Application of Forward Osmosis Membrane Technology for Oil Sands Process-Affected Water Desalination

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Oil Sands Research and Information Network

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Table of Contents

LIST OF TABLES

LIST OF FIGURES

REPORT SUMMARY

The extraction process used to obtain bitumen from the oil sands produces large volumes of oil sands process-affected water (OSPW). As a newly emerging desalination technology, forward osmosis (FO) has shown great promise in saving electrical power requirements, increasing water recovery, and minimizing brine discharge. With the support of this funding, a treatment system was constructed using a cellulose triacetate (CTA) forward osmosis membrane to test the feasibility of OSPW desalination and contaminant removal. The forward osmosis systems were optimized using different types and concentrations of draw solution. The forward osmosis system using 4M NH_4HCO_3 as a draw solution achieved 85% water recovery from OSPW, and 80% to 100% contaminant rejection for most metals and ions.

A water backwash cleaning method was applied to clean the fouled membrane, and the cleaned membrane achieved 77% water recovery, a performance comparable to that of new forward osmosis membranes. This suggests that the membrane fouling was reversible.

The forward osmosis system developed in this project provides a novel and energy efficient strategy to remediate the tailings waters generated by oil sands bitumen extraction and processing.

ACKNOWLEDGEMENTS

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1 INTRODUCTION

The oil sands resources in Northern Alberta are the third-largest source of oil reserves in the world (after Saudi Arabia and Venezuela). The Athabasca oil sands deposit in Fort McMurray is the largest deposit in Northern Alberta, covering an area of more than 100,000 square kilometres. It is estimated that the Alberta oil sands contain over 1.8 trillion barrels of crude oil with over 178 billion barrels recoverable under current economic conditions. In 2008, the rate of oil production reached approximately 2 million barrels per day (Giesy et al. 2010), and it is anticipated that production may increase a few-fold within the next two decades (Siddique et al. 2008).

The crude oil production process in the mineable oil sands industry is composed of four major steps: mining, extraction, primary upgrading, and secondary upgrading. During extraction, oil sands are mixed with hot water, crushed, and then filtered through screens. The mixed slurry is then transported via pipeline (i.e., hydro-transport) to the bitumen extraction plants and fed to a separation vessel, where bitumen, water, and sands are separated through a "frothing" process. Fluid wastes generated from bitumen extraction are deposited into tailings ponds for storage on-site (Sanders et al. 2000). Since 1967, oil sands processing has resulted in production of over a billion cubic metres of tailings (Fakhru'l-Razi et al. 2010, Jordaan 2012). Once in the tailings ponds the coarse solids settle, leaving fine tailings in slurry and relatively solids-free oil sands process-affected water (OSPW) at the surface. The expansion of mineable oil sands operations will lead to increasing quantities of OSPW, treatment of which has become a significant issue for the industry.

Given the considerable volume of impounded wastewater and the need for reducing the consumption of fresh water sources, oil sands companies have been developing new technologies to maximize their ability to recycle water (Government of Alberta 2008). Syncrude Canada Ltd. recycled 85.0% of its tailings pond water and minimized the water use intensity (Manuel et al. 2009). Suncor Energy Inc. recycled 75.0% of its water in 2010 and has reduced its reliance on fresh water resources from the Athabasca River by 12.0% since 2009 (Suncor Energy Inc. 2011).

1.1 Motivation

Bitumen extraction from oil sands currently uses water-based extraction processes that produce 4 m^3 of tailings for every 1 m^3 of bitumen (Siddique et al. 2006); consequently, there are more than 180 square kilometres of tailings ponds in the oil sands region. At the same time, the demand for increasing amounts of fresh water from the Athabasca River is becoming a bottle-neck for future oil sands development. Recycling of oil sands process-affected water reduces the amount of fresh water used but it concentrates the total dissolved solids (TDS) from ore extraction chemicals and oil sands ores in OSPW. Therefore, desalination of OSPW is urgently needed to decrease the concentration of dissolved species to allow the water to be further

recycled in the bitumen extraction process or returned to the environment (Allen 2008a,b). Table 1 indicates the treatment targets of selected ions/metals that typically occur in OSPW[1].

Table 1. Treatment objectives for environmental discharge of OSPW. After Allen (2008b), CCME (2014).

Parameter (mg/L)	Typical OSPW	Environmental Guideline	Treatment objective (% removal)
Ammonia	14	0.800 to 1.300	64 to 93
Bicarbonate	775 to 950	500	50
Chloride	80 to 540	120	70
Sulphate	218 to 290	50	80
TDS	1,900 to 2,221	1,340	50 to 60
Aluminium	0.070 to 0.500	0.750	<80
Arsenic	0.006 to 0.015	0.005	<67
Chromium	0.003 to 2	0.074	<63
Copper	0.002 to 0.900	0.002	>95 – 99
Iron	0.800 to 3	0.300	<50
Lead	0.040 to 0.190	0.003	94 to 99
Nickel	0.006 to 2.800	0.052	93 to 99
Zinc	0.010 to 3.200	0.03	96

Motivated by a lack of cost effective and energy efficient technology for the desalination of OSPW, the present study was performed to investigate the potential application of forward osmosis (FO) technology to desalinate OSPW and remove toxic ions and metals. Information obtained from the study can be utilized to develop facilities for OSPW treatment.

1.2 Objectives

Our research is developing a novel, low-cost, and environment-friendly forward osmosis process to remove ions and metals in OSPW. This will allow less turbid water to be generated, which may be used for recycling in the oil sands extraction process or to be returned safely to the environment. The specific objectives were to:

1. Test the feasibility of forward osmosis technology in OSPW desalination;
2. Optimize the conditions of FO technology in OSPW treatment;
3. Evaluate the influence of draw solution on the performance of FO technology; and

[1] For a detailed review of metals, salts and organics in OSPW see Li, C., A. Singh, N. Klamerth, K. McPhedran, P. Chelme-Ayala, M. Belosevic and M. Gamal El-Din, 2014. Synthesis of Toxicological Behavior of Oil Sands Process-Affected Water Constituents. OSRIN Report No. TR-50. 101 pp. http://hdl.handle.net/10402/era.39659

4. Explore the fouling of the FO membrane and the possibility of reusing FO membranes after cleaning.

1.3 Report Organization

Proposed theories and experimental design of the forward osmosis process are discussed in sections 2 and 3. The effectiveness of FO technology in OSPW desalination under different experimental conditions is explored in section 4. Fouling of the FO membrane and the possibility of membrane reuse is also investigated in section 4.

2 BACKGROUND

2.1 Existing Desalination Technologies for OSPW Treatment

Our research group has been investigating various OSPW desalination techniques. Nanofiltration (NF), reverse osmosis (RO), and electrodialysis (ED) using novel nanocomposite membrane materials have been evaluated and optimized for OSPW treatment (Kim et al. 2011, 2012a,b,c, 2013a). An NF membrane with a molecular weight cutoff as low as 300 to 400 Da can reject >90% of multivalent ions and dissolved organics from contaminated water, although monovalent ions and volatile organics tend to pass through it (Kim et al. 2011). Reverse osmosis, on the other hand, can remove >90% of monovalent ions, as well as >98% of multivalent ions and dissolved organics. ED is an electrochemical membrane process using a combination of ion exchange (ion selective) membranes that selectively separate dissolved ions from water with electric current as a driving force. The average ED rejection rates of ionic species in OSPW are greater than 98% (Kim et al. 2013b).

