OIL REMOVAL FOR PRODUCED WATER TREATMENT AND MICELLAR CLEANING OF ULTRAFILTRATION MEMBRANES

A Thesis

by

SCOTT JAY BEECH

Submitted to the Office of Graduate Studies of
Texas A&M University
in partial fulfillment of the requirements for the degree of

MASTER OF SCIENCE

August 2006

Major Subject: Biological and Agricultural Engineering

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Approved by:

Chair of Committee,	Bruce J. Lesikar
Committee Members,	David Burnett
	Zivko Nikolov
Head of Department,	Gerald Riskowski

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ABSTRACT

Oil Removal for Produced Water Treatment and Micellar Cleaning of Ultrafiltration Membranes. (August 2006)

Scott Jay Beech, B.S., Texas A&M University

Chair of Advisory Committee: Dr. Bruce J. Lesikar

Produced water is a major waste produced from oil and natural gas wells in the state of Texas. This water could be a possible source of new fresh water to meet the growing demands of the state after treatment and purification. This thesis describes a research project that evaluated the treatment of brine generated in oil fields (produced water) with ultrafiltration membranes. The characteristics of various ultrafiltration membranes for oil and suspended solids removal from produced water were studied to test whether they could be used in a pretreatment method. The research measured the effect of pressure and flow rate on performance of three commercially available membranes for treatment of oily produced water. Oil and suspended solids removal were measured by using turbidity and oil in water measurements taken periodically.

The study also analyzed the flux through the membrane and any effect it had on membrane performance. The research showed that an ultrafiltration membrane provided turbidity removal of over 99% and oil removal of 78% for the produced water samples. The results indicated that the ultrafiltration membranes would be useful as one of the first steps in purifying the water.

Membrane cleaning of produced water-fouled membranes by micellar solutions was investigated. A neutral pH and ambient temperature micelle solution for effective cleaning of oily water-fouled membranes was developed and studied. The performance of cleaning solutions on ultrafiltration membranes was investigated on laboratory size membrane testing equipment. Different micro emulsion solutions were studied to evaluate the effect of solution properties on cleaning performance. Three types of multiple membranes were studied, each having the same polyvinylidene fluoride (PVDF) material but with different nominal separation or flux characteristics. The data showed that the use of a micelle solution to clean the produced water-fouled membranes was a feasible and effective method. The study showed with further adjustment of the micelle solution the cleaning effectiveness could be optimized to provide double the effectiveness of current industry methods for membranes fouled by produced water.

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1. INTRODUCTION

Advances in membrane technology have allowed the development of an effective onsite treatment system for the conversion of produced water into a potable fresh water resource. Produced water represents waste generated by the oil and gas industry. If it is cleaned and desalinate, it can help in meeting future fresh water needs in the state of Texas.

The goal of this project was to determine the best membrane technology for the economical onsite pretreatment of produced water. This project included a study of the feasibility of using micellar solutions to clean the membrane fouling that occurs during onsite operation.

The specific objectives of this research has been 1) to determine the most effective commercial available ultrafiltration membrane and effect of operation parameters for onsite produced water pretreatment, 2) to determine whether micelle solutions for membrane cleaning are effective, 3) and to determine effects of different micelle solution compositions for membrane cleanup.

The research data are compiled and presented as two separate studies:

- The screening and evaluation of the most effective ultrafiltration membranes for use in oilfield brine pretreatment for turbidity and oil removal to meet feed water quality requirements for desalination.
- To evaluate cleaning parameters and use of micelle solutions to remove fouling caused by produced water fouled ultrafiltration membranes under ambient temperature and pH for an onsite treatment system.

This thesis follows the style and format of Journal of Membrane Science.

1.1. Background

The oil and gas industry produces large amounts of wastewater as one of the byproduct of production. This wastewater is commonly referred as produced water or oilfield brine. In Texas, the oil and gas industries produce 250 billion gallons of produced water annually [1]. This produced water, treated currently as waste, could be a major resource to reduce water shortages in Texas [1].

Currently produced water is typically disposed in injection wells as waste or for pressure maintenance of the reservoir [1-2]. Produced water disposal and handling is covered by the Clean Water Act and United States Environmental Protection Agency (EPA) and is treated as a non-hazardous waste from oil and gas production and is exempt from the Resource Conservation and Recovery Act (RCRA) for monitoring specific constituents [2-3]. These disposal wells are tightly monitored and controlled to prevent groundwater contamination through overfilling or too high contaminant loads [3]. These restrictions on injection wells size, depth, and capacity were developed by the EPA to prevent pollution of current underground fresh water supplies or future sources of fresh water. The current regulation on produce water is based on the Best Practicable Technology (BPT) for onshore production [3]. The BPT limit set by the EPA is 35 mg/L oil and grease daily max for use as an agricultural or wildlife reuse or no onsite discharge for onshore production facilities [3].

Produced water in Texas has widely varying composition [2, 4]. Produced water contains suspended oil and grease, organics, dissolved and suspended solids, salts and various other trace metals. Their characteristics differ depending on the particular

location of the oil well. They are typically saline with total dissolved solids (TDS) concentrations ranging from 100 ppm to over 300,000 ppm [2, 4]. Produced water also typically contains between 50 to a 100 ppm total oil and grease along with low concentrations of minor and trace metals [2, 4].

1.2. Produced Water Treatment Technologies

Produced water treatment and purification was accomplished through a variety of chemical and physical separation techniques. Since produced water composition varies from location to location, a proven purification method has been difficult to develop. Depending on the exact characteristic of the particular source of produced water different pretreatment processed are applied. Hydrocyclones, centrifuges, membrane filtration, and activated carbon or depth filters are all techniques that have been tested to perform produced water treatment [2, 4-6]. Removal treatments have concentrated on suspended solids and oil and grease. Removal of the dissolved and suspended oil and grease has been especially difficult. Membrane treatment used to reduce or eliminate the oil and grease also achieved the necessary removal for trace metals. Oil removal to the 35 mg/L required by the EPA precluded the use of hydrocyclones or centrifuges. The secondary concern is salt removal. The common techniques currently used for desalination are multistage flash or reverse osmosis [7]. New techniques for desalination of produced water are being researched including membrane pervaporation [7] and electrodialysis [8].

Most oil removal technologies cannot achieve the separation required to meet water quality standards [9]. These separation technology mechanisms did not remove the entrained or suspended oils. The concern or problem with use of the first two types of

technologies for treatment of produced water was that the minute amounts typically found in produced water sources fall below the required concentration to make the technology operate efficiently or economically. For example, hydrocyclones are typically utilized to achieve separation between the crude oil and the brine. The suspended oil concentration remaining in the produced water was near the minimum that the separation technologies were able to economically obtain. Absorption techniques can and would provide separation required but were limited by the suspended solids or by trace contaminates found in different sources that could react with absorption material and introduce different contaminates that would later need to be removed. Filtration techniques were capable of most of the necessary reduction in oil content and suspended solid removal. Membranes, a type of filtration, technology that provided the separation while minimizing replacement of filters or membranes.

