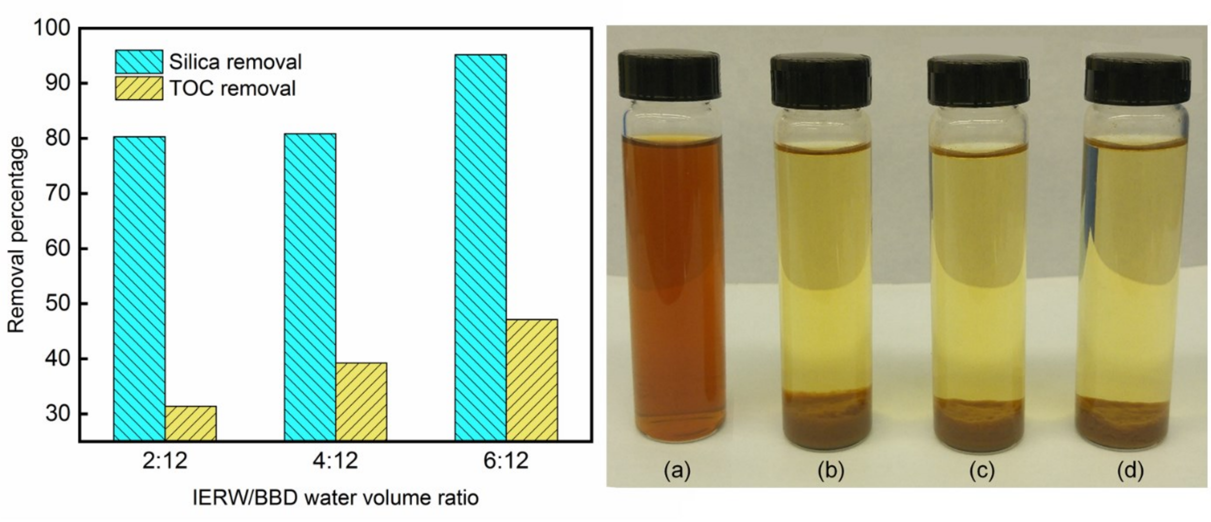


Figure 2.11: Demonstrate the treatment of BBD water using IERW as coagulant. The silica and TOC removal percentages using IERW for the treatment of BBD are depicted in the graph. The solution labelled (a) is Athabasca BBD and the (b), (c) and (d) represent the mixture solution after sedimentation with 2:12, 4:12, 6:12 IERW/BBD volumetric ratio, respectively.

These results confirm that the precipitation of the magnesium hydroxide was effective in removing the silica particles and organic matters in the BBD water by the coagulation-flocculation process.

2.4 Conclusion

In the present work, a systematic study has been conducted to investigate the feasibility of using IERW as a coagulant for the treatment of BBD. It was observed that the IERW is capable of reducing some major impurities, which are responsible for reducing the plant water recycling and efficiency of the OSTG, from the BBD and this takes into account not only the silica removal but also the organic matter presented in the BBD. The efficiency of silica and TOC removal is 98.72% and 81.34%, respectively, which can be considered effective in a chemical treatment process. The turbidity measurements indicate that when the temperature decreased from 80 °C to 40 °C, the number of settled particles was reduced. Moreover, it was observed that using mixing and increasing the temperature and dosage of the IERW improved the flocculation process significantly and larger flocs were formed and precipitated. However, the concentration of calcium increased after this treatment; this problem was solved by using soda ash softening process to remove the calcium from the solution. The sludge characterization supported the hypothesis of silica and organic matter removal by coagulation-flocculation of magnesium hydroxide. The usage of IERW was found to be effective for the treatment of Athabasca BBD. The removal efficiency improved by increasing the dosage of IERW, implying that the addition of more magnesium ions led to a higher removal efficiency.

Chapter 3

3 Evaluation of Integrated Membrane/Chemical Coagulation Process for Treatment of Oil Sand Produced Water

3.1 Introduction

Recently, the treatment of SAGD produced water has attracted more attention to mitigate the water consumption issue of this operation. SAGD is a commonly used method, which is applied for the extraction of bitumen from oil sands reservoir in Alberta, Canada. In this method, steam is produced from OTSGs and injected into the production wells to extract the bitumen by reducing its viscosity. The mixture of water and bitumen is pumped out to the surface for bitumen separation. After oil and water separation, the produced water is treated to be reused as the boiler feed water (BFW) [2,4,12–14,31,83]. The BFW used for OTSGs should meet the minimum boiler requirement to achieve a reasonable efficiency by avoiding scaling and fouling in the boiler tubes and other equipment. Currently different chemical pre-treatments are being applied to purify the SAGD proceed water, such as, warm lime softening, which is being used to reduce the concentration of the silica. One of the common methods for the removal of the hardness is ion exchange regeneration. Ion exchangers can remove calcium and magnesium ions by exchanging it with sodium ions in the resin bed. In the regeneration process, a concentrated sodium chloride solution is used to replace the sodium ions with the hardness ions. As a result, this process produces a waste stream named IERW, which contains a high concentration of sodium, calcium and magnesium. Some studies explored different methods to reuse the IERW for different purposes like sodium chloride recovery or the biological denitrification application [8–11]. Currently, in the SAGD operations, the IERW is being transferred to the disposal tank. Furthermore, some portion of the BBD water produced from the OTSG after the steam generation is also being disposed. The BBD water usually contains a higher concentration of organic matter, silica and TDS compare to the BFW. In the SAGD application, a portion of the BBD water is being recycled back to the water treatment process. However, the disposal of the BBD has demonstrated serious technical and environmental issues due to the silica-organic matter co-precipitation, which results in the blockage of the disposal wells [4,12,13]. Thus, many works have reported different alternatives to treat the BBD water and prevent the problems associated with its disposal. The usage of acidification, membrane filtration and Fenton oxidation has been investigate to treat the BBD water. Recently, membrane technology has proven to be a promising technology for the treatment of oil sand produced water owing to its compact design and lower operation expanse and energy consumption. In particular, pressure driven membrane processes such as nanofiltration (NF), reverse osmosis (RO) and forward osmosis (FO) have been widely applied to provide a higher quality BFW for the OTSG because of their high capability to remove silica, TOC and TDS. It is worth noting that water containing low concentration salt and organic matters do not cause significant scaling so the conventional methods for the BFW treatment do not target the removal of the TDS (salt) and TOC. However, the BBD has a higher concentration of dissolved solids compare to BFW making the treatment of BBD with membrane, very challenging since this treatment is usually followed by fouling and scaling due to presence of silica and organic matter [12–16,26,37]. Therefore, developing efficient and environmental friendly methodologies for the treatment of BBD and IERW streams has attracted significant attention from the oil sands companies.

In the conventional treatment process for SAGD operations, the silica and hardness are removed using different methods like warm lime softening and ion exchange regeneration. However, these treatment methods do not target the removal of organic matter and even increase the concentration of TDS. The successful usage of RO and NF has been reported for the removal of dissolved solids, silica, hardness and organic matter from the oil sand produced waters [13,32]. However, the treatment of saline water is not without difficulty since the high concentration of the salt will lead to high osmotic pressure and can increase the effect of concentration polarization (CP). CP is the phenomena representing the accumulation of the rejected ions near the surface of the membrane. It can mitigate the efficiency of the membrane treatment by reducing the permeate flux and salt rejection [36]. The pressure-driven membranes like RO and NF operate by applying pressure to overcome the osmosis pressure between the feed and permeate to force the water molecules through the membrane. The osmosis pressure depends on the concentration difference between the concentrations of ions in the feed and permeate side of the membrane. Thus, in treating saline water, a higher pressure is needed on the feed side to force the water through the membrane and achieve a similar flux to pure water flux [35]. The usage of NF and RO in treating wastewater with high salinity has been reported and the effect of different parameters on this treatment was explored. The applicability of different NF membranes for the desalination of the seawater was explored. It was demonstrated that tight NF membrane (NF90 commercial membrane) is capable of rejecting a reasonable amount of salt from saline water; the salt rejection for NF 90 was about 90% for a feed with a salt concentration of 5000 ppm [38]. NF90 membrane also showed that is capable of removing not just monovalent but also divalent ions from wastewaters. The NF membranes resulted in a higher permeate flux, and salt rejection as the feed pressure increased [84]. RO was also used to provide a higher quality water from saline wastewaters but this method required a higher energy consumption compare to NF applications [39,85]. Additionally, RO was explored in many studies as a viable option to treat high salinity wastewaters including seawater [86–88]. The treatment of BFW using the FO process has also been studied. It was observed that the FO membrane was relatively less prone to fouling compare while treating the BFW, which contained a high concentration of organic matter [15,89].