OSPW desalination using RO and ED can produce high quality permeate water; however, these conventional water desalination technologies generally require intensive heat or electrical energy input, produce large volumes of concentrated wastewater or brine streams that need to be managed, and are highly vulnerable to membrane fouling (Elimelech and Phillip 2011). In addition, OSPW consists of high concentrations of organic compounds and suspended solids that cause severe and irreversible fouling of equipment components under the highly pressurized operational conditions.

Recent studies show that average capital and operational costs to desalinate OSPW in Fort McMurray are extremely high (Godwalt et al. 2010, Kim et al. 2012a). It is reported that the electrical energy for seawater desalination consumed by FO is 0.24 kWh/m^3, which is only 8% of the energy consumed by RO (3.02 kWh/m^3) (McGinnis and Elimelech 2007). Any advance in energy and cost efficiency that can be applied to desalination technology will have a profound impact on the future application of water desalination.

2.2 Forward Osmosis Technology

Forward osmosis (FO) technology applies a single salt (e.g., ammonium bicarbonate, NH_4HCO_3) draw solution that has a high total dissolved solids (TDS) concentration, to move water from the wastewater (in this case, OSPW) to the draw solution by way of natural osmotic pressure

(Figure 1). The draw solution is then easily desalinated by simply changing the pH or by moderate heating (< 60 °C at atmospheric pressure) since NH_4HCO_3 decomposes to NH_3, CO_2 and water at moderate high temperature. This natural tendency of water to move from a relatively low solute concentration region (wastewater) into a region of high solute concentration (single salt draw solution) does not require external pressure (energy).

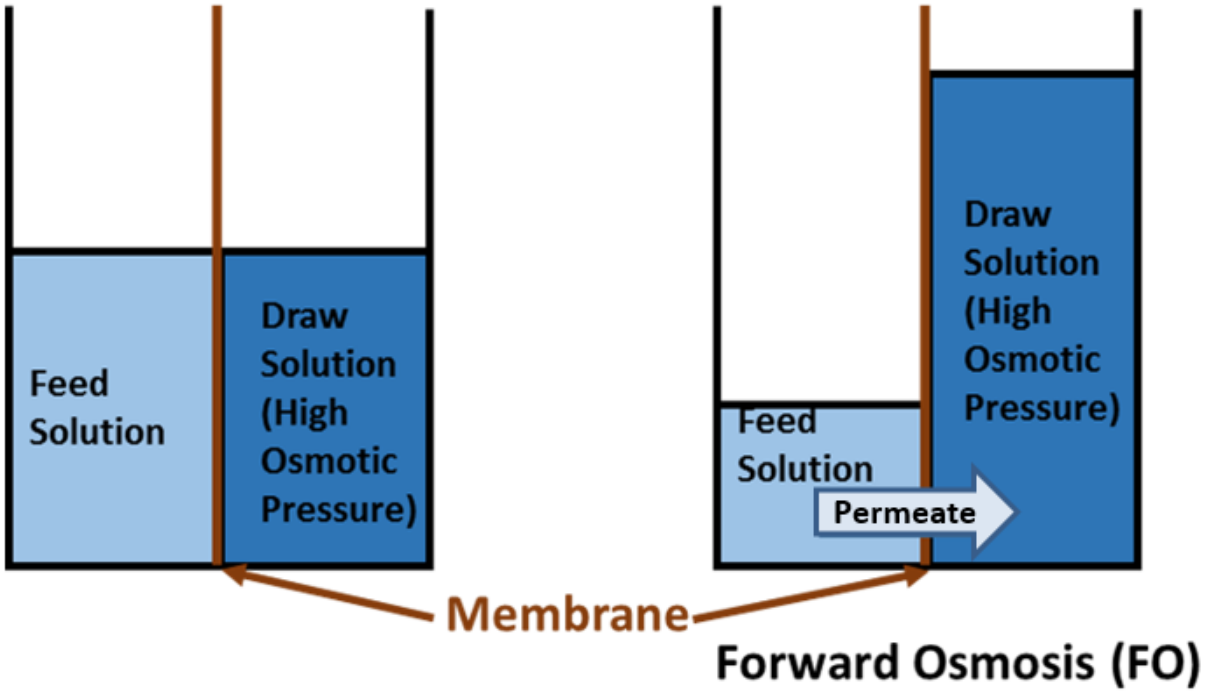

Figure 1. Principle of a forward osmosis treatment system.

Although this is a simple concept, the advantages of FO technology for water desalination have only recently been realized. Based on a recent search of the Web of Science database, only three academic papers on FO desalination were published before the year 2005; however, more than 150 academic papers have been published since then (around 100 papers of which were published after 2010). In general, studies on FO desalination (for examples see Cath et al. 2005a,b, Jiao et al. 2004) have shown the enormous potential of forward osmosis compared to other desalination methods for saving electrical power (e.g., 72% in McGinnis and Elimelech (2007)) and contributing to continued and sustainable development of the oil sands. A recent case study reported on the FO desalination of wastewater from oil and gas well fracturing in the U.S. (Hickenbottom et al. 2013)[2].

[2] See also http://oasyswater.com/case-study

Key advantages of FO systems are: (1) operation at very low or no hydraulic pressure (Cath et al. 2006, Zhao et al. 2012) and (2) high feed water (OSPW in current research) recovery. Due to a low hydraulic operating pressure, FO significantly reduces the potential for membrane fouling. This property is extremely beneficial for the treatment of water with high concentrations of organic and inorganic foulants (as in case of OSPW) (Kim et al. 2011, 2012c).

Energy costs greatly contribute to the operating costs of water treatment (McGinnis and Elimelech 2008) and these costs are critical considering the industry's long-term water treatment needs. Higher water flux rates (up to 10 times) and recoveries are possible with FO compared to RO because the fabric layers that protect the RO membrane from high pressures are unnecessary for FO membranes and because FO membranes can withstand osmotic driving forces greater than the hydraulic forces necessary to drive RO (McCutcheon et al. 2005).

3 METHODOLOGY

3.1 Set-up of an FO Membrane for OSPW Desalination

FO desalination reactors were set up in the laboratory according to the design shown in Figure 2. Ammonium bicarbonate (NH_4HCO_3) and urea (CH_4N_2O), a widely used fertilizer in Alberta, were used to prepare single salt draw solutions. A commercially available cellulose triacetate (CTA) FO membrane (Hydration Technology Innovations[3], Scottsdale, AZ, USA) was applied to separate the draw solution and OSPW held within two chambers with a functional surface area of 48 cm^2. The FO membrane was positioned with the active layer of the membrane facing the feed solution (OSPW) and the support layer facing the draw solution. The initial draw and feed solution volumes were 1,500 mL and 500 mL, respectively. Peristaltic pumps applied on both sides of the membrane produced a constant feed solution and draw solution flow with a flow rate of 21 mL/min (hydraulic retention time was 9 minutes). The system was operated in ambient laboratory conditions with a room temperature of 21 ± 1 °C.