1.3. Membrane Filtration

Membrane filters are classified into types based on their nominal size or molecular weight cutoff (MWCO). These classifications are commonly classified as microfiltration, ultrafiltration, nanofiltration, and reverse osmosis and correspond to the size of particle that is rejected by the membrane. Microfiltration rejects suspended solids ranging from 0.10 μm to about 100 μm [10]. Ultrafiltration membranes provide separation from 1000 to 100,000 MWCO or 0.001 μm to 0.02 μm for macromolecules and suspended solids [10]. Nanofiltration membranes increase the rejected range to include sugars, divalent salts, and dissociated acids below the 1000 MWCO range [10]. Reverse osmosis membranes are normally classified for ideal rejection of all components except solvent (e.g., water) [10].

The membrane technologies are also developed into four configurations for industrial applications. These four configurations are tubular membranes, hollow fibers, plate and frame, and spiral membranes. Each configuration has distinct advantages or disadvantages in their operation. Tubular membranes are able to handle larger size particles, higher flow rates, easier cleaning by clean-in-place techniques, but lowest surface area to volume ratio [10]. Hollow fiber membranes have the characteristics of highest surface area to volume ratio, back flushing capability, but require smaller particles in the feed to prevent plugging [10]. Plate and frame membranes provide easy onsite membrane replacement and visual observation of permeate for sample collection and detection of leaks [10]. Spiral membranes provide turbulent flow due to the feed spacers breaking up the laminar flow and adding turbulence, fairly high surface area to volume ratio, and lowest energy consumption due to low flow rates, pressure drops, and relatively high turbulence.

Membrane filtration technology developments are resulting in an increasing range of material of construction, provide better membrane performance, higher temperature limits, and larger pH ranges. The membranes currently being manufactured include cellulose acetate, polysulfone, polyamide, nylon, PVDF, polytetrafluoroethylene, polypropylene, and others [10]. These materials provide increased temperature, pH, and chemical compatibility ranges. Also, membranes have been developed with different membrane structures including thin film composites [10].

Membrane filtration operations are affected by the feed water composition, temperature, and flow rate and turbulence [10]. These factors affect the flux of the membrane due to concentration polarization of the membrane [10]. Concentration

polarization refers to the development of another layer on the membrane surface besides the boundary layer and the membrane that provides resistance to permeate flow. Concentration polarization effects can be minimized by increasing cross flow velocity or turbulence and lowering transmembrane pressure (TMP) with varying membrane configurations.

Fouling also occurs during membrane operation. Fouling is the result of interactions between the membrane surface chemistry and the solutes being separated. Membrane fouling by minerals, organics, particles and colloids, and microbial growth is a major operational factor that requires periodic cleaning [11-15]. Any of these four types of membrane fouling may occur during membrane filtration depending on the nature of the feed. Fouling of membranes is considered a consequence of the separation process itself [15]. The fouling of the membrane surface requires techniques to remove the fouling layers. Both physical and chemical methods are employed. Important parameters when cleaning fouling are the type of fouling, cleaning agent, pH, concentration, temperature, and time [11-12, 14-15]. The typical cleaning agents for membrane cleaning are bases, acids, enzymes, surface active agents, sequestering agents, detergents, and disinfectants [11-12]. Each type of cleaning agent has benefits and drawbacks for use with produced water. For example, an acid cleaning of an oily wastewater ultrafiltration membrane resulted in an appreciable increase of permeate flux but became time dependent, while an alkaline solution resulted in a lower flux with time independence [12]. Studies have been reported that examined the effect of chemical and physical aspects of cleaning organic fouled membranes [16], enzymatic cleaning [17], and biological cleaning [18]. In 2005, Ang, Lee, Eleimelech showed that the by

optimizing the chemical reaction between the organic foulant and the cleaning chemical along with physical components of cleaning an efficient cleaning procedure was developed for the organic fouled reverse osmosis membranes [16]. Enzymatic cleaning of protein and lipid fouled ultrafiltration membranes were shown to be an effective method to recover the membrane flux by using specific enzymes to remove the protein and lipid fouling the membrane surface [17]. Also in 2005, Pavlova showed that biological fouling could be treated similarly with the disinfectants specific to the membrane chemistry [18].

Membrane filtration has been proven effective in treating oily water in other industries including municipal wastewater [19-21], engine rooms [22], and industrial wastewater [2,4-6, 21]. Membrane technologies also have been utilized in the production of fresh water from surface water [23] and seawater [2, 4-6, 19-20, 22]. The cost effective use of membrane technology is determined by the reliability of the system and maintenance of the permeate flow rate. The industry has developed a wide range of materials and techniques to improve the efficiency and applications of the membranes compared to the first cellulose acetate membranes. These new materials allow the technology to be used with new feeds including produced water. Membranes available for industrial use include thin film polyamide membranes on a polysulfone support, ceramic membranes, and stainless steel [10]. Novel bentonite clay membranes have been tested for produced water treatment but with high TDS [24].

Produced water with its wide range of composition of feed causes significant operational problems. These problems include the fouling of the membrane surface, the loss of flux through the membrane surface, poor rejection characteristics, and membrane

failure due to chemical reactions with the membranes. The major operational concern is typically the fouling of the membranes. For efficient operation, pretreatment reduces the fouling of the membranes without creating other problems [15]. Also, operation conditions can be selected to minimize the concentration polarization and membrane fouling with resultant increased operational permeate flux.

As mentioned, produced water and oily water can cause severe fouling problems on most membranes. Produced water can cause all four categories of particle, organic, mineral, biological membrane fouling and must be pretreated to minimize the fouling of the membranes used for RO desalination. Proper pretreatment and system design should include steps to reduce the suspended particles, oil and grease, mineral deposit, and biofilm formation through pretreatment or to select an appropriate membrane configuration. In actual operation, membrane fouling is not completely avoidable, thus periodic cleaning is required

2. MATERIAL AND FEED SAMPLE COLLECTION

2.1. Feed Sample Collection

Produced water samples were obtained from transport trucks delivering brine to a Key Energy salt water disposal well in Brazos County, Texas. The raw water feed samples were stabilized (for transportation and temporary storage) by addition of commercially available and industry recommended oilfield chemicals, RSI 224sp, RSI 676, and RSI 513. At the pilot plant, the water was pumped through a 10 μm (nominal) depth filter for bulk particle and oil separation of material possibly added during transport and collection.