The practice of chemical pre-treatment for membrane desalination has proved to play an important role in improving membrane performance. These pre-treatments normally are applied to the wastewaters prior to membrane treatment to reduce the effect of fouling and scaling [90–93]. Fouling can reduce the performance of the membrane significantly, and the need for cleaning can increase the maintenance cost of the membrane filtration. The membrane fouling can be due to organic, colloidal, inorganic and biofouling. The organic fouling is caused by the presence of organic matters such as humic acid. The inorganic fouling might occur by the precipitation of mineral scales on the membrane. As for the colloidal fouling, it can happen when the size of the colloidal particles in the wastewater are bigger than the pore size of the membrane and they deposit on the surface of the membrane forming a cake layer. Biofouling occurs by the attachment of microorganisms resulting in forming a biofilm on the feed side of the membrane [93–96]. Coagulation is one of the standard techniques for removing unwanted impurities from the wastewaters. During the coagulation process, the small particles aggregate through manipulating their surface charge and are removed by sedimentation or filtration [97]. Previously, coagulation has been used as the pre-treatment to remove the organic matter, colloid and suspended solids from different wastewater before applying the membrane process. During the chemical pre-treatment process, some colloids like silica, which might precipitate and aggregate on the surface or within the pores of the membrane, can be removed by the flocculation and sedimentation. It was observed that after using pre-treatments, the permeate flux of the membrane was improved by mitigating the effect of fouling, resulting in a lower energy consumption and maintenance cost. The scaling effect of magnesium and calcium on the membrane can be minimized using chemical water softening methods such as soda and caustic softening [12,90–94].

Membrane filtration needs to provide a sufficiently high water recovery (more than 70%) to be economically applicable. Water recovery percentage shows the amount of water which is collected as the treated permeate water. Fouling is being considered as one of the major issues standing in the way of reaching a high water product recovery [98]. It was demonstrated by Sadrzadeh et al. that NF and RO were successful for the removal of TDS and TOC from the warm lime softener inlet water (the produced water guided to lime softeners). Additionally, It was proven that the a NF membrane can be more efficient in the treatment of oily wastewaters because it is able to achieve a higher flux with a lower operating pressure compare to RO and still achieve a high TDS and TOC rejection according to the boiler requirement [13]. However, in the majority of the cases, the oil sand produced water (WLS and BBD) contains a high concentration of organic matter and silica, which can lead to fouling and scaling of the membrane filtration [13,26,31,84]. Therefore, the oil sand wastewaters treatments using NF and RO were followed by several flux declines. Furthermore, the treatment of wastewaters containing a high concentration of calcium and magnesium with membrane filtration is challenging because these divalent ions can reduce the efficiency of the filtration and increase the energy usage and maintenance cost by causing scaling [98]. Scaling is the deposition of inorganic salts on the surface of the membrane, which usually happens when membrane allows the passage of water and reject other ions from passing through it to the dissolved salts in the feed side become oversaturated and deposit on the membrane [36,99,100]. The scaling potential of different inorganic salts has been investigated to show the effect of scaling on the performance of membrane processes. It was observed that precipitation of calcium carbonate caused significant permeate flux decline. Furthermore, it was demonstrated that at a lower pH (less than 7), calcium carbonate has lower chance of depositing on the surface of the membrane [100–102].

The purpose of this work was to investigate the efficiency of different membrane-based treatment methods to produce BFW by treating the BBD and IERW. Previous work involved applying chemical treatments with the IERW and sodium bicarbonate. It was observed that this chemical treatment removed a significant amount of organic matter and silica from the BBD, but they resulted in increasing the TDS. The produced water by IERW waste contained high concertation of sodium ions and although high salt concentration usually is not capable of causing significant scaling in OTSGs, the requirement of the OTSGs suggest avoiding a high TDS feed water to achieve a proper steam generation efficiency [5]. Thus, different membrane-based hybrid process were used to evaluate the performance of each treatment. Purification efficiency was studied by exploring water recovery and water product quality of membrane filtrations. Based on these parameters, different membrane processes were compared to nominate an efficient application for the treatment of the BBD water.

3.2 Materials and method

3.2.1 Experimental design

The BBD water and IERW samples were provided by EXEN Pro Ltd. located in Calgary. The Table 3.1 presents the characteristic of BBD water and IERW.

Three membrane-based treatment methods were applied to treat the BBD water and IERW stream. In the first approach, NF was applied to purify the pre-treated BBD by IERW conditioning with and without soda ash softening. In the second method, the contaminated BBD was directly treated with NF. Finally, the last method explored the potential of recovering water from BBD by using it as feed solution in FO process and using IERW as the draw solution.

Table 3.1: Properties of BBD and IERW wastewaters.

Parameter	Unit	IERW	BBD
TDS	ppm	66625±375	6525±25
pH	-	6.20±0.11	11.66±0.01
Turbidity	NTU	0.25±0.05	0.86±0.06
UV absorbance at 254 nm	-	0.07±0.01	0.72±0.04
$SUVA_{254}$	-	1.04±0.15	0.77±0.08
TOC	ppm	6.71±0.07	229.80±3.23
Silica as dissolved	ppm	5.22±0.48	77.6±1.5
Mg^{2+}	ppm	2201±351	0.24±0.03
Ca^{2+}	ppm	9455±1059	2.97±2.59
Na^{+}	ppm	22165±3244	1806±130
Cl^{-}	ppm	80650± 4203	40±6

Figure 3.1 demonstrates the schematic design of different treatments. These methods are explained in more detail below:

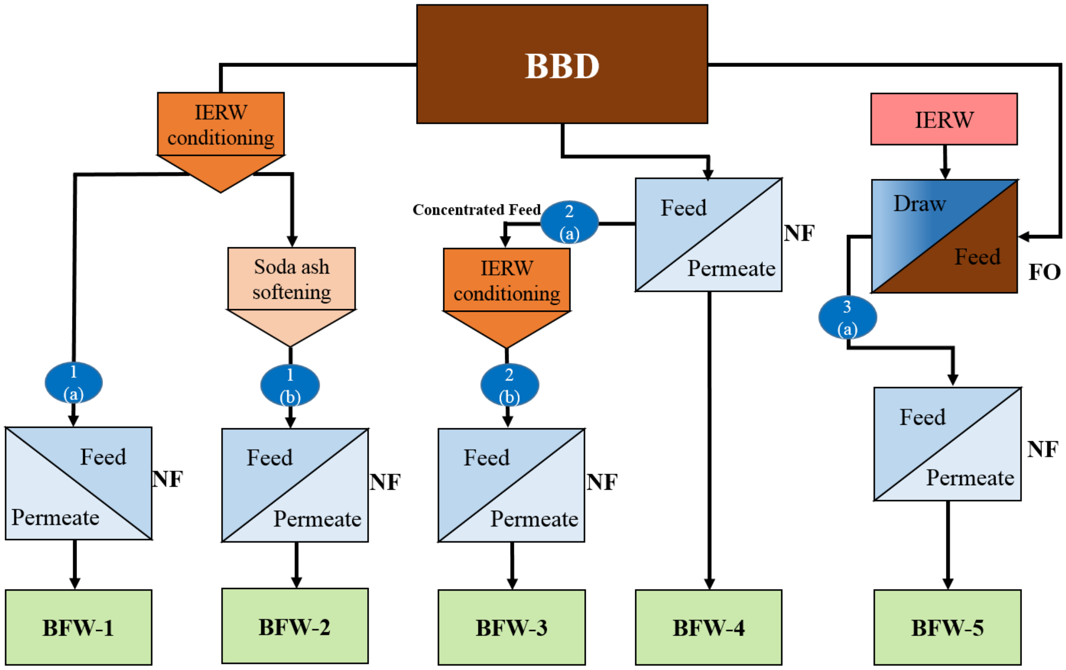


Figure 3.1: Schematic view of the experimental design presenting different membrane-based treatments for the BBD wastewaters.

3.2.2 Purification of pre-treated BBD by NF

This method involved applying IERW conditioning and then using NF as the final treatment. The complete details about this pre-treatment is provided in the previous work. As a brief summary: the chemical pre-treatment was conducted by addition of IERW as a chemical coagulant to BBD for 30 minutes at 2:12 (IERW:BBD) ratio. After 30 minutes of sedimentation, the supernatant was extracted and was used as the Feed 1a. The properties of the Feed 1a is provided in Table 3.2. After IERW chemical treatment, most of the organic matter and silica were removed from the BBD, but the concentration of the calcium dissolved ions increased significantly. In order to further purify the Feed 1a, two approaches were considered. The first method was treating the water after IERW conditioning with NF. The other method involved using sodium bicarbonate (dosage of 5 g/L) as the coagulant to remove the calcium as calcium carbonate [82,103]. The experimental procedure for the calcium removal was mixing the coagulant for 30 minutes at a low stirring speed. Then, the supernatant was extracted after 30 minutes of precipitation. After coagulation and precipitation process, the supernatant was guided to the filtration setup as the Feed 1b (Table 3.2). At this stage, the Feed 1b contained a low concentration of impurities and a high concentration of sodium.