As this was a proof-of-concept project there were no replicates in the experiments described below and therefore determining statistical significance of the results is not possible.

3.2 Characterization of OSPW and FO Membrane

Raw OSPW obtained from an oil sands tailings pond was used in this project. The OSPW was stored at 4 °C in a 158.9 L (one barrel) plastic container, and, after natural gravity settling, the supernatant was used in the experiment. To characterize OSPW, pH and electrical conductivity were measured, anion concentrations were measured by ion chromatography (IC), and metal concentrations were measured by inductively coupled plasma mass spectrometry (ICP-MS). Scanning electron microscopy (SEM) was used to observe the topography and surface structure of the CTA membrane.

[3] See http://www.htiwater.com/technology/forward_osmosis/index.html

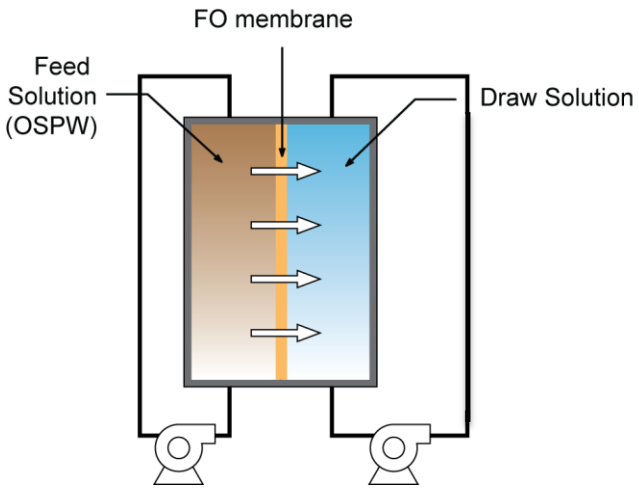

Figure 2. Forward osmosis system design for OSPW treatment.

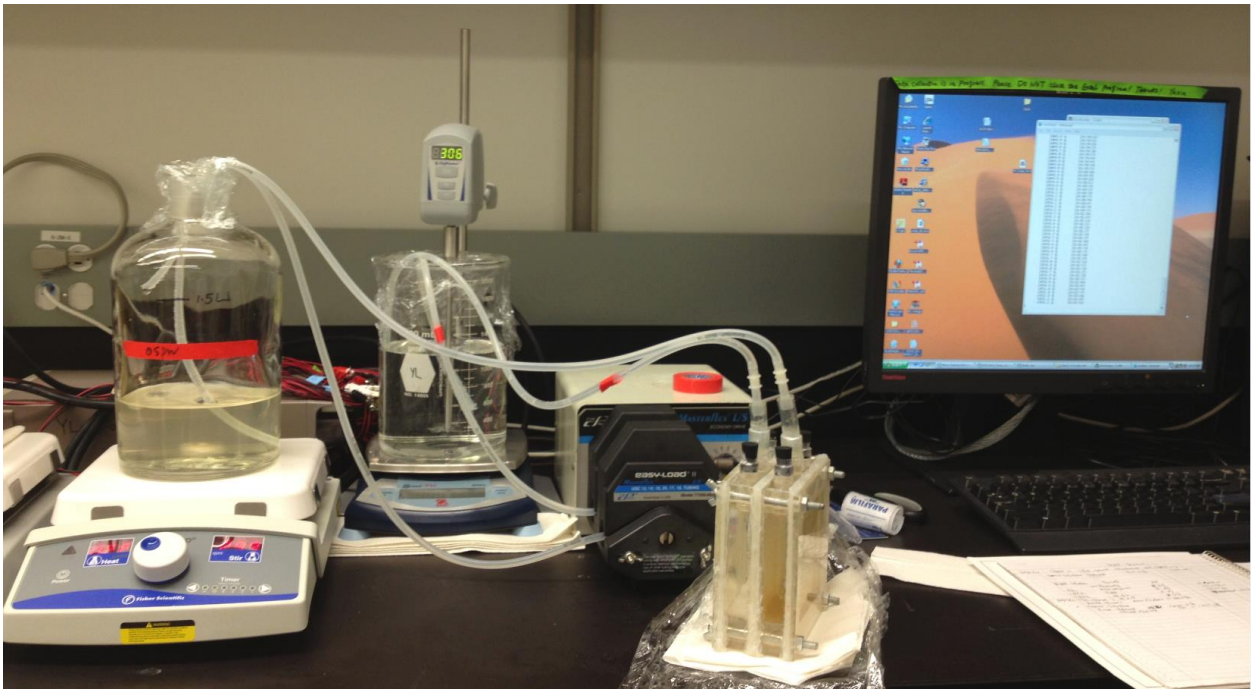

Figure 3. Laboratory scale forward osmosis system for OSPW treatment.

3.3 Performance of FO Membrane Desalination of OSPW

To evaluate the ability of the FO membrane to desalinate OSPW, water flux, water recovery, and ion and metal rejection were measured under a range of osmotic driving forces. Water flux was determined by dividing the weight change over time of the draw solution by the membrane area.

Water recovery was determined by the volume change of feed solution after 28 hours of FO as shown in the following equation:

$$\text{Recovery}(\%) = \frac{V_{\text{permeate}}}{V_{\text{feed}}} \times 100\%$$

Where, V is the volume of the permeate (determined by the weight change of the draw solution) or the feed.

In this report, the term *water recovery* is used to describe the volume change of feed solution (as a result of water movement to the draw solution) after 28 hours FO treatment. We did not take the next step of desalinating the draw solution to actually *recover* the cleaned OSPW water. This could be done by simply changing the pH, moderate heating (< 60 °C at atmospheric pressure), or additional RO treatment with much reduced fouling potential and enhanced water flux.

Ion and metal rejection were determined by the following equation:

$$\text{Rejection}(\%) = (1 - \frac{C_{\text{permeate}}}{C_{\text{feed}}}) \times 100\%$$

Where, C is the concentration of the permeate (determined by dividing the draw solution mass change by its volume change) or the feed.

OSPW quality before and after treatment was assessed by measuring pH, conductivity, and ion and metal concentrations.

Ion concentrations were determined by IC and ICP-MS. Samples were filtered and acidified prior to measure by ICP-MS. Firstly, samples were filtered by 0.45 μm Teflon filters. Sequentially, 10 mL samples were diluted to 50 mL using 1% trace metal grade HNO_3. Thereafter, the samples were analysed by ICP-MS (Elan 9000, PerkinElmer). ICP-MS Multi-Element Solution 2 w/o Mercury (#CLMS-2N) obtained from SPEX CertiPrep® was used as the standard.