The produced water feed, after filtration, was stored in barrels and sealed to reduce aeration and increase duration of water stability before 6-8 liter feed samples were aliquoted for testing. The quality of the produced water was visually monitored for a noticeable change in produced water color while obtaining feed samples. The stored feed water was periodically replaced as dictated by a visible color change in feed water samples.

2.2. Description of Experimental Setup and Equipment

The experiments were performed by using the GE Sepa™ CF II Med/High Foulant System (GE, YCFHFSYS01) for membrane testing designed for 140 cm^2 flat sheet membranes shown in *Figure 1*.

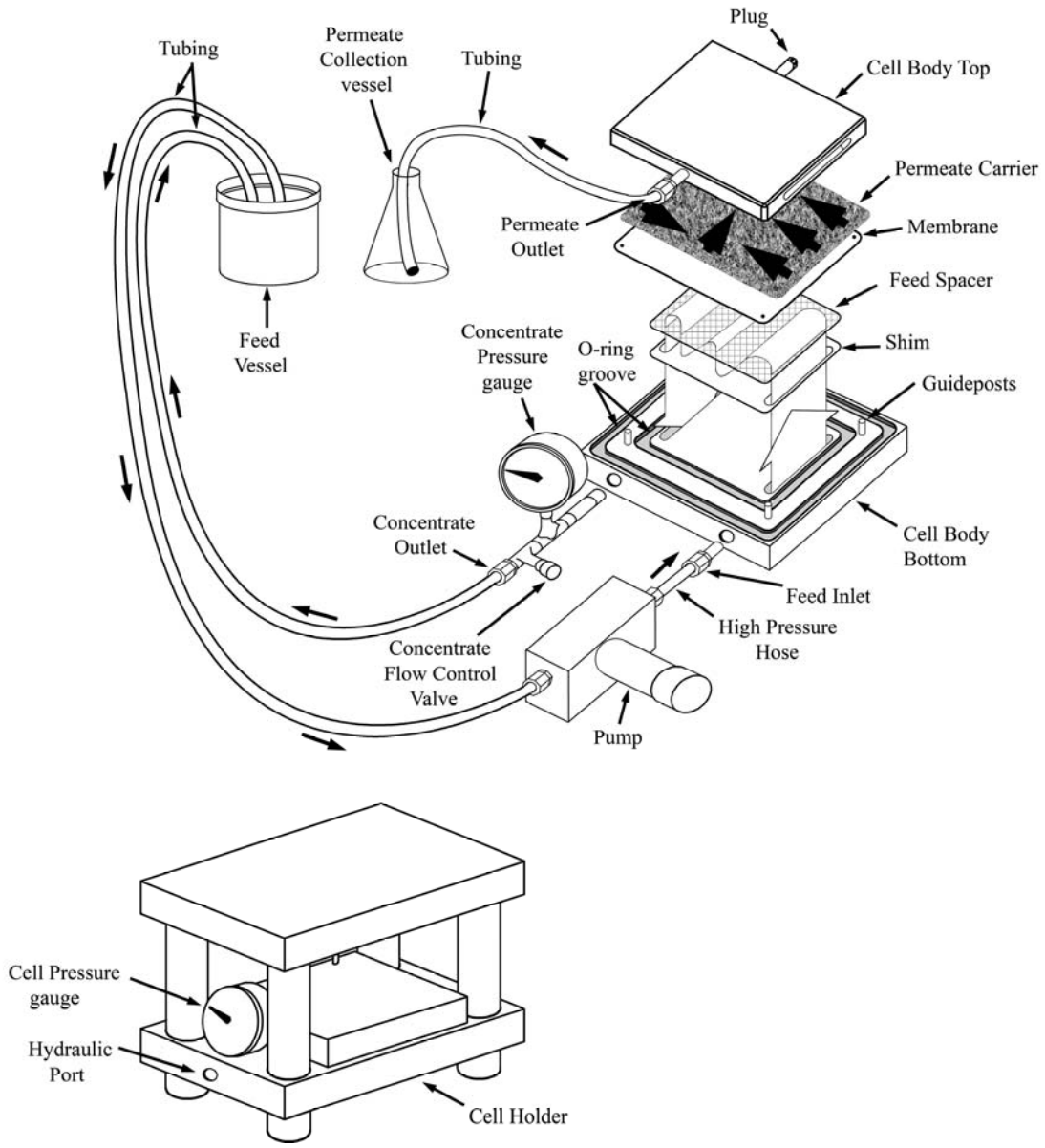


Figure 1 GE Sepa™ CF II Med/High Foulant System operation schematic (modified from [25])

Figure 1 shows the placement of the feed spacers, permeate carrier, and membrane that model operation of spiral membranes. The apparatus includes a 15 liter feed tank, pulse dampener, high pressure pump with variable speed control, and pressure and temperature gauges to monitor inlet and outlet conditions.