3.2.3 Direct BBD filtration with NF

In the second method, BBD was purified with NF directly. Furthermore, the concentrated retentate after 50% water recovery was next to another cycle of IERW conditioning followed by NF. The properties of this concentrated feed are summarized in Table 3.2. This solution had a higher concentration of silica and organic matter compared to the initial BBD water therefore; IERW conditioning was applied to remove these contaminants before NF treatment.

3.2.4 FO approach

The last approach was conducted to evaluate the efficiency of IERW for the treatment of BBD water as the draw solution of the FO process. The IERW contained a high concentration of sodium chloride (Table 3.1) that provides a high osmotic pressure for the FO application [15,104,105]. After, the FO process, the diluted draw solution was treated with NF to reduce the concentration of sodium, calcium and magnesium. The properties of the diluted draw are written in Table 3.2 as the Feed 3a.

Table 3.2: The properties of the Feed 1a, 1b, 2a, 2b, 3a.

Parameter	Unit	Feed 1a	Feed 1b	Feed 2a	Feed 2b	Feed 3a
TDS	ppm	11350	16665	8500	16750	34120
pH	-	10.75	10.96	10.9	11.6	6.20
Turbidity	NTU	1.4	1.8	0.9	1.2	0.8
TOC	ppm	17	16.6	443.30	107.7	3
Silica as dissolved	ppm	1.43	0.93	111	3.17	3
Mg^{2+}	ppm	1.29	0.01	0.16	0.07	1010
Ca^{2+}	ppm	1084	0	2.78	3.82	5000
Na^{+}	ppm	4311	6973	3975	8069	11000

3.2.5 Membrane

The NF&RO filtration was performed using DOW FILMTEC BW30, XLE-4040 and NF90. These commercial membranes were used to evaluate the efficiency of the membrane separation process for the treatment of wastewaters. For the FO process, a commercial polyamide thin film composite (TFC) membrane was purchased from Hydration Technology Innovation (HTI).

3.2.5.1 Membrane filtration setup

Membrane filtrations tests were performed in three different operational modes, namely (i) crossflow, (ii) FO, (iii) dead-end setup.

3.2.5.2 Crossflow setup and analysis of filtration

Figure 3.1 depicts the schematic view of the crossflow membrane setup. The operating transmembrane pressure and feed flow rate were adjusted using a backpressure regulator and a bypass valve. The flow rate was kept constant at 1 Liter Per Minute (LPM) for all of the filtration tests. The temperature of the feed solution was controlled using a recirculating chiller (Isotemp 3013, Fisher Scientific). A conductivity meter and balance (Mettler Toledo) were used to measure the conductivity and mass of the permeate water, respectively. The permeate water flux (J_w) was calculated as follow:

$$J_w = \frac{\Delta m}{\rho A \Delta t} \tag{3.1}$$

Where A is the active surface area of the membrane (the effective membrane area was 0.00206 m^2) and Δm is the mass of collected permeate water over a certain time period which is represented by Δt. The permeate flux was directly calculated using LabVIEW data acquisition software. Furthermore, the rejection (R) of the TDS was measured as:

$$R\ (\%) = \left(1 - \frac{C_p}{C_f}\right) \times 100 \tag{3.2}$$

Where C_p and C_f express the concentration of permeate and feed water, respectively.

The fouling properties of the commercial membranes were evaluated in the following steps: 1) pure water filtration for 30 minutes, 2) wastewater filtration for 3 hours, 3) hydraulic washing of the membrane and then filtering pure water for 30 minutes. The Total flux decline ratio (DR_t), reversible flux decline ratio (DR_r), irreversible flux decline ratio (DR_{ir}) and flux recovery ratio (FRR) were measured by the following equations:

$$DR_t\ (\%) = \left(1 - \frac{J_p}{J_{w1}}\right) \times 100 \tag{3.3}$$

$$DR_r\ (\%) = \left(\frac{J_{w2} - J_p}{J_{w1}}\right) \times 100 \tag{3.4}$$

$$DR_{ir}\ (\%) = \left(\frac{J_{w1} - J_{w2}}{J_{w1}}\right) \times 100 \tag{3.5}$$

$$FRR\ (\%) = \left(\frac{J_{w2}}{J_{w1}}\right) \times 100 \tag{3.6}$$

Where J_{w1}, J_{w2} and J_p are the pure water flux at first, pure water flux after hydraulic cleaning and permeate water flux of the wastewater solution, respectively. In order to obtain the permeate water flux of the wastewaters, the average between the 2:45 to 3 H of the wastewater filtration was calculated.

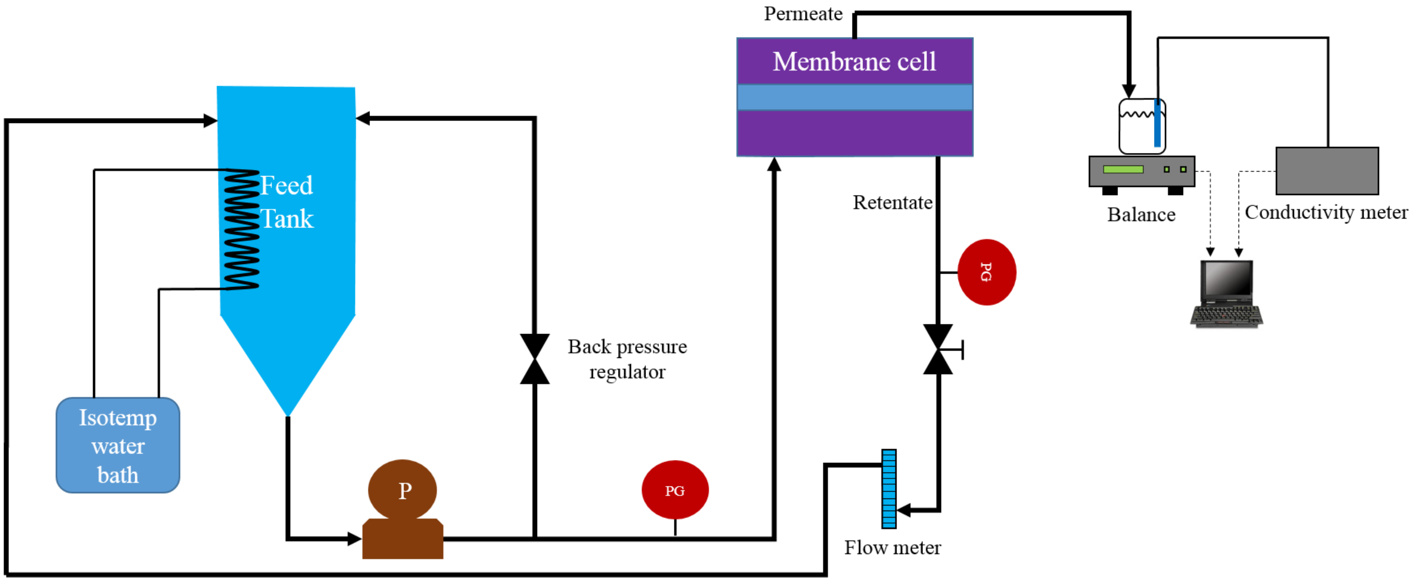


Figure 3.2: Schematic of the cross-flow filtration setup.

3.2.5.3 Schematic view of the FO setup

Figure 3.2 illustrates a schematic view of the FO setup. Two gear pumps were used to circulate the flow rate of the feed and solution. A flow rate of 2.5 liters per minute (LPM) was selected. The active layer of the membrane faced the feed side for the FO tests but for the PRO experiments, the active layer was positioned towards the draw solution. The temperature of the feed and draw solution was adjusted using the recirculating chillers (Isotemp 3013, Fisher Scientific). The volume of the feed and the draw solutions for all of the tests was 1 L. The conductivity was monitored using a conductivity meter and a digital weight balance measured the volume of the draw solution. The flux was calculated with the same procedure as crossflow setup using the Equation 3.1. The effective membrane area of the illustrated membrane cell was 140 cm^2. Furthermore, the reverse solute passage (J_s) was calculated as follows [106]:

$$J_s = \frac{C_t V_t - C_0\,V_0}{A\Delta t} \qquad (3.6)$$

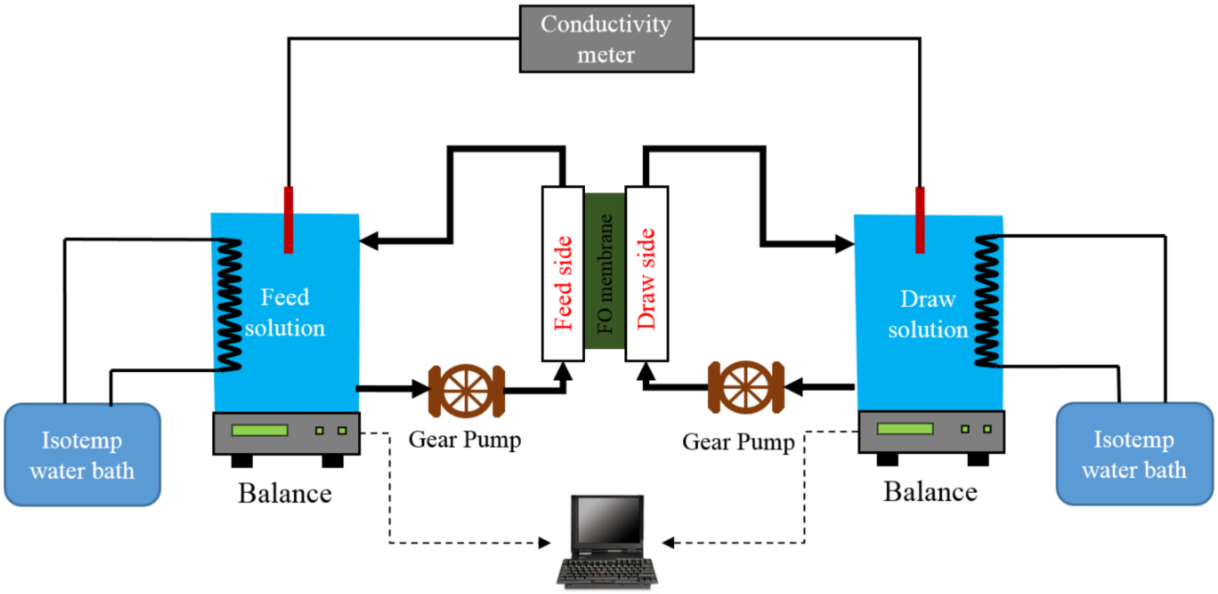


Figure 3.3: Schematic view of the FO setup.

3.2.5.4 Dead-end membrane filtration setup

Figure 3.4 shows different components of the dead-end setup. A nitrogen tank was used to provide the required pressure. In order to prevent the deposition of the contaminants and concentration polarization on the surface of the membrane, the solution was stirred using a magnetic stirrer at 500 rpm through the experiments. The collected permeate water was weighted using the digital weight balance, and the flux and rejections were calculated using Equation 3.1 and 3.2 with the same procedure.

3.2.6 Characterization of water and membrane samples

The total organic carbon (TOC) was analyzed using a non-purge able organic carbon method using the Shimadzu TOC-VCSH analyzer. The concentration of the calcium, magnesium, sodium and silica was obtained using inductively coupled plasma optical emission spectroscopy (ICP-OES). A Hach DR 5000 spectrophotometer was employed to measure the UV absorbance. Moreover, the turbidity was analyzed with a turbidity meter with a unit of nephelometric turbidity unit (NTU). Field emission scanning electron microscopy (FESEM, Zeiss Sigma 300 VP) was used to analyze the morphology of the deposited materials on the fouled membranes.

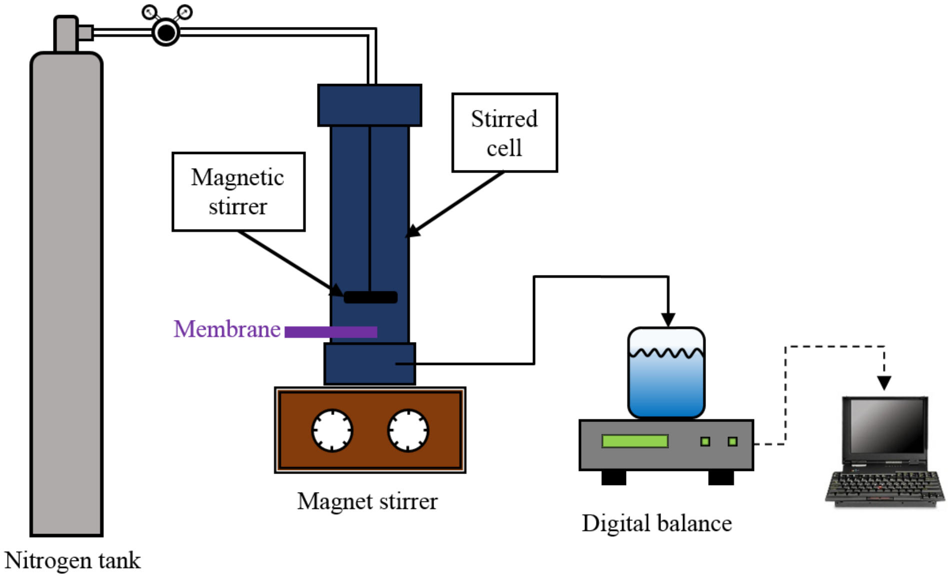


Figure 3.4: The schematic view of the dead-end stirred cell.

3.3 Results and discussion

3.3.1 NF process with chemical pre-treatment

The Figure 5 (a) and (b) show the permeate flux, TDS rejection and fouling properties of NF90 for the Feed 1a and 1b. As can be observed for both Feed 1a and 1b, the water flux of NF90 was significantly lower compare to when the pure water was used. The initial flux of NF90 for the Feed 1(a) was higher than the initial flux of filtration for the Feed 1b due to having a lower TDS concentration. This is because of the concentration polarization phenomena, which is less significant in the solution with lower TDS concentration. However, the water flux of NF process for the Feed 1b was almost constant during the experiment unlike the filtration of Feed 1a, which was followed by flux decline; this flux decline can be attributed to the combined effect of concentration polarization and fouling. In order to evaluate the fouling behavior of the membranes, the membranes were washed and were tested again by using pure water as the feed. It was observed that the NF process for the Feed 1a and 1b demonstrated a total flux decline of 88% and 87%, respectively (Figure 5(b)). The flux recovery ratio and reversible flux decline of NF for the Feed 1(b) were 29% and 25% more than the Feed 2a, respectively. The NF method for the Feed 1b showed an irreversible fouling was as low as 1.3%, which implies that most of the deposited materials on the surface were washed away by cleaning. In contrast, the irreversible fouling of filtration for the Feed 1a was as high as 30%, which was probably due to the deposition of calcium ions on the surface of the membrane. Furthermore, the TDS rejection of NF90 for the Feed 1a was 5 % higher than the Feed 2b. This observation is higher concentration of dissolved solids in the Feed 1b than Feed 1a [22]. In the pressure driven membrane filtration, the effect of concentration polarization becomes more severe when the feed solution has a high TDS concentration. A significant solute concentration difference between the feed side and the permeate side results in large osmotic pressure difference that causes the solutes to move to the permeate side to maintain the osmotic balance. Thus, in the treatment of Feed 1b, the accumulation of dissolved ions on the membrane surface was higher compare to the filtration of Feed 1a leading to a higher salt passage through the membrane, which resulted in a lower TDS rejection. Additionally, the NF90 showed a calcium rejection as high as 98% for the Feed 1a, which is significantly higher than its TDS rejection. The reason for this high rejection of calcium ion can be attributed to the effect of Donnan exclusion mechanism, which explains that the monovalent ions have a larger charge density and interaction compare to the divalent ions. Additionally, the divalent ions such as magnesium and calcium have a larger size than the sodium ions so the NF process is capable of removing more divalent ions compare to monovalent ions [23,48].