For IC measurement, samples were filtered through 0.45 μm Teflon filters then analysed by IC (ICS-2100, Dionex). Seven Anion Standard II (Dionex # 057590) stock solution were used as the standard solution.

3.4 Optimization of FO Desalination of OSPW

To optimize OSPW desalination by FO, the performance of different types and concentrations of draw solution (2M NH_4HCO_3, 4M NH_4HCO_3, and 4M urea) was compared by the experimental methods described above. The osmotic pressures of 2M NH_4HCO_3, 4M NH_4HCO_3, and 4M urea are 91.00, 182.01, and 0.024 bar respectively.

3.5 Characterization of Fouled FO Membrane

Membrane surface morphology was observed using scanning electron microscopy (SEM) before and after OSPW treatment. For SEM imaging, the membrane samples were coated with a 5 nm

gold layer by sputter coating (Edwards S510B sputter coater, VHH Ltd., Crawley, United Kingdom). The coated membrane was visualized with a Vega-3 SEM (Tescan, Brno, Czech Republic).

4 RESULTS AND DISCUSSION

4.1 Characterization of Oil Sands Process-Affected Water (OSPW) and Forward Osmosis (FO) Membrane

4.1.1 *Characterization of OSPW*

Ion and metal concentrations, and the pH and conductivity of the fresh OSPW used in this study, were measured to characterize OSPW properties (Table 2). The values of pH, conductivity, and concentrations of ion and metal, are comparable to previous measurements (Kim et al. 2012).

Table 2. Characterization of the oil sands process-affected water in this study.

Major Ions	**Concentration (mg/L)**	**Environmental guideline (CCME 2014)**
F^-	3.3 ± 1.8	0.12
Cl^-	517.0 ± 37.3	120
NO_2^-	253.4 ± 134.9	0.006
SO_4^{2-}	177.7 ± 20.1	50
Br^-	140.9 ± 21.4	N/A
NO_3^-	62.0 ± 11.9	13
Na	980.6 ± 23.8	N/A
Mg	10.7 ± 0.5	N/A
K	17.9 ± 1.7	N/A
Ca	18.6 ± 3.8	N/A
Si	10.9 ± 8.1	N/A
Trace element	**Concentration (µg/L)**	
Al	91.5 ± 43.0	750
P	208.5 ± 237.4	100 (eutrophic lake)
Ni	10.1 ± 0.9	25 (hardness 50 mg/L $CaCO_3$)
Cu	10.3 ± 2.0	2 (hardness 50 mg/L $CaCO_3$)

Trace element	**Concentration (µg/L)**	
Se	13.9 ± 3.1	N/A
Sr	679.0 ± 26.7	N/A
Mo	151.8 ± 5.9	73
Ba	67.3 ± 16.4	N/A
Cr	322.0 ± 282.3	74
Fe	149.1 ± 110.3	300
pH	8.8 ± 0.2	
Conductivity	3.8 ± 0.3 (mS/cm)	

4.1.2 *Characterization of FO Membrane*

A cellulose triacetate (CTA) FO membrane (Hydration Technology Innovations, Scottsdale, AZ, USA) was applied to separate the draw solution and OSPW between two chambers. The surface area is 8 × 8 cm^2, and the chamber volume is 128 cm^3.

SEM was used to observe the topography of active and support layers. Figure 4 shows typical SEM images of FO membranes. Pore structures found on the active layer were consistent with the reported structure of CTA membranes (Wang et al. 2012).

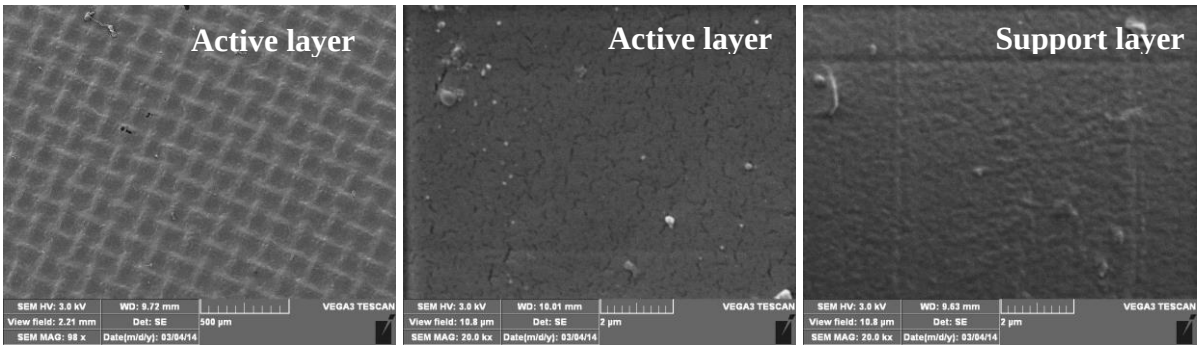

Figure 4. Typical SEM images of FO membranes.
A forward osmosis membrane was coated with 5 nm gold by sputter coating and visualized with a Vega-3 SEM.

4.2 Performance of FO for OSPW Treatment using 4M NH_4HCO_3 as a Draw Solution

4.2.1 *Water Flux and Water Recovery of FO System*

NH_4HCO_3 is used widely as an effective draw solution in FO technology because it has good solubility in water and is able to generate high osmotic pressure, which is crucial for achieving good water flux and water recovery (Ng et al. 2006). Also, NH_4HCO_3 is easily decomposed by heating to produce fresh water (Ng et al. 2006). In this project, 4M NH_4HCO_3 was applied as a draw solution to test the feasibility of its application to FO desalination of OSPW.

Figure 5 shows the changes in water flux as a function of operating time. The water flux reached a maximum of around 68 L/m^{2}h at the beginning of FO, then dropped quickly and stabilized around 5 L/m^{2}h. Our observation is comparable to the reported 1 to 10 μm/s (3.6 to 36 L/m^{2}h) for NaCl desalination using NH_4HCO_3 as a draw solution at a laboratory scale (McCutcheon et al. 2006). In another report regarding FO treatment of drilling wastewater using 260 g/L NaCl as a draw solution, the maximum water flux reached 14 L/m^{2}h, then decreased to a final water flux of 2 to 4 L/m^{2}h (Hickenbottom et al. 2013). A pilot scale FO process to treat frac flowback (McGinnis et al. 2013) using NH_4HCO_3 as a draw solution, achieved 2.6 L/m^{2}h water flux and 64% water recovery.

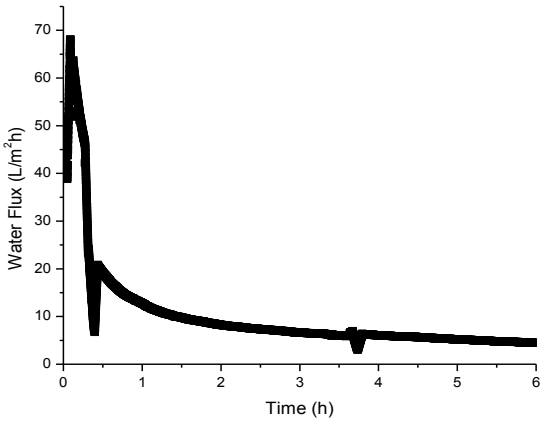

Figure 5. Permeate water flux through FO membrane using 4M NH_4HCO_3 as a draw solution.