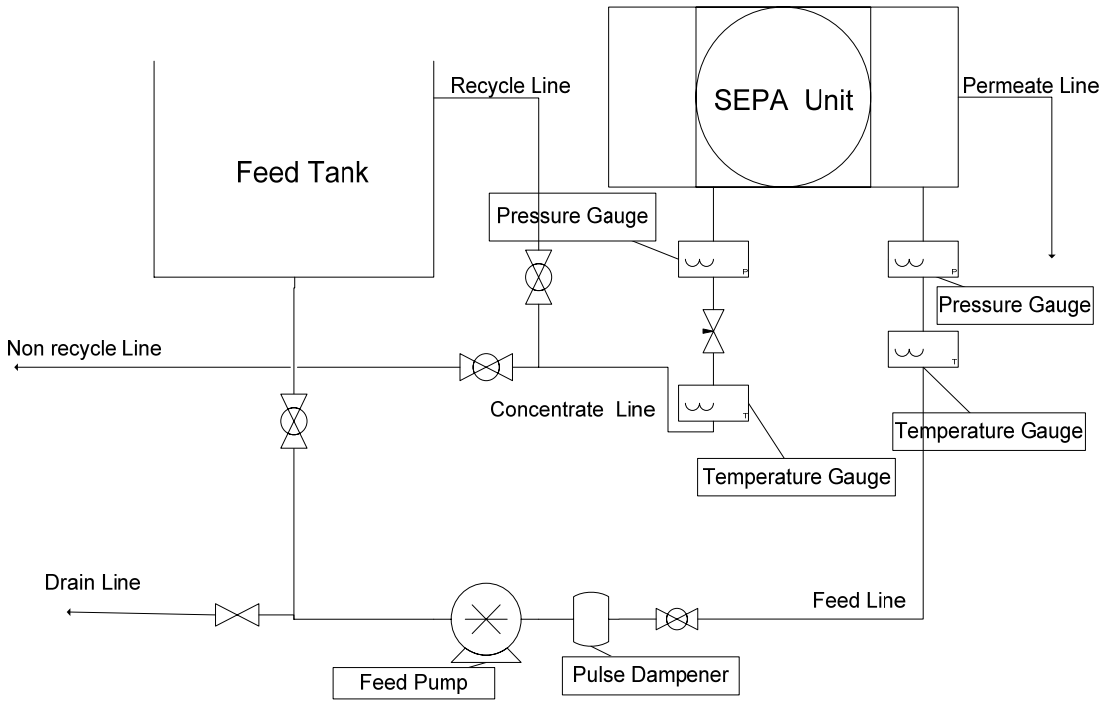


Figure 2 Laboratory process experimental schematic

A schematic of the laboratory process (*Figure 2*) indicates the location of instrumentation and flow control valves for different operating conditions. The pump and variable speed control were tested using a stopwatch and graduated cylinder to establish steady feed flow rates at specific frequency readings as indicated in *Table 1*.

Table 1 Pump flow rate control specification

Variable Speed Drive Frequency (Hz)	Feed Flow Rate (LPM)	Approximate Reynolds Number @293 K
3.5	1.9	488
7.3	3.8	977
11.5	5.7	1465
16.0	7.6	1953
21.4	9.5	2442

Standard pH paper was used to monitor the pH of the feed tank during testing. Permeate flow rate was measured by stopwatch and graduated cylinder as needed for cleaning analysis.

2.3. Obtaining membrane samples

Membrane manufacturers were contacted for ultrafiltration membrane recommendations for use in oily water separations. Three membranes were chosen each having a spiral membrane configuration type for compact design configuration. Membranes also had a range of MWCO and expected compatibility with the micelle solutions. Flat sheet samples were obtained of each selected membrane and cut to fit the Sepa unit and the 140 cm^2 test area. The differences in the three membrane types are provided in *Table 2* and each membrane type are referred to as JW, 5k, and BN.

Table 2 Membrane specifications

Test Code	JW	5k	BN
Membrane manufacturer	General Electric	PTI	Snyder
MWCO	30k	5k	30k
Material	PVDF	PVDF	PVDF
pH range	1-11	3-10	1-11
Operating pressure range (psi)	10-50	15-50	10-150

3. OIL AND SUSPENDED SOLIDS REMOVAL FOR PRODUCED WATER TREATMENT BY ULTRAFILTRATION MEMBRANES

3.1. Overview

The first sets of experiments were performed to treat produced brine to measure the performance of ultrafiltration membranes for oil and turbidity removal. The research focused on the effect of pressure and flow rate on membrane performance with respect to flux and contaminant removal from produced water with three selected membranes. Oil and suspended solids were evaluated using turbidity and oil in water measurements taken every 30 minutes. The studied showed that ultrafiltration membranes achieved turbidity removal of over 99% and oil content removal of greater than 87 %.

3.2. Introduction

The difficulty with produced water cleanup is the need to design for the extreme variability of produced water from different sources and wells. Robust treatment systems should handle the bulk of potential contaminants in produced water and be effective on most produced water sources. One method to help achieve this goal is to design the treatment system in stages with increasing water quality or separation requirements as you progress through the treatment train. Two of the major contaminants that need to be removed from oilfield brine to meet water quality standards are suspended and dissolved oil and grease and suspended solids. Removal of dissolved solids has been commercially available for seawater and utilize well characterized technologies like reverse osmosis and multistage flash evaporation. These technologies require a high quality of water feed for efficiency to minimize the energy requirement.

For suspended solids or turbidity removal, some form of filtration is the typical method used in industry. Filtration can be used after treatment of the water by a coagulant such as for municipal water treatment. The concern with using filtration technology to remove the suspended solids from oilfield brine is the need to replace standard filters frequently if the water source has a high concentration of suspended solids, (the case for most sources of produced water). Other techniques that have been tested for produced water suspended solids treatment include activated carbon [26], ceramic microfiltration [9], and ceramic ultrafiltration [2]. Oil removal or organics removal has been investigated using various technologies including electroflocculation [27], carbonaceous absorbent [28], bioreactors [29], wetland treatment [30], ultrafiltration [2, 31] and nanofiltration [32]. These studies have given varying results for oil content removal. The use of ultrafiltration using new types of membranes offer the most promise for produced water pretreatment for later desalination. The use of ultrafiltration membranes for pretreatment to meet established feed conditions for reverse osmosis or multistage flash evaporation can be used to make the onsite treatment of produced water economically viable. Membrane technology utilized cross flow filtration to provide the treatment and was allowed to reduce the accumulation of suspended solids and oil content on the membrane surface.

With membrane technology, produced water can be treated onsite to meet feed water conditions of less than 5 normalized turbidity units (NTU) and high removal of oil content for treatment by reverse osmosis. Ultrafiltration membranes were selected to be compatible with oily water and to provide better separation without causing higher capital cost due to higher operation pressures. This study examined and evaluated the

use of commercially available ultrafiltration membranes to achieve the desired reduction in both turbidity and oil content of the produced water. The study examined whether ultrafiltration membranes could be used for onsite produced water pretreatment for both turbidity and oil content removal before produced water desalination. The study examined the effect of operation pressure and flow rate on the effectiveness of membrane treatment to meet the desalination feed requirements.

3.3. Materials and Methods

3.3.1. Experimental method

Evaluation of commercial ultrafiltration membranes for use in produced water treatment has been conducted. Ultrafiltration membranes should provide the necessary pretreatment separation for desalination with minimum space and cost requirement. Each membrane type obtained was tested for produced water treatment under two operational factors of pressure and flow rate under a 3X2 factorial design with no replication based on the membrane specification provided by the membrane manufacture. The membrane specifications for the three ultrafiltration membranes suggested an operational pressure of about 30 psi or 207 kilopascals (kPa). This pressure indicated three factor levels of 20, 30, and 40 psi (corresponding to 138, 207, and 276 kPa) for the factorial design experiments were appropriate. Limits on flow rates recommended by the Sepa System lab equipment and high fouling feed spacer indicated a maximum flow rate of approximately 8 liters per minute (LPM) for high fouling tests provided for flow rate operation levels of 1.9 and 3.8 LPM in the factorial design. Each experiment was monitored for temperature, flow rate, pressure, pH, operation time, and feed and permeate quality.