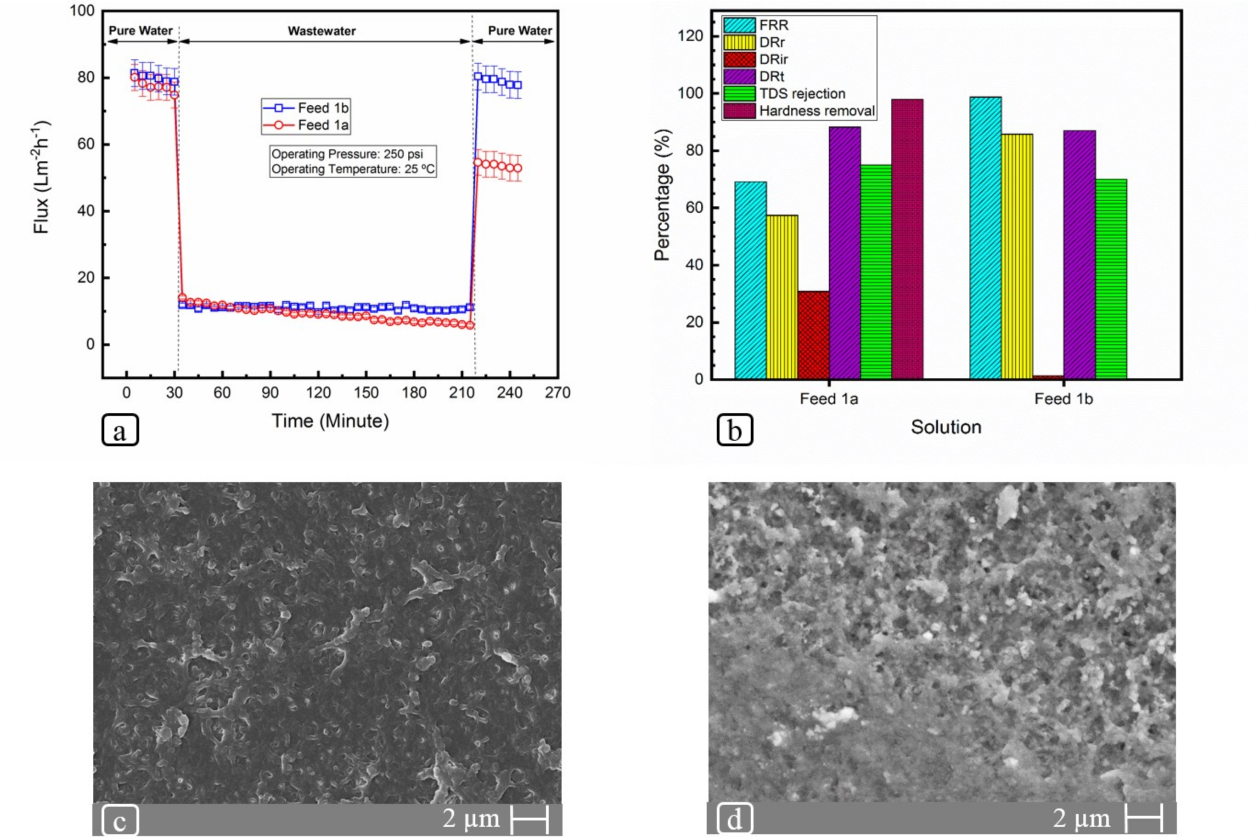


Figure 3.5: (a) the permeate flux of the NF, (b) fouling characteristics (FRR, DRr, DRir, DRt, and rejection of TDS, TOC, and silica. SEM images of NF90 membrane: (c) before and (d) after filtration of Feed 1a.

The Appendix B provides more details about the purification of Feed 1b by different commercial membranes. Figure 3.5 (c) and (d) illustrate the SEM images of the NF90 membrane before and after filtering Feed 1(a), respectively. Based on the morphologies of the foulants on the membrane surface, the deposition of the calcium ions resulted in a dense foulant layer further proving the relatively high irreversible fouling ratio value observed in the filtration test.

3.3.2 NF-treatment of BBD

The permeate flux of NF process for the purification of the BBD water and the Feed 2b, which is the concentrated retentate of BBD filtration after IERW conditioning, is depicted in Figure 6 (a). The initial flux of NF90 for the BBD was higher than the Feed 2b due to having a lower TDS concentration. Whereas, the filtration of the Feed 2b was followed by a lower flux decline compare to BBD filtration. The observed flux decline was The Figure 6 (b) shows the fouling characteristic for the BBD and the Feed 2b. The total fouling ratio of the BBD filtration was 83%. The NF treatment for BBD water had a flux recovery and reversible fouling ratio of 97% and 80%, respectively. Moreover, the irreversible fouling was as low as 4% demonstrating that the flux decline was attributed to concentration polarization and fouling, which were easily removed through hydraulic washing. Moreover, this filtration succeeded in achieving a TDS, silica and TOC rejection of 80%, 88% and 90%, respectively. The NF process for the Feed 2b showed a lower initial flux as result of having a higher TDS concentration. The treatment of the Feed 2b showed a similar fouling behavior to the NF of the BBD water proving that only a low percentage of fouling was irreversible. The TDS, silica and TOC rejection of this filtration were 74%, 85% and 92%. The observed fouling of NF90 for the BBD water and the Feed 2b could have been due to the concentration polarization and deposition of the organic matter and silica particles on the surface of the membrane. In conclusion, both of the filtrations demonstrated a relatively high flux recovery ratio and low irreversible fouling ratio. The morphology of the deposited contaminants on the NF90 membrane was analyzed using the SEM technique. Figure 3.6 (c) and (d) show the NF 90 membrane before and after filtration of BBD water. The observed coating of the rejected contaminants were presumably due to the precipitation of the silica and organic matter on the surface of the membrane.

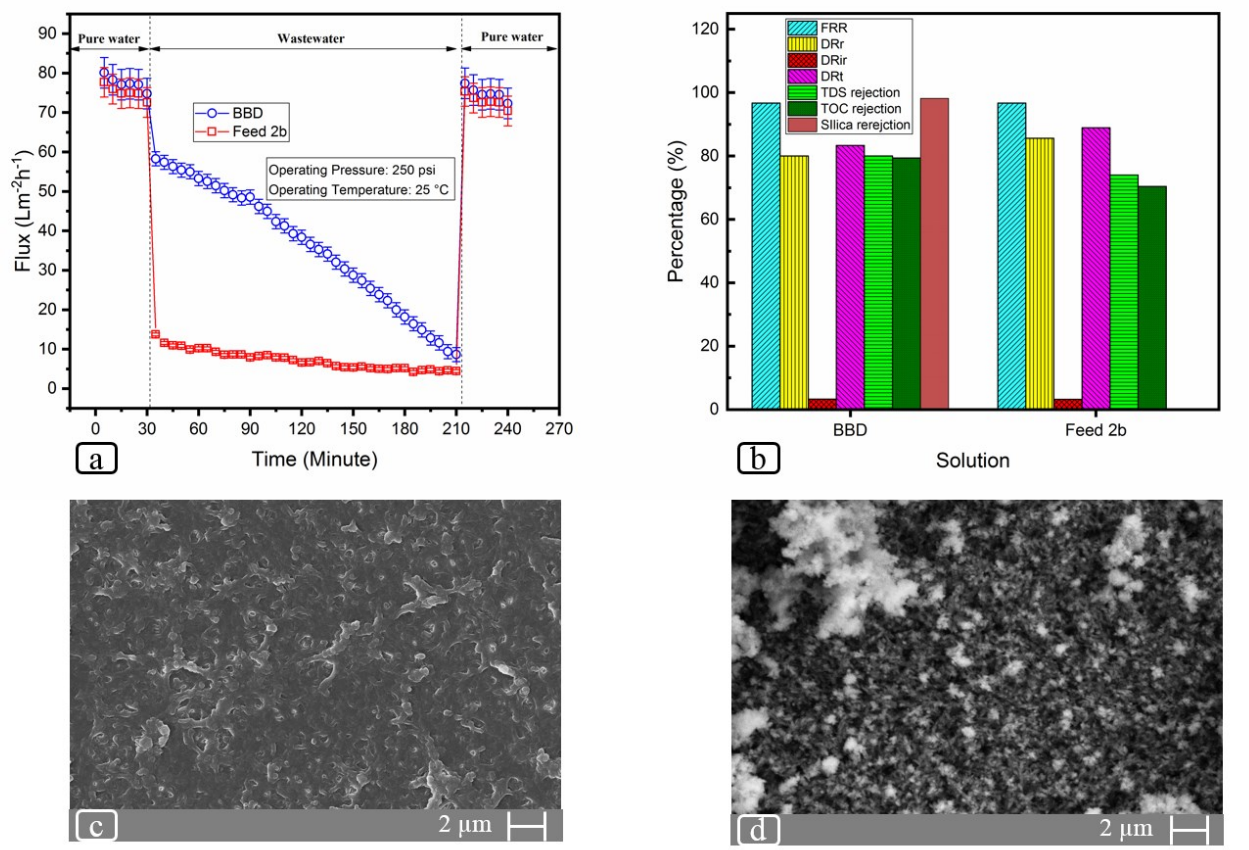


Figure 3.6: The permeate flux and fouling characterization of the NF while treating the BBD along with the concentrated retentate stream. SEM images of NF90 membrane: (c) before and (d) after filtration of BBD water.

3.3.3 FO for the treatment of the BBD

The water flux and salt passage of the FO and PRO process are depicted in the Figure 7 (a) and 7 (b), respectively. As it can be seen the PRO configurations had a higher initial flux compare to the FO tests. This was expected because in FO, the porous support layer of the membrane was placed on the draw side allowing the passage of salt through the membrane. This salt passage can cause internal concentration polarization (ICP) inside the porous layer, which can lead to a lower water flux. However, in PRO, the support layer of the membrane is faced to the feed side preventing the ICP [49,50]. The Figure 7 (a) and (b) show that the water and reverse salt flux increased for all of the tests when the temperature was enhanced from 25 °C to 45 °C. This is due to the decrease of the solution viscosity and increase of the diffusion at the raised temperature. Additionally, the increased temperature probably boosted the movement of molecular chain of the membrane resulting in the passage of more water molecule and solute ions through the membrane [51–53]. All of the FO tests showed constant flux during the experiment but the PRO runs were followed by flux decline and fouling. The fouling in the PRO tests was presumably due to the precipitation of silica and organic matter on the support layer of the membrane, which was avoided in the FO configuration because the active layer was in contact with the feed side.