The water flux achieved in this project was much higher than the water flux in Hickenbottom et al. suggesting that NH_4HCO_3 can be used as a competitive draw solution for industrial wastewater treatment using FO technology.

In this project, the recovery of water from OSPW was 85% after 28 hours operation (since the weight of draw solution stopped increasing after 28 hours operation, we assume no water could be recovered after 28 hours), a result comparable to the reported 75% to 85% water recovery in previous reports (Hickenbottom et al. 2013, McCutcheon et al. 2006). The water recovery achieved in this project was slightly lower than the reported 80% to 95% achieved by the reverse

osmosis (RO) system (e.g., 95% for dairy industrial wastewater treatment) (Vourch et al. 2008). The conductivity of feed OSPW increased from 3.8 mS/cm to 35.5 mS/cm during deionization.

4.2.2 *Solute Rejection in FO System*

Reverse solute transportation, or solute rejection, is another important factor in FO membrane performance. Figure 6 shows the ions and metals rejected in the FO process using 4M NH_4HCO_3 as a draw solution. The CTA membrane applied in this experiment showed good rejection (70% to 100%) of Cl^-, F^-, NO_2^-, Br^- ions and Al, Ca, Fe, Sr, Mo, Ba metals; and moderate rejection of SO_4^{2-}, Na, K, and Se (30% to 70%). It is interesting that little to no rejection of NO_3^-, Mg, Si, P, Cr, Ni, and Cu was observed, and further experiments are needed to fully address this result.

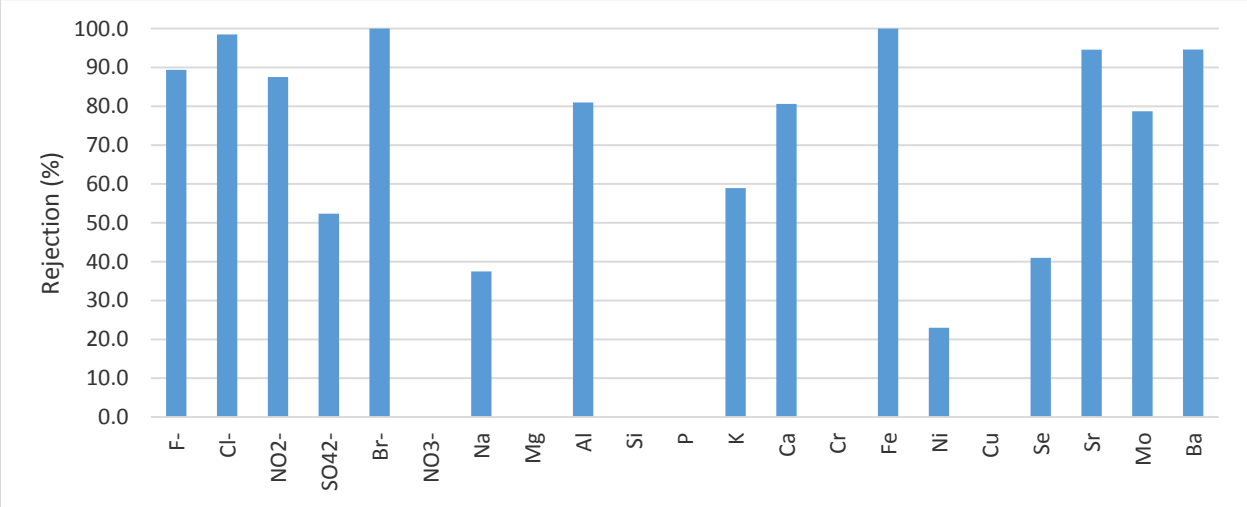

Figure 6. CTA forward osmosis membrane rejection of ions and metals in OSPW.

4.3 Backwash Cleaning of Fouled Membrane

During FO desalination of OSPW, membrane fouling was caused by contaminants in OSPW. Membrane cleaning was necessary for efficient membrane reuse. After 28 hours of operation using 4M NH_4HCO_3 as a draw solution, water backwash was applied to clean the FO membrane. The cleaned CTA membrane was reapplied to desalinate OSPW.

Water flux through the backwashed membrane as a function of time is shown in Figure 7. The maximum permeate water flux was 122.8 L/m^2h, which is much higher than the maximum water flux of the original membrane (68 L/m^2h). This suggests that pre-treatment of the membrane using water might help to improve the water flux; therefore, in other experimental tests the FO membrane was pretreated by soaking in distilled deionized water for 24 hours before application in the FO system. However, the water flux dropped quickly, and the recovery of water from OSPW was 77% after 28 hours FO, which was slightly lower than water recovery

with the original membrane (85%). The conductivity of feed OSPW increased from 3.8 mS/cm to 25.9 mS/cm during the second desalination trial.

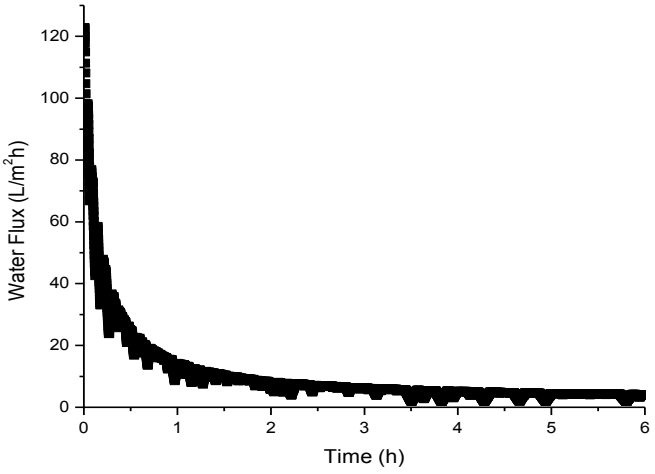

Figure 7. Permeate water flux through FO membrane after water backwash.

4.4 Performance of FO in OSPW Desalination using Different Draw Solutions

4.4.1 *Performance of FO in OSPW Desalination using 2M NH_4HCO_3 as Draw Solution*

To test the impact of draw solution concentration on FO performance, 2M NH_4HCO_3 was applied as the draw solution for OSPW desalination. Permeate water flux as a function of time is shown in Figure 8A and Table 3. The maximum water flux using 2M NH_4HCO_3 was 120 L/m^{2}h compared to a maximum water flux of 68 L/m^{2}h using 4M NH_4HCO_3. However, water recovery after 28 hours of operation was 57.7% using 2M NH_4HCO_3 and 85% using 4M NH_4HCO_3, and the conductivity of feed OSPW was 15.25 mS/cm using 2M NH_4HCO_3 vs. 35.5 mS/cm using 4M NH_4HCO_3 during desalination (Table 3).