3.3.2. Experimental procedure

The test consisted of a batch operation with full concentrate recycle. Each experiment consisted of placing approximately 7 liters of produced water feed into the feed tank (see *Figure 2*). The test consisted of operating the Sepa system (*Figure 1*) for 2 hours while maintaining the operational flow rate and pressure for the particular test with concentrate being continuously recycled to the feed tank. Approximately 30 milliliter (mL) feed samples were taken before and after the two hour test duration to monitor the change in feed conditions during testing. Inlet and outlet pressure were constantly monitored and adjusted during the experiment to maintain the TMP, average of the inlet and outlet pressures, at the specified level. Temperature, permeate flow rate, pressure measurements were taken every 30 minutes to monitor change in flux. Also, approximately 30 mL permeate samples were collected every 30 minutes to measure water quality achieved by the membrane. Finally pH of the produced water feed was monitored throughout the duration of the experiment for any major change.

3.3.3. Data analysis

Flux measurements were temperature adjusted for viscosity to a common temperature of 298 K and reported as liters per square meter per hour (LMH). The data collected during each of the runs were analyzed and computed to provide direct flux performance comparisons between the different membranes through plots: 120min Flux vs. TMP at 1.9 and 3.8 LPM and flux vs. time or fouling curve for direct comparison of the data for each membrane under the same operating conditions. The samples were analyzed for turbidity a reflection of suspended solids and oil. Water samples were

measured for an estimated oil content to provide separation characteristics of the membranes. The classification and selection of the best membrane will be based on the 120min flux, lowest TMP, and high rejection characteristics of the membrane obtained.

3.3.4. Water sample analysis

Water sample analyses consisted of two measurements, turbidity and oil content. Turbidity analyses were conducted using a Hach 2100p turbidity meter calibrated with factory standards for NTU. Oil analyses were conducted using the TD-500 oil in water meter developed by Turner Designs Hydrocarbon Instruments, Inc. The TD-500 oil in water meter involved use of a solvent extraction procedure with high accuracy and repeatability and correlates to EPA and other industry accepted laboratory methods for oil and grease measurements in water. The TD-500 utilized the FastHEX procedure with the high accuracy and repeatability. The FastHEX procedure involved the extraction of the suspended and dissolved oil from the water samples then using ultraviolet light to detect the oil concentration in the solvent. The analysis method was compatible with all popular solvents including hexane, Vertrel, AK-225, Freon, xylene, and others. The water sample analyses used hexane as the extraction solvent and were calibrated to known oil concentrations. Each sample collected during an experiment was tested three times for instrument error and averaged to calculate the turbidity and oil content of a particular sample. The two feed samples were averaged and the five permeate sample averages were then averaged for a combined feed average and permeate average for both the turbidity and oil content. The average values were used to calculate removal percentages for the test as follows in *Eq. 1.*

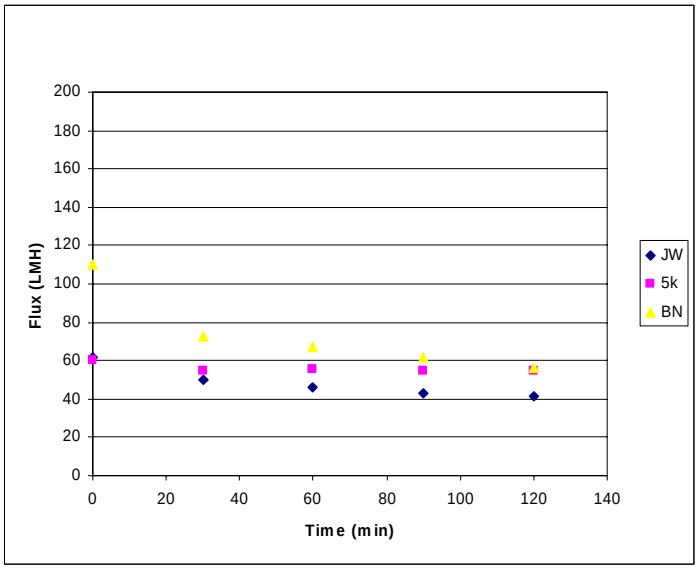
$$Percent\ \ Removal\ \ (\%) = \left(1 - \frac{permeate\ \ average}{feed\ \ \ average}\right) * 100 \qquad (1)$$

The calculated removal percentages were used in evaluating the separation characteristics under the same flow and pressure for each membrane type.

3.4. Results.

3.4.1. Flux curves

The temperature adjusted fouling curves or flux versus time for each membrane was shown in *Figure 3*.



a)

Figure 3. Brine fouling curves at TMP of 20 psi (138 kPa), for the two feed flow rates. The flux decay was monitored for the membranes at 298K. (a) 1.9 LPM, and (b) 3.6 LPM.

b)

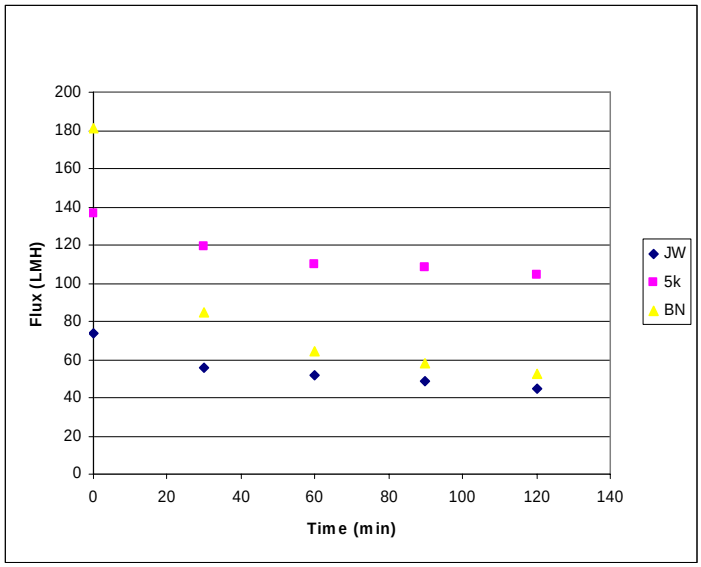


Figure 3. Continued.

Figure 3 showed that the flux decays were slight and steady over the time period for the 5k and JW. For the BN membrane, *Figure 3* showed a major drop in the flux within the first 30 minutes followed by a slow decline for the rest of the experiment. *Figure 4* showed similar curves on the membrane types for a 207 kPa TMP. *Figure 4* showed similar behavior for the 207 kPa TMP at both flow rates and the JW membrane at the higher flow rate. The figure also indicated that only a moderate decline occurred for the JW membrane at the low flow rate and for the 5k membrane. *Figure 4* also showed that the flux decay for the BN membrane occurred mainly within the first 30 minutes and then stabilized.