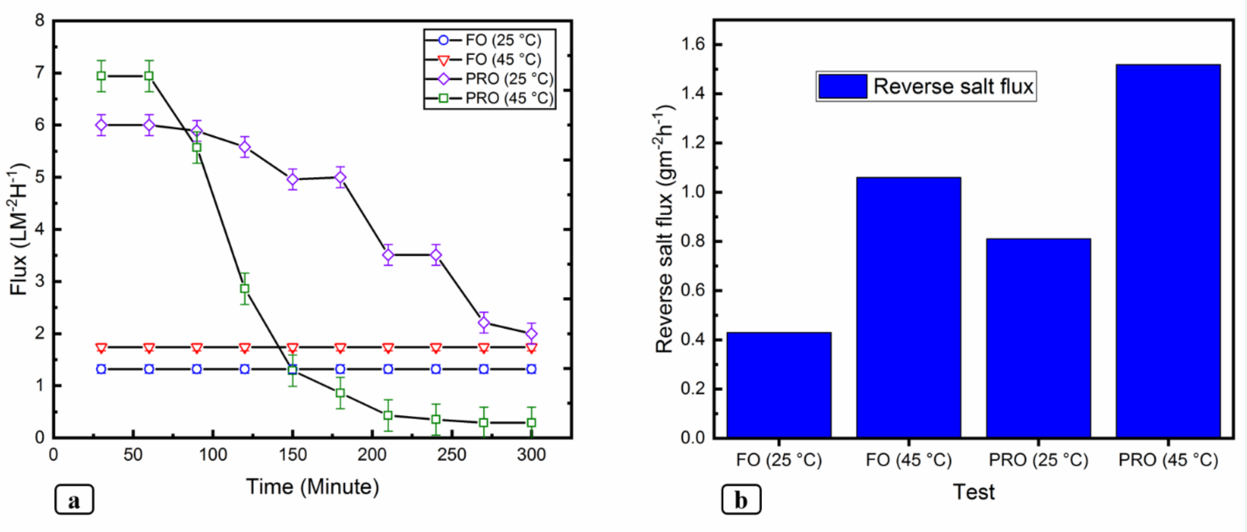


Figure 3.7: Demonstration of FO process by the (a) water flux and (b) reverse salt flux of the FO and PRO tests at different temperatures.

The results from the treatment of the diluted draw (Feed 3a) by NF is depicted in Figure 8. The TDS concentration of this feed was relatively high (see Table 4) and did not show any permeate flux at operating pressure of the 250 psi. Thus, in order to achieve a proper permeate flux, the operating pressure and stirring speed had to be raised to 350 psi and 1500 rpm, respectively. As it can be seen, the water flux of this filtration was comparably low based on the operating pressure of 350 psi, which is 100 psi more than previous filtrations. The total flux decline of this filtration was as high as 95%, which is in agreement with the flux trend observed in the Figure 8 (a). The

TDS, calcium and magnesium rejection for NF of the Feed 3a was 86%, 97% and 97%, respectively. The high TDS rejection of this filtration compare to the other cases can be due to two reasons. Firstly, the Feed 3a contained a high concertation of the calcium and magnesium and as mentioned before the NF have a higher capability of removing these ions compare to sodium ions. Secondly, the increase in the stirring speed could have also hindered the effect of concentration polarization leading to less solute passage through the membrane and increasing the rejection. Previously, it was observed that the filtration of the feed solutions containing calcium and magnesium was highly depended on the pH and was more calcium scaling was observed while treating a high pH wastewater. This is due to the fact the solubility of the magnesium and calcium ions is higher at low pH [48]. Thus, the reason for this low value of irreversible fouling can be due to the low pH (6.2) of the Feed 3a.

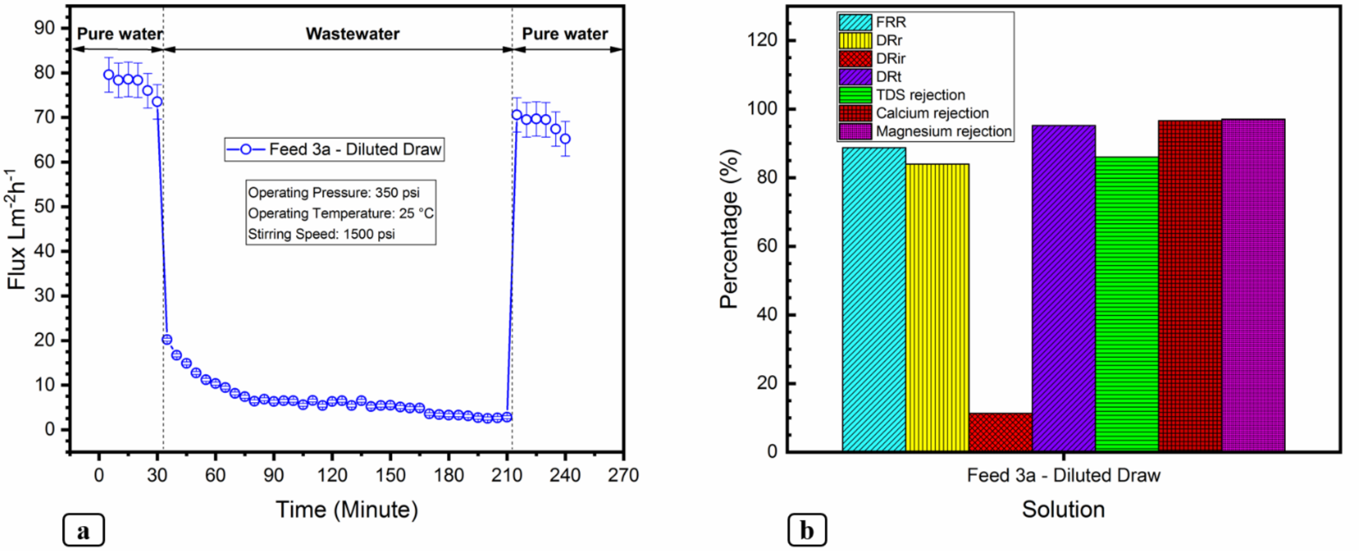


Figure 3.8: Water flux (a) and filtration analysis (b) for the treatment of the concentrated feed after IERW conditioning (Feed 2b).

3.3.4 Comparison of the different methods

In order to compare the efficiency of the filtration tests, the total flux decline and flux recovery ratio of all of the runs was depicted in the Figure 9. It should be mentioned that in this case, the initial flux of treatment was considered as the wastewater flux in the total flux ratio calculations since the flux recovery can demonstrate the fouling behavior and the total flux decline can show the efficiency in terms of achieving a higher volume of the treated water. The FO/NF filtration clearly did not showed a proper efficiency in terms of having a low flux recovery ratio and requiring a high-energy consumption. Even though the filtration of the Feed 1a showed a proper flux decline ratio, its flux recovery ratio indicates severe irreversible fouling, which can increase the maintenance cost in the long-term operations. The Feed 1b resulted in high flux recovery ratio but due to having a high TDS, achieved a relatively high flux decline demonstrating low capability in terms of achieving a low water recovery. However, the BBD filtration showed very promising results since it achieved the lowest flux decline ratio and still was able to obtain a high flux recovery ratio. Moreover, the concentrated solution of BBD water was purified by IERW conditioning and was filtered as the Feed 2b. The filtration of Feed 2b showed the same behavior as the Feed 1b and a slightly better flux decline ratio compare to the filtrations in the first and third scenario. Overall, it can be concluded that the second method, which was a combination treatment of the BBD water and the Feed 2b showed the highest efficiency because it took advantage of the low TDS concertation of BBD water by treating it with NF and refining the concentrated BBD water to increase the water recovery volume of the filtration.