Table 3. Performance of FO for OSPW desalination using different draw solutions.

	Water flux (L/m^{2}h)	Recovery (%)	Conductivity (ms/cm)
4M NH_4HCO_3	68.08	85.0	35.50
4M NH_4HCO_3 H_2O backwash	122.80	77.0	25.90
2M NH_4HCO_3	120.00	57.7	15.25
4M Urea	110.00	22.5	4.57

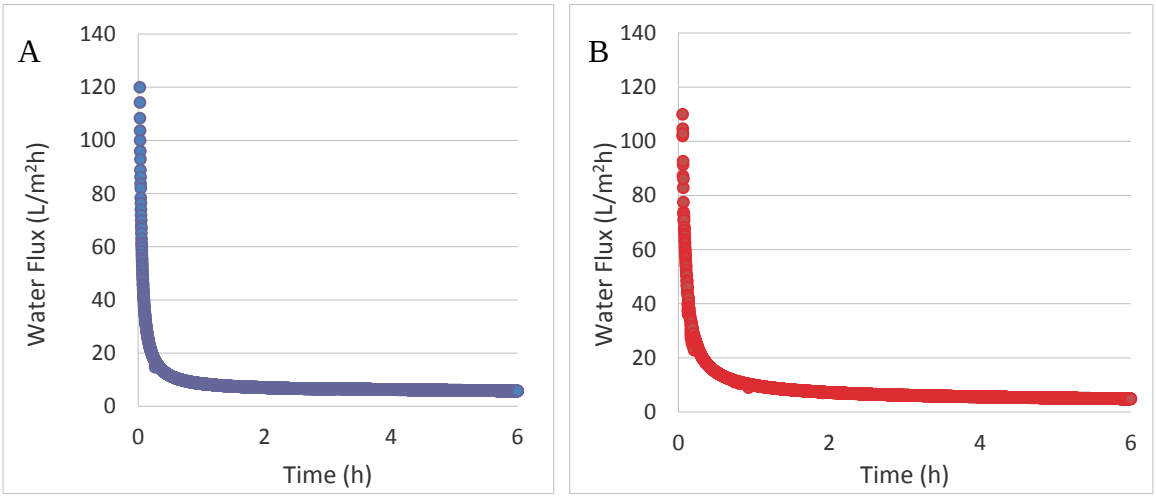

Figure 8. Permeate water flux through forward osmosis membrane for OSPW treatment using 2M NH_4HCO_3 (A) and 4M urea (B) as draw solutions.

4.4.2 *Performance of FO in OSPW Desalination using 4M Urea as Draw Solution*

Another promising area of FO application is desalination of OSPW for irrigation using fertilizers as draw solutions. When fertilizers are used as draw solutions, the diluted draw solution after FO treatment can be directly used for fertigation (assuming no contaminants were imported from the feed); therefore, there is no need for separation and recovery (Phuntsho et al. 2012).

Urea is one of the most widely used fertilizers in Alberta. In the present study, 4M urea solution was applied as a draw solution in the FO process. The TDS of 4M urea was 240 g/L. The water flux is shown in Figure 8B and Table 3. The maximum water flux using 4M urea was 110 L/m^{2}h, comparable to that of FO treatment using 2M NH_4HCO_3 as a draw solution, however water recovery and OSPW conductivity were considerably lower (Table 3).

4.4.3 *Comparison of the Performance of FO in OSPW Desalination using Different Draw Solutions*

Water flux, water recovery, and ion and metal rejection during FO desalination of OSPW using different draw solutions are compared in Figures 8 and 9. 4M NH_4HCO_3 was the most effective draw solution in FO desalination of OSPW, and recovery of water from OSPW reached 85% after 28 hours of operation. However, water recovery after 28 hours of FO using 4M urea as a draw solution was only 22.5%, which was much lower than water recovery using NH_4HCO_3 (Figure 9). And the conductivity of feed OSPW increased only slightly from 3.8 mS/cm to 4.57 mS/cm during desalination using urea (Table 3).

As shown in Figure 10, rejection of ions and metals was different for different draw solutions. To better compare the ions and metals rejection, the rejection performance of ions and metals by different draw solutions has been divided into three levels: good (70% to 100%), moderate (30%

to 70%), and poor (0% to 30%). Table 4 shows the comparison of rejection based on the three levels:

- 2M NH_4HCO_3 showed
  - good rejection of NO_2^-, SO_4^{2-}, Br^-, NO_3^-, Ca, Cr, Fe, Sr, Mo, Ba
  - moderate rejection of Cl^-, Na, Al, Si, P, K, Ni, Cu, Se, and
  - little to no rejection of F^- and Mg.
- 4M Urea solution showed the best performance in rejection of ions and metals (all but Fe were in the good range).
- With the exception of Cl^-, the FO system using 4M NH_4HCO_3 after water backwash showed similar or better performance than the 4M NH_4HCO_3 without backwash:
  - good rejection of F^-, NO_2^-, Br^-, Al, Ca, Fe, Sr, Mo, Ba,
  - moderate rejection of Cl^-, SO_4^{2-}, Na, K, Cr, Ni, Cu, Se, and
  - little to no rejection of NO_3^-, Mg, Si, P.

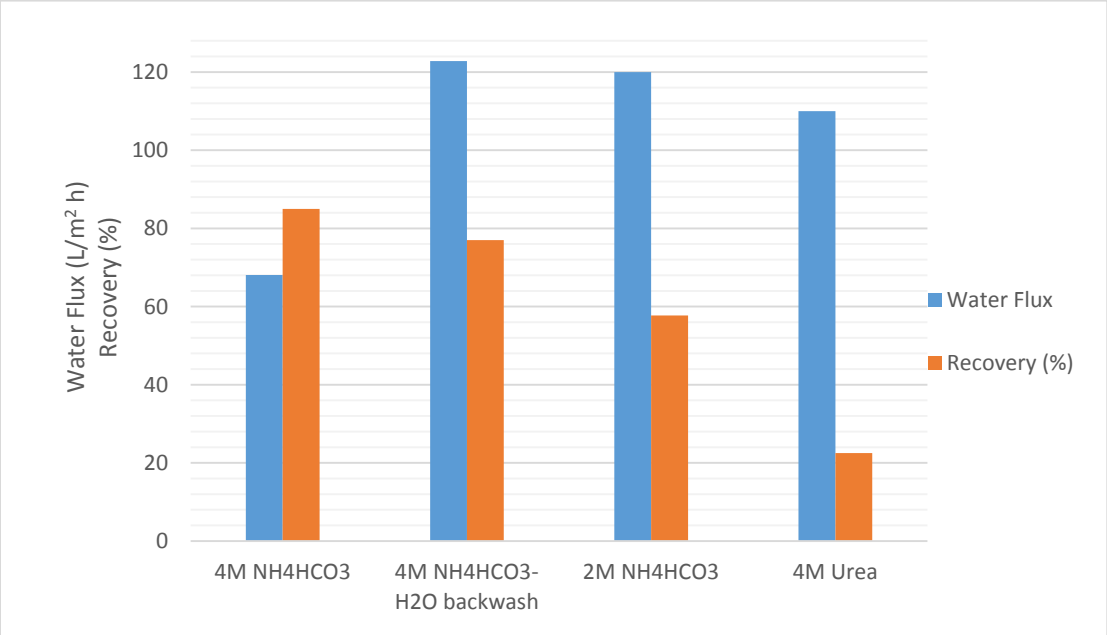

Figure 9. Comparisons of water flux and water recovery through FO membrane using different draw solutions.