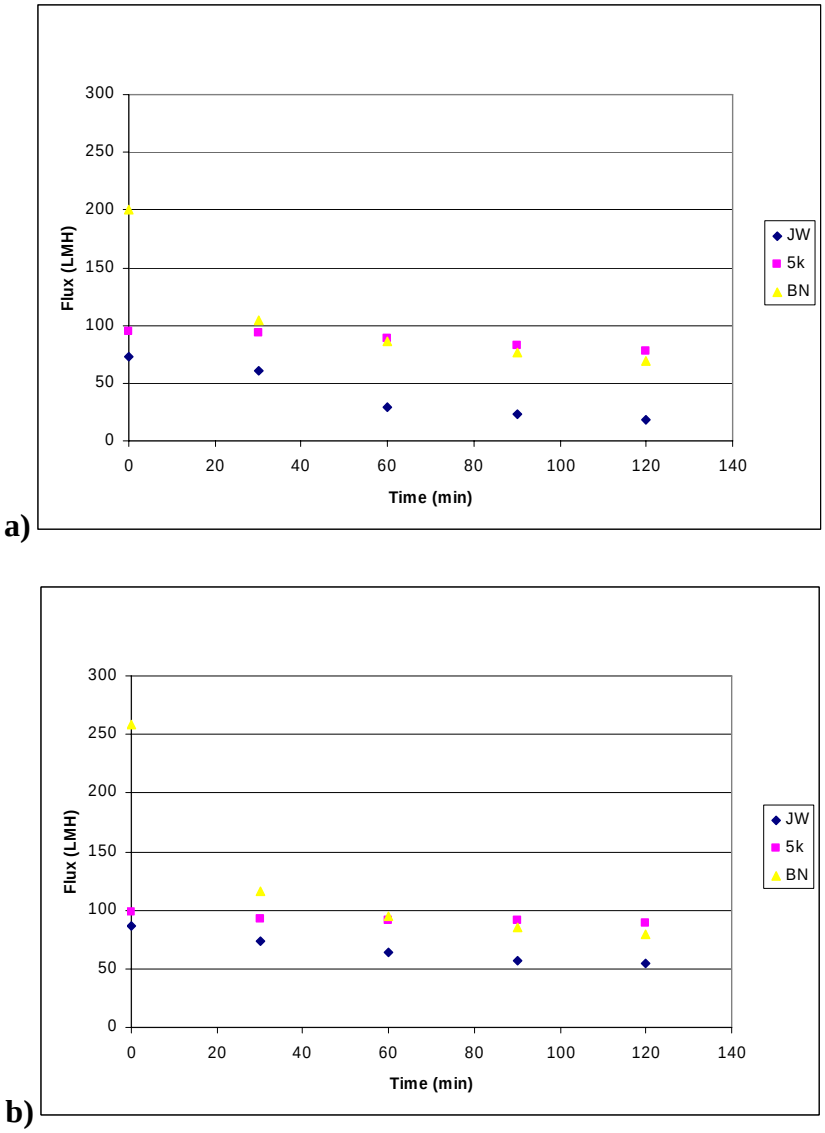
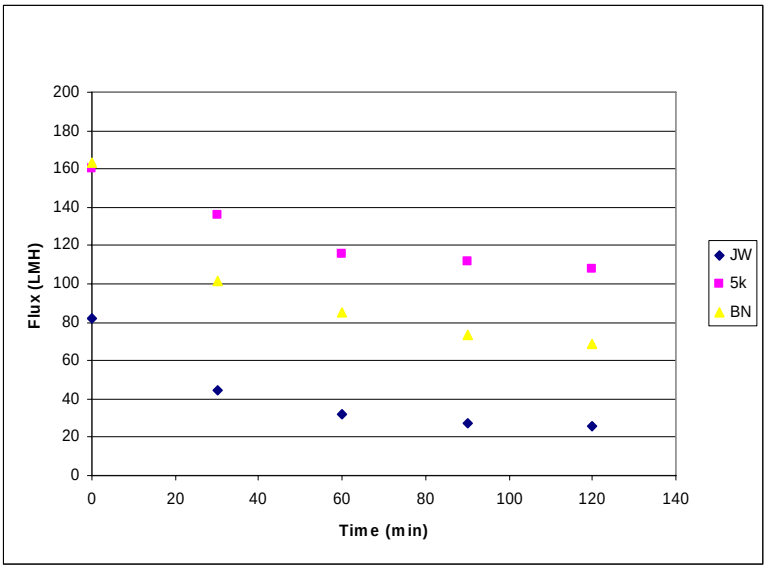


Figure 4. Brine fouling curve at TMP of 30 psi (207 kPa), for the two feed flow rates. The flux decay was monitored for the membranes at 298K. (a) 1.9 LPM, and (b) 3.6 LPM.

These curves indicate a major decay for the three membranes during the experiment with the exception for the 5k membrane under the high flow. *Figure 5* showed the highest pressure flux decline for the three membrane types.

a)



b)

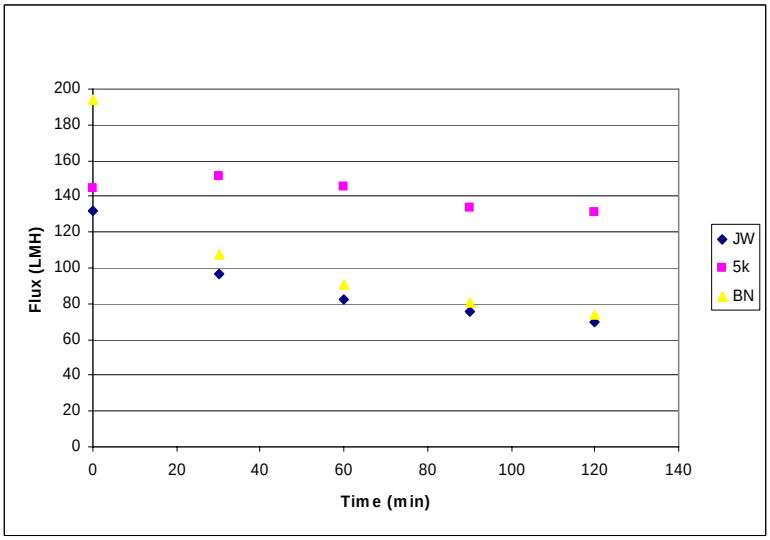


Figure 5. Brine fouling curve at TMP of 40 psi (276 kPa), for the two feed flow rates. The flux decay was monitored for the membranes at 298K. (a) 1.9 LPM, and (b) 3.6 LPM.