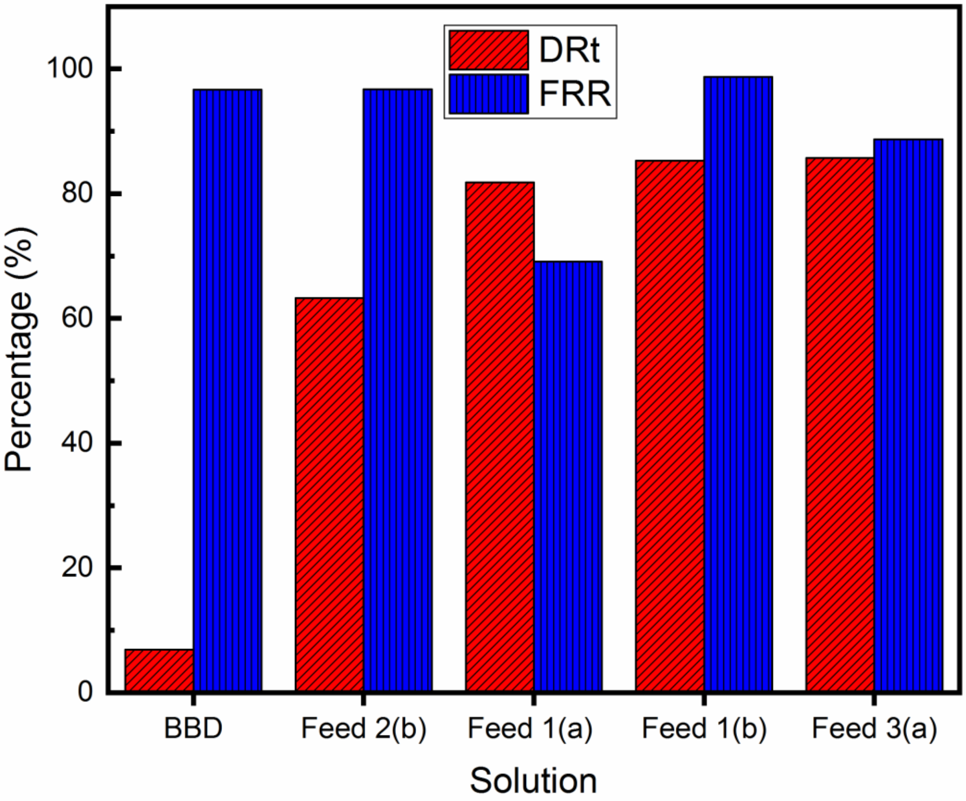


Figure 3.9: The total flux decline and flux recovery ratio for all of the runs.

3.4 Conclusion

This study evaluated different integrated chemical/membrane processes for the purification of BBD water indented to be reuse as the BFW. The first method involved purifying the pre-treated BBD with IERW conditioning, which was followed by 31% irreversible fouling due to the presence of calcium ions. Another chemical pre-treatment by soda ash softening was applied to reduce the calcium concentration and mitigate the irreversible fouling issue. The NF of the pre-treated BBD water with soda ash softening showed an irreversible fouling as low as 1%. However, the total flux decline ratios of these filtrations were relatively low because of their feeds solution had a high TDS concentration. Nonetheless, the efficiency of NF for the Feed 1b was more than the Feed 1a, which indicates the beneficial impact of using soda ash softening as a pre-treatment for NF. Another approach elaborated the direct usage of the NF process for the purification of BBD water, which demonstrated a high initial water flux with 4% reversible fouling. Furthermore, this process was followed by applying an integrated IERW conditioning and NF process to purify the concentrated retentate. The concentrated retentate after IERW coagulation had a relatively high TDS concentration and a low silica and TOC concentration compare to the initial BBD water. The filtration of concentrated BBD water had a relatively low total flux decline ration and an irreversible fouling ratio as low as 3%. In the third scenario, the BBD water was tested as the feed solution and the IERW was placed as the draw solution of the FO process, the resulted diluted draw was purified by NF. This NF did not show a proper efficiency in terms of requiring a high-energy consumption and achieving a relatively high total flux decline ratio. Overall, the direct treatment of the BBD by NF was the most promising method since it achieved low total flux decline and irreversible fouling ratio. Moreover, by treating the concentrated retentate, it was able to achieve the highest water recovery compare to other methods. Therefore, it is recommended to treat the BBD directly with NF and further purifying the concentrated by IERW conditioning and NF.

Chapter 4

4 Concluding Remarks and Future Works

4.1. Conclusion

Water consumption in SAGD plants will most probably will be the main obstacle for the sustainable production of oil in Alberta. Hence, reduction of freshwater use by innovative treatment of produced water is one of the main priority area of oil sands companies. The objective has always been to effectively treat, recycle and reuse more water. In this study different scenarios for the treatment of SAGD BBD water were evaluated. First, IERW conditioning was studied, as a novel approach, to treat the BBD water by using an existing waste stream, i.e., IERW in the SAGD plant. Then, various membrane-based hybrid methods, with or without IERW conditioning and chemical pre-treatments, were used to purify the BBD water.

IERW conditioning has removed as high as 98.72% and 81.34% of silica and TOC, respectively. The main mechanism responsible for the coagulation of BBD water and IERW mixture solution was the formation of magnesium hydroxide and co-precipitation of silica and organic matter. Chemical characterization of sludge has proved the presence of magnesium hydroxide. It was demonstrated that increasing the temperature, IERW dosage and mixing speed could lead to higher turbidity removal. The optimized condition was 2:12 (IERW:BBD) mixing ratio, 60 rpm mixing rate, and 80 °C temperature. Under this condition, larger flocs were formed and were separated through precipitation. Although mixing IERW with BBD water has led to the removal of silica and organic matter, it increased the calcium concentration in the solution. This problem was resolved by soda ash softening of IERW conditioning product. The soda ash removed all the calcium ions with a ratio of 5 g/l, however it increased the amount of sodium in the solution. The characterization of the produced sludge revealed the presence of silica, magnesium and calcium, which shows a high potential for resource recovery. The potential of using the IERW for the treatment of another BBD water stream with a higher concentration of organic matter was also investigated. In this case, IERW conditioning was successful in removing about 80% of silica concentration and 35% of organic matter.

In the second part of this thesis, several membrane-based hybrid methods were employed to treat the BBD water after IERW conditioning. It was observed that NF process, after the IERW conditioning, provides a higher performance by applying the soda ash softening through reducing the effect of irreversible fouling. The potential of using a hybrid FO/NF process was also explored by using the IERW as the draw solution and the BBD water as the feed solution of FO, followed by treating the diluted draw with NF. However, the NF of the diluted draw required a higher operating pressure due to the high TDS of the diluted draw. This filtration also resulted in a high total flux decline ratio proving to be an inefficient treatment. Additionally, a direct approach of using NF for BBD purification was evaluated with further treating the concentrated retentate. The direct filtration of the BBD water showed the lowest total flux decline ratio and resulted in a relatively low irreversible fouling ratio. Overall, it was concluded that the combination of the direct treatment of BBD by NF and purifying the concentrated retentate by the combination of IERW conditioning and NF, was the most promising method for the treatment of BBD water.

4.2. Future work

The use of IERW as a coagulant in the first chapter can be further investigated by adding an MF process after the coagulation-flocculation. Previously, it was observed that the mixing ratios of 1:12 to 2:12 (IERW:BBD) showed almost the same silica and TOC removal but the lower dosage of coagulant resulted in a solution with relatively high turbidity. Hence, lower dosages of IERW can be employed to achieve the same removal efficiency, which will probably result in a highly turbid solution. The high turbidity is an indicator of the high amount of suspended solids, which can be removed using MF. This procedure will help to use a lower dosage of IERW for the coagulation, which might also resolve the issue of the calcium addition through the IERW conditioning. Moreover, the IERW can be used to treat other types of wastewaters with a higher concentration of organic matter. In this case, if the IERW conditioning is not capable of removing most of the organic matter, magnesium can be added separately to increase the removal efficiency of the process.

Membrane filtrations test in the second chapter can be conducted at different conditions since the flux and fouling behaviour of the membrane separation process is profoundly affected by different operating parameters such as temperature, pressure, and pH. That would be interesting to do the membrane filtration at higher temperatures since the BBD stream in the SAGD operation has a high temperature (about 80 °C). At high temperature, it is expected to achieve a higher flux and lower rejection. Moreover, the fouling behaviour at high temperature can be different. For example, the precipitation of calcium and magnesium ions is more intense at high temperature, so the scaling effect of these ions will be more significant. Moreover, different commercial membranes such as BW30 and XLE can be used to produce a BFW with a lower TDS. It is recommended to use these membranes for all of the proposed scenarios. This will provide a valuable insight, as the permissible concentrations of contaminants are different for different boilers in SAGD plants. Therefore, some of the SAGD operations might need a BFW with a lower TDS level.

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6 Appendices

Appendix A: Calculation of removal percentage by mass balance

In order to explain the procedure for obtaining the removal percentage, an example for the calculation of the magnesium removal percentage is provided here.