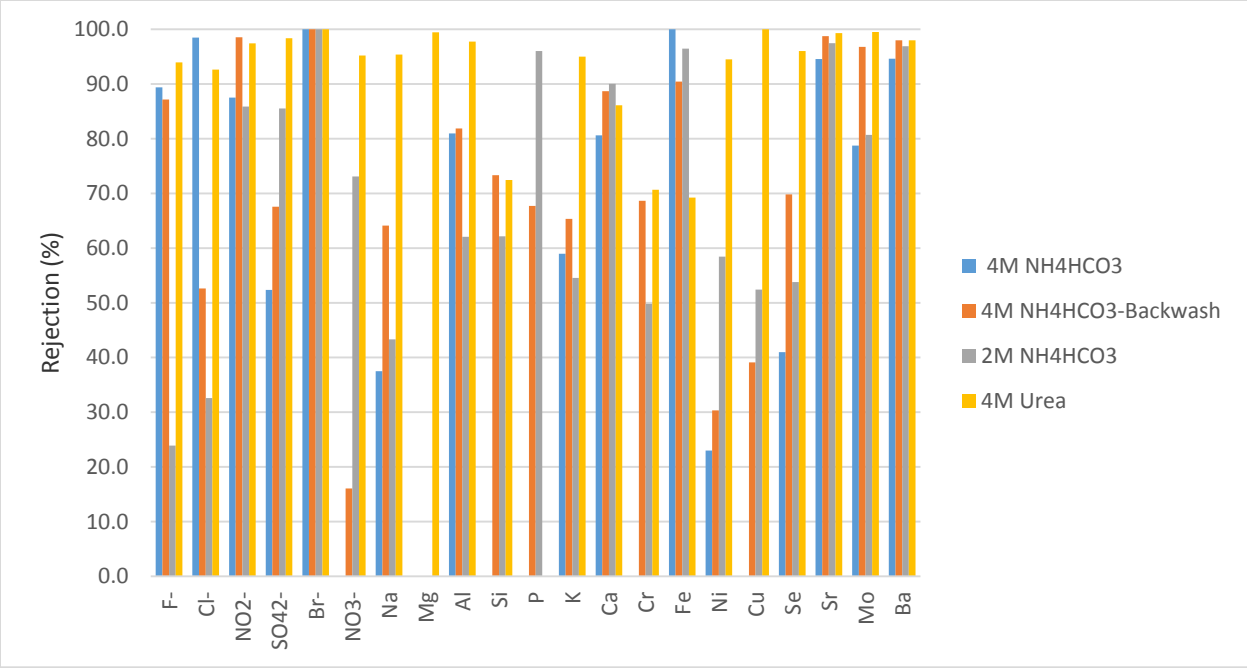

Figure 10. Ion and metal rejection by an FO membrane using different draw solutions.

Table 4. Comparison of ion and metal rejection by an FO membrane using different draw solutions.

Draw Solution	Rejection		
	Good (70% to 100%)	***Moderate (30% to 70%)***	***Poor (0% to 30%)***
4M NH_4HCO_3	F^-, Cl^-, NO_2^-, Br^-, Al, Ca, Fe, Sr, Mo, Ba	SO_4^{2-}, Na, K, Se	NO_3^-, Mg, Si, P, Cr, Ni, Cu
4M NH_4HCO_3 with water backwash	F^-, NO_2^-, Br^-, Al, Ca, Fe, Sr, Mo, Ba	Cl^-, SO_4^{2-}, Na, K, Cr, Ni, Cu, Se	NO_3^-, Mg, Si, P
2M NH_4HCO_3	NO_2^-, SO_4^{2-}, Br^-, NO_3^-, Ca, Cr, Fe, Sr, Mo, Ba	Cl^-, Na, Al, Si, P, K, Ni, Cu, Se	F^-, Mg
4M Urea	F^-, Cl^-, NO_2^-, SO_4^{2-}, Br-, NO_3^-, Na, Mg, Al, Si, P, K, Ca, Cr, Ni, Cu, Se, Sr, Mo, Ba	Fe	

4.4.4 *Characterization of Fouled FO Membrane*

SEM was used to observe the foulant layer on membrane surfaces. Figure 10A shows an OSPW fouled FO membrane after using 4M NH_4HCO_3 as a draw solution; Figure 10B shows the membrane after cleaning by water backwash. Figures 11C and 11D show OSPW-fouled

FO membranes after using 2M NH_4HCO_3 and 4M urea, respectively, as draw solutions. OSPW foulant displayed a different morphology on each membrane.

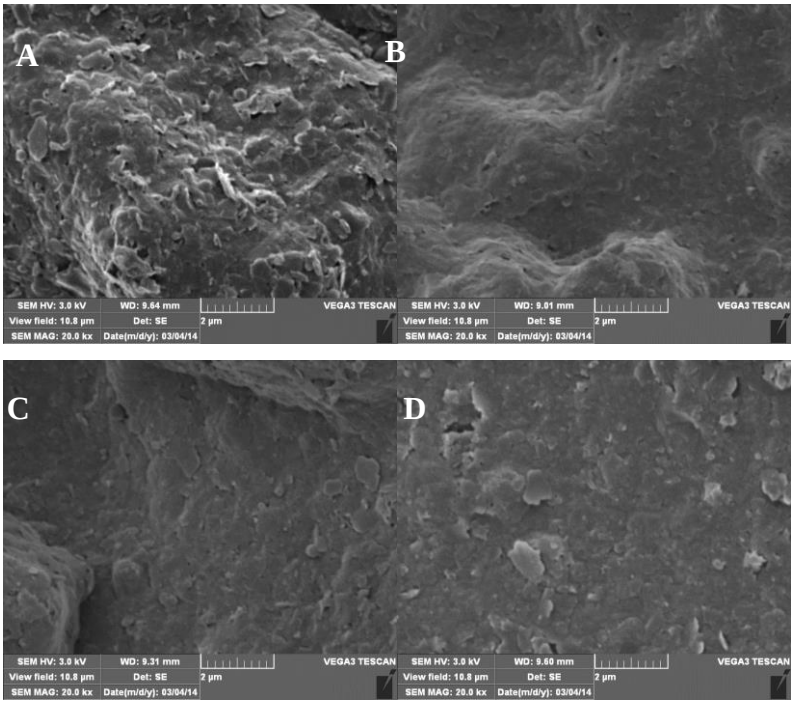

Figure 11. SEM images of OSPW fouled FO membranes.
FO was performed using 4M NH_4HCO_3 (A, B), 2M NH_4HCO_3 (C), and 4M urea (D) as draw solutions. The membrane in B is shown after water backwash.