Figure 5 shows the major decay in flux in the first 30 minutes. After 30 minutes, the data show only a steady slow decline in the flux performance. *Figure 6* shows that 120 minute fluxes were the highest for the 5k membrane except for TMP of 176 kPa and 1.9 LPM flow rate.

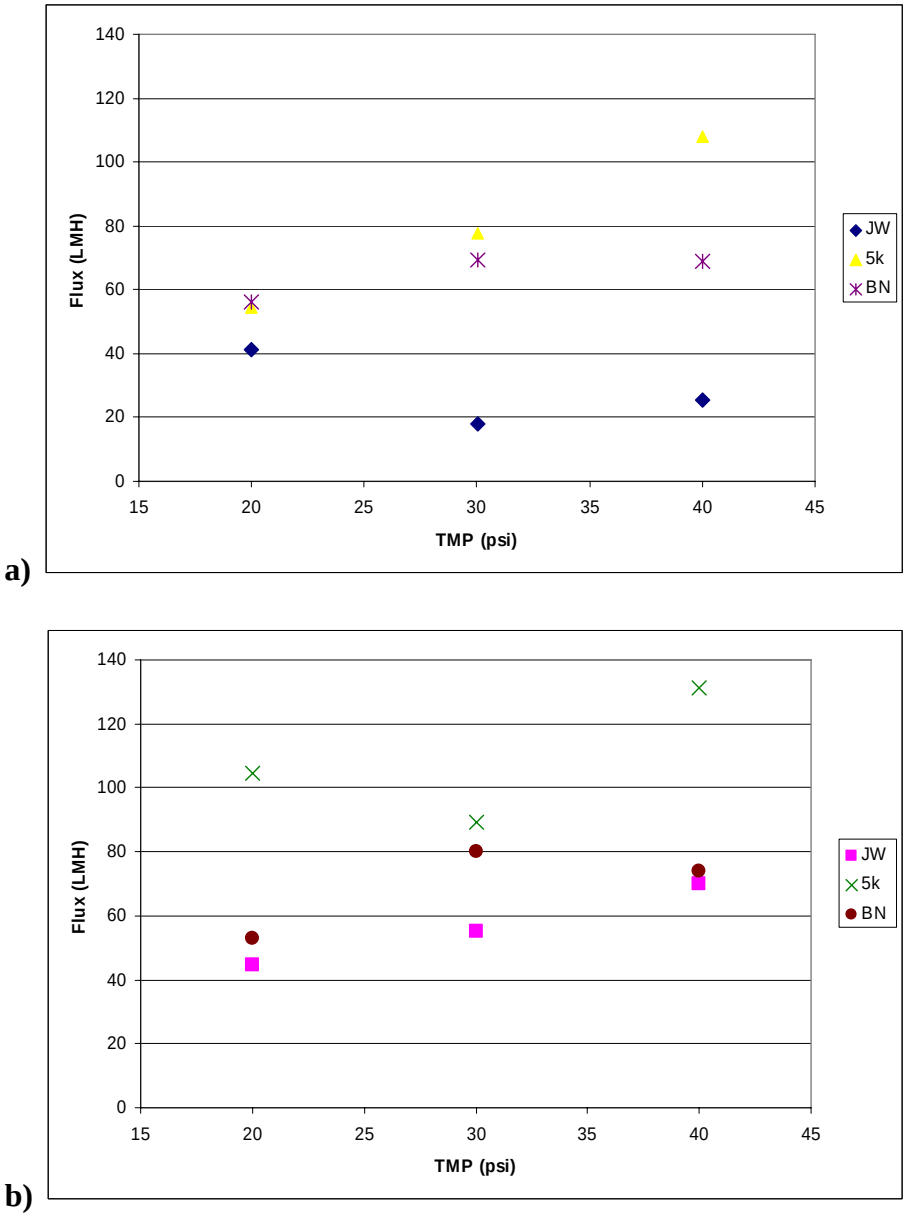


Figure 6. Brine flux @ 120 min versus TMP, corrected to 298K and for the two flow rates. (a) 1.9 LPM, and (b) 3.8 LPM.

The data in *Figure 6* show that doubling the feed flow rates improved flux for each membrane but only slightly. It is also seen that the JW membrane provided the lowest flux at all pressure and flow rates. The data in *Figure 6* showed that increasing pressure yielded higher fluxes than doubling the flow rate provided.

3.4.2. Separation performance

Water quality analyses for turbidity and oil content were computed and averaged for every experiment and shown in *Table 3.*

Table 3 Water quality results

Experiment parameters	Feed Turbidity Average (NTU)	Permeate Turbidity Average (NTU)	Turbidity % Removal	Feed Oil content Average (ppm Oil)	Permeate Oil Content Average (ppm Oil)	Oil content % Removal
JW: 1.9LPM/138kPa	627.8	2.5	99.60%	363.5	34.8	90.43%
JW: 1.9LPM/207kPa	412.2	1.6	99.61%	1927.8	573.3	70.26%
JW: 1.9LPM/276kPa	238.2	1.7	99.27%	1509.0	188.1	87.53%
JW: 3.8LPM/138kPa	252.3	1.1	99.57%	28.0	11.3	59.52%
JW: 3.8LPM/207kPa	1000.0	1.3	99.87%	204.3	47.7	76.64%
JW: 3.8LPM/276kPa	1000.0	1.9	99.81%	156.3	26.9	82.81%
5k: 1.9LPM/138kPa	365.8	3.7	98.99%	43.8	15.6	64.41%
5k: 1.9LPM/207kPa	868.7	1.6	99.82%	48.0	7.9	83.61%
5k: 1.9LPM/276kPa	1000.0	2.4	99.76%	62.8	8.0	87.27%
5k: 3.8LPM/138kPa	565.2	2.6	99.55%	76.0	26.3	65.44%
5k: 3.8LPM/207kPa	954.7	8.8	99.07%	192.2	30.9	83.94%
5k: 3.8LPM/276kPa	832.8	35.4	95.75%	44.2	23.3	47.32%
BN: 1.9LPM/138kPa	1000.0	1.8	99.82%	136.0	7.7	94.31%
BN: 1.9LPM/207kPa	875.8	2.5	99.71%	61.8	7.7	87.60%
BN: 1.9LPM/276kPa	922.5	2.3	99.75%	98.2	7.9	91.92%
BN: 3.8LPM/138kPa	1000.0	1.8	99.82%	121.0	7.3	93.94%
BN: 3.8LPM/207kPa	1000.0	1.8	99.82%	76.8	9.3	87.94%
BN: 3.8LPM/276kPa	974.0	1.8	99.81%	42.5	9.3	78.20%

The data in *Table 3* show that the turbidity and the oil content of the feed were different for each experiment but within the range for produced water. *Table 3* displayed values for turbidity of the permeate water samples calculated below 5 NTU. The removal percentage for the turbidity ranged from 95.75% to 99.87%. *Table 3* also shows that the oil contents of the water samples were influenced by the feed concentrations. The oil removal percentages for the experiments ranged from 47.32% to 94.31%. The results indicated that all three membranes achieved the turbidity removal less than 5 NTU necessary to meet feed quality requirements for desalination technologies. *Table 3* also showed that the oil removal percentages were the highest for the BN membrane and

that the permeate oil content was the lowest concentration achieved by the membranes and averaged below 10 ppm oil. Finally, *Table 3* indicated that increased TMP or feed flow rates did not improve the oil content separation removal percentages or obtained oil content concentration characteristics of three membranes.

3.5. Discussion

3.5.1. Flux curves

The results indicated that the three membranes were able to provide a high flux to treat the oilfield brine. The fouling curves indicate that the 5k membrane was able to reduce fouling by the produced water over the duration of the experiment. This could be the result of a lower MWCO for the membrane. The lower MWCO could prevent the pores of the membrane surface from being plugged by the suspended and dissolved oils. The JW and the BN membrane or higher MWCO membranes showed large flux decays which were possibly explained by the filling of the larger pores on the membrane surface, but more likely explained by surface fouling.

The flux curves indicated that the increased feed flow rates increased performance of the membranes without any loss in water quality. The 120 minute flux showed higher flux for the increased TMP for each membrane type as you would expect for most membrane systems. The flux data indicate that the higher pressure caused faster fouling while significantly decreasing the flux rate of the fouled membrane. The higher pressure caused the formation of the fouling layers to occur at a faster rate by forcing the oil deposits or particles within the produced water feed to plug the membrane pores or increasing the surface fouling of the membrane. The fouling curves also indicated two

distinct regions of fouling of the membrane, the rapid initial flux decline during the first 30 minutes and the second gradual flux decay during the rest of the experiment.

3.5.2. Water analysis

The water analyses indicated that even though the produced water feed samples were taken from the same 10 micron filtered sources the quality of the feed varied significantly for the experiments. This variation led to the treatment of some produced water with higher concentrations of oil and suspended solids and some treatment with lower concentrations of oil and suspended solids in the produced water feed. The analysis showed that even for the feed samples with the higher concentration of contaminates the membrane was able to treat the produced water. The higher concentrations of the suspended solids or oils indicated by the high or maximum turbidity on most feed samples provided no noticeable effect on the water quality of the permeate samples when compared to the lower feed turbidity experiments. The membranes were capable of providing the required suspended solid or oil removal of a turbidity of about 5 NTU for subsequent TDS treatment. The oil separation characteristics provided by the membranes showed that increased pressure and feed flow rate forced oil content through the membrane while also increasing the fouling rate. This indicated that increased pressure reduces the performance of two of the ultrafiltration membranes while increasing the fouling rate of the produced water. The BN membrane showed that the increased TMP while causing the faster fouling, did not hinder the water quality of permeate obtained. This suggested that the membrane prevented the oil content for being forced through the membrane by the higher flow rate and pressures.

3.6. Conclusions

The treatment of produced water by ultrafiltration membranes was a logical treatment step for an onsite system before the desalination of the brine. The commercial available membranes were able to treat the produced water to the desired water quality for later desalination. The results indicated that the system would be operated at very low pressure and high flow rates that would provide low capital and operational costs. The testing showed that increased flow rate would provide the necessary throughput while limiting the fouling rate and improving water quality.

The PVDF membranes selected for testing each had different separation characteristics for the produced water. The three ultrafiltration membranes all had a capability of at least 30,000 MWCO. The MWCO generally was not an indicator of the separation capable of the membranes. The BN membrane provided the overall best treatment of the produced water with high flux rate and the best separation characteristics. The 5k membrane was the second effective membrane with the highest flow rates but reduced water quality. The JW membrane was the least effective membrane tested.

The study showed that the treatment of produced water with ultrafiltration membranes onsite can be effective. The study showed the operation pressure and flow rate affected the treatment of the water with only two of the membranes. The study indicates that the commercially available BN membrane would be a good choice for the onsite application of produce water treatment because the water quality obtained by the membrane was suitable for later reverse osmosis desalination. The study also showed

that for the BN membrane the feed flow rate, TMP, feed suspended solids concentration, and feed oil content provided no change in the membrane effectiveness.

4. MEMBRANE CLEANING AFTER PRODUCED WATER TREATMENT WITH A MICELLAR SOLUTION

4.1. Overview

The second objective of this research was to test the effectiveness of a new type of membrane cleaning agent. A neutral pH and ambient temperature micro emulsion cleaning agent has been developed that effectively cleans oily water fouled membranes. The performance of the cleaning solutions on produced water fouled ultrafiltration membranes was tested on laboratory membrane testing equipment. Micro emulsion chemical make-up and solubilizing characteristics were varied to determine their effect on cleaning performance. Physical cleaning factors were studied for the micelle solution cleaning performance along with the multiple membranes of the same PVDF material but different nominal separation or flux characteristics. The results indicated the micellar solution was effective in cleaning the produced water fouled ultrafiltration membranes. Physical factors that influenced the micelle solution cleaning effectiveness included the cleaning flow rate, rinse time, and membrane size.

4.2. Introduction

Membrane filtration has been utilized in various industries for the treatment of water and wastewater. These membrane systems are designed for treatment of a specific known water source and remove the desired contaminants to meet environment regulations or desired water quality for industrial use. These contaminants can have a wide range of characteristics that will allow them to be separated through membrane technology. The concern with using membranes in the treatment of wastewater was to

increase efficiency of the treatment system by minimizing the fouling and to efficiently clean the membranes after fouling.

To efficiently clean membrane fouling, the fouling type caused by the wastewater should be known. The degree of fouling is related to the wastewater characteristics and the amount of filtration desired. In a typical membrane application the wastewater characteristics are almost constant and have known concentrations, but for produced water treatment the water characteristics will vary from well to well and over time causing additional concerns when developing a cleaning protocol. Also, temperature an important factor for cleaning membranes required additional consideration, especially for remote filtration units for well sites where high temperature cleaning might not be practical. A cleaning solution that will work at ambient conditions would also reduce costs. An ambient temperature micelle solution would be a possible solution to the temperature limitation. Micro emulsion solutions consist of micelles formed by surfactants to create a hydrophobic cell within an aqueous environment.

As explained earlier, produced water has caused all four types of membrane fouling but typically mineral and oil deposits dominate. The mineral and oil deposits on the membrane were the primary concern since they will occur from every produced water source and require a different cleaning approach than biological fouling. Particulate fouling can be cleaned