For the coagulation treatment process, 143 ml of IERW was mixed with 857 ml of BBD. The concentration of magnesium in the IERW and BBD water was 2201 ppm and 0.24 ppm, respectively. Thus, the total input mass of the magnesium ($M_{Mg-input}$) can be calculated as follows:

$$M_{Mg-input} = M_{Mg-SAC} + M_{Mg-BBD} = 336.75\,mg + 0.21\,mg = 336.96\,mg \qquad \text{(A1)}$$

Where M_{Mg-SAC} and M_{Mg-BBD} are the mass of the magnesium in the IERW and BBD water, respectively.

The total output mass of the magnesium ($M_{Mg-output}$) was obtained with the same procedure. Based on these values, the total solid mass of the precipitated sludge ($M_{mg-solid}$) was measured using the following equation

$$M_{Mg-solid} = M_{Mg-input} - M_{Mg-output} = 336.96\,mg - 2.24\,mg = 334.72\,mg \qquad \text{(A2)}$$

Finally, the removal percentage of the magnesium was calculated as follows:

$$\text{Removal percentage of magnesium} = \left(\frac{M_{Mg-solid}}{M_{Mg-input}}\right) * 100 = \left(\frac{334.72}{336.96}\right) * 100 = 99.34\% \qquad \text{(A3)}$$

All of the remaining removal percentages for other ions were calculated following the same method.

Appendix B: Comparison of different commercial membranes for the treatment of the Feed 1b

In order to achieve a higher quality of BFW different commercial membranes were used to treat the Feed 1b. Cross-flow filtration set up was used for all of these tests. The operating pressure for all of the membranes was 200 psi. The permeate flux and the rejection of these commercial membranes are presented in Figures B1 and B2, respectively. For all of the membranes, the flux increased by increasing the feed temperature. The flux decline observed in Figure B1 is presumably due to the compaction of membranes at higher temperature. Moreover, it can be seen that the BW30 had the lowest flux and the highest rejection (87%). In addition, the NF 90 had the highest flux with a slightly lower rejection compare to the XLE. The permeate flux of XLE membrane was higher than the BW30 but did not show a significant increase in the TDS rejection. Therefore, the BW30 is capable of producing a BFW with lowest TDS concentration due to its high TDS rejection capability.

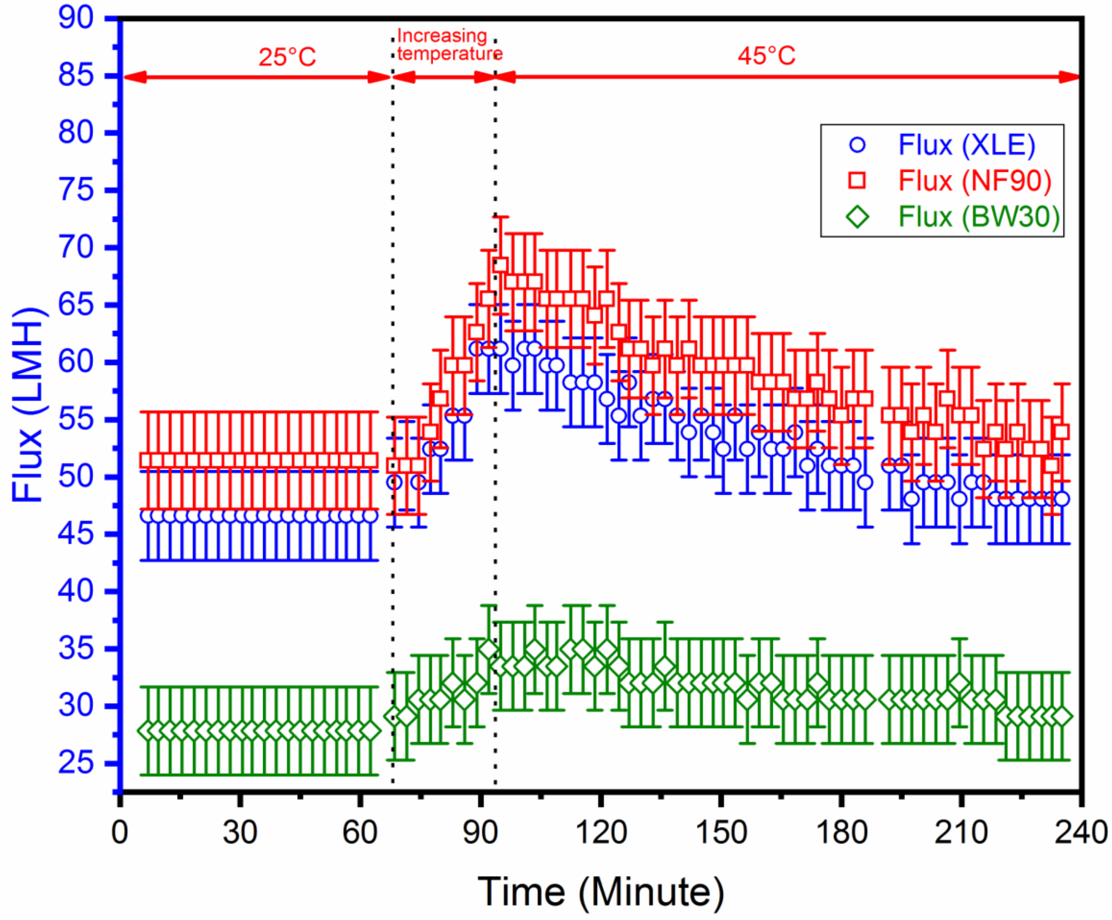

Figure B1: Permeate flux through different commercial membranes.

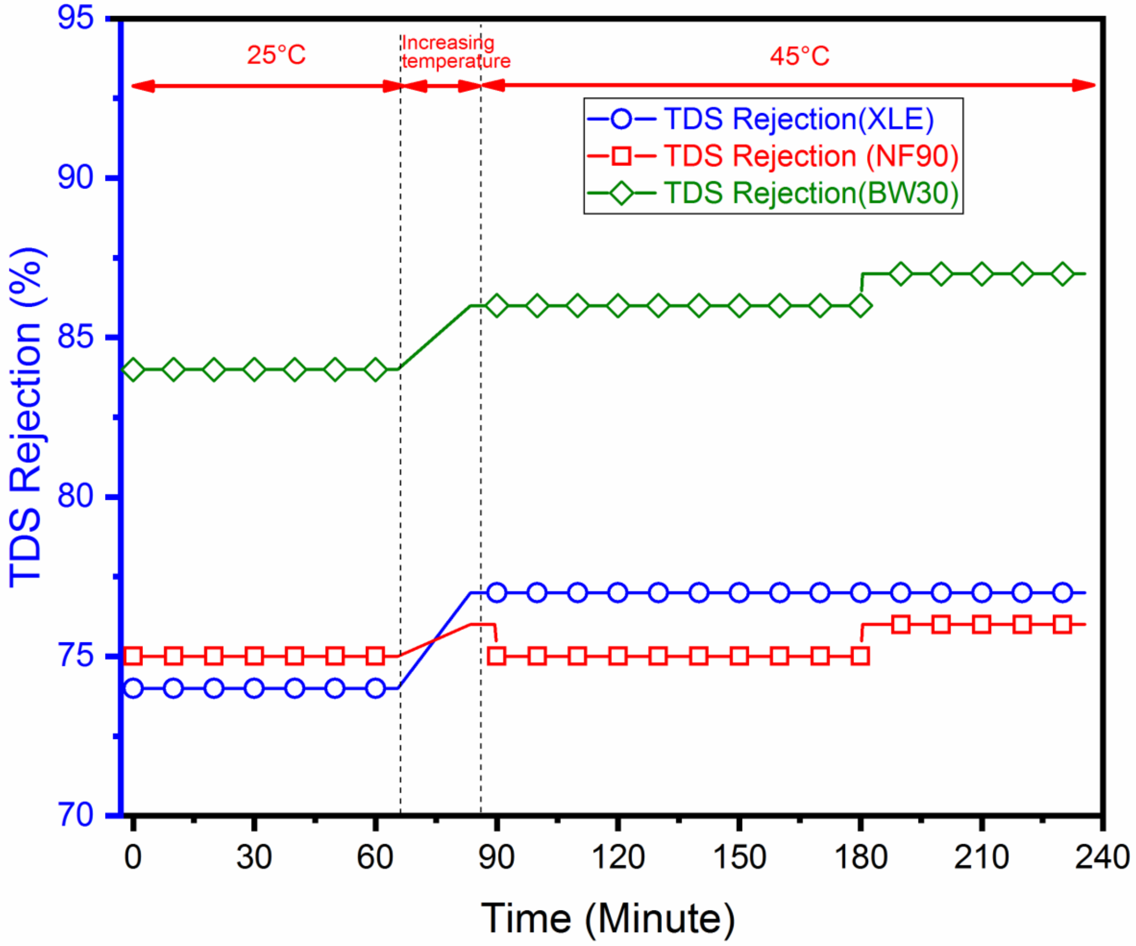

Figure B2: TDS rejection for all studied commercial membranes.