5 CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

FO desalination of OSPW with 4M NH_4HCO_3 as a draw solution achieved the highest recovery of water within 28 hours of operation, although the permeate water flux of FO using 4M NH_4HCO_3 was not the highest. Therefore 4M NH_4HCO_3 was the most suitable draw solution in this study. The findings suggest that a forward osmosis system developed with the methods described here is a promising technology to remove inorganic ions and metals from oil sands wastewater with lower energy consumption compared to traditional desalination technologies, e.g., reverse osmosis. Results of this project will benefit the oil sands and other industries across Canada that produce high salinity and contaminated wastewater.

The findings of the experiments performed in this research are summarized below:

- With 4M NH_4HCO_3 as a draw solution, the FO system reached a maximum of around 68 L/m^2h water flux to treat OSPW, and the recovery of water from OSPW was 85% after 28 hours of operation. The CTA membrane applied in this

experiment showed good rejection (70% to 100%) of Cl^-, F^-, NO_2^-, and Br^- ions and Al, Ca, Fe, Sr, Mo, and Ba metals; and moderate rejection (30% to 70%) of SO_4^{2-}, Na, K, and Se. It is interesting that little to no rejection of NO_3^-, Mg, Si, P, Cr, Ni, and Cu was observed. Further experiments are needed to fully address this result.

- The water back wash method was applied to clean the FO membrane after 28 hours of operation using 4M NH_4HCO_3 as a draw solution, to test the possibility of reuse of FO membranes. With the reused FO membrane, the maximum permeate water flux was 122.8 L/m^{2}h and the recovery of water from OSPW was 77% after 28 hours of FO, which was slightly lower than the water recovery with the original membrane (85%). The rejection rates of different ions before and after backwashing were comparable for most ions (Figure 9). These results suggest that the membrane is reusable in this FO system. This system showed good rejection of F^-, NO_2^-, Br^-, Al, Ca, Fe, Sr, Mo, Ba, moderate rejection of Cl^-, SO_4^{2-}, Na, K, Cr, Ni, Cu, Se, and little to no rejection of NO_3^-, Mg, Si, P.
- 2M NH_4HCO_3 was also applied as a draw solution for OSPW desalination to test the impact of draw solution concentration on FO performance. The maximum water flux using 2M NH_4HCO_3 was 120 L/m^{2}h compared to a maximum water flux of the backwashed membrane of 122.8 L/m^{2}h using 4M NH_4HCO_3. However, water recovery after 28 hours of operation was 57.7% using 2M NH_4HCO_3 and 85% using 4M NH_4HCO_3. 2M NH_4HCO_3 showed good rejection of NO_2^-, SO_4^{2-}, Br^-, NO_3^-, Ca, Cr, Fe, Sr, Mo, Ba, moderate rejection of Cl^-, Na, Al, Si, P, K, Ni, Cu, Se, and little to no rejection of F^- and Mg.
- Urea, one of the most widely used fertilizers in Alberta, was applied as a draw solution in the FO process to test the feasibility of the application of desalinated OSPW in fertigation. The maximum water flux using 4M urea was 110 L/m^{2}h, which is comparable to that of FO treatment using NH_4HCO_3 as a draw solution. However, after 28 hours of operation, the FO water recovery using 4M urea as a draw solution was only 22.5%, which was much lower than the FO water recovery using NH_4HCO_3 as a draw solution. The system using 4M urea showed good rejection (70% to 100%) of F^-, Cl^-,NO_2^-,SO_4^{2-}, Br^-, NO_3^-, Na, Mg, Al, Si, P, K, Ca, Cr, Ni, Cu, Se, Sr, Mo, Ba, and moderate rejection of Fe (30% to 70%).
- The FO systems using different draw solutions showed different rejection of ions and metals. Generally, the rejection performance of FO systems for ions and metals showed a reverse relationship with their water flux and water recovery performance; 4M urea solution showed the best performance in rejection of ions and metals.

5.2 Recommendations

Additional research could further explore the possibility of using FO technology in the oil sands industry. Although successful commercial applications of FO have been demonstrated for oil field wastewater treatment, this is the first study evaluating FO applications on OSPW

desalination. To better optimize the FO process for industrial application, future studies should investigate:

- Options for draw solution reuse,
- Disposal options of concentrated OSPW by the FO system,
- Conditioning of membranes,
- Influence of draw solution on membranes,
- Losses in draw solutions (through membrane and during recovery),
- Optimize the FO process under pilot and full scale conditions.

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7 GLOSSARY

7.1 Terms

Desalination

Desalination refers to any of several processes that remove some amount of salt and other minerals from saline water.

Draw Solution

Draw solution, also called osmotic agent, draw agent, etc., has a high solute (salt) concentration.

Feed Solution

Feed solution is the solution with low solute (relative to draw solution) concentration. The wastewater to be treated; in this case OSPW.

Foulant

Foulant refers to materials in water that cause membrane fouling during osmosis.

Hydraulic Retention Time

Hydraulic retention time refers to the average length of time that a volume of water remained in a system. Hydraulic retention time is calculated as the volume of the system divided by the inflow rate.

Ion/Metal Rejection

Ion rejection is determined by the ion concentration change after 28 hours of FO as shown in the following equation.

$$\text{Rejection}(\%) = (1 - \frac{C_{\text{permeate}}}{C_{\text{feed}}}) \times 100\%$$

Where, C is the concentration of the permeate (determined by dividing the draw solution mass change by its volume change) or the feed.

Membrane Fouling

Membranes are fouled during osmosis when solute particles deposit onto the membrane surface or into membrane pores. Membrane fouling inhibits the membrane's performance, reducing water flux and lowering the quality of the water produced.

Permeate

Permeate is the solute which diffuse through the FO membrane from feed solution to draw solution.

Water Flux

Water flux is determined by dividing the weight change over time of the draw solution by the membrane area.

Water Recovery

Water recovery is determined by the volume change of feed solution after 28 hours of FO as shown in the following equation:

$$\text{Recovery}(\%) = \frac{V_{\text{permeate}}}{V_{\text{feed}}} \times 100\%$$

Where, V is the volume of the permeate (determined by the weight change of the draw solution) or the feed.

7.2 Acronyms

CHWE	Clark Hot Water Extraction
ED	Electrodialysis
FO	Forward Osmosis
IC	Ion Chromatography
ICP-MS	Inductively Coupled Plasma–Mass Spectrometry
MFT	Mature Fine Tailings
NF	Nanofiltration
OSPW	Oil Sands Process-Affected Water
OSRIN	Oil Sands Research Information Network
RO	Reverse Osmosis
SEE	School of Energy and the Environment
SEM	Scanning Electron Microscopy
TDS	Total Dissolved Solids

7.3 Chemicals

CH_4N_2O	Urea
CTA	Cellulose Triacetate
NH_4HCO_3	Ammonium Bicarbonate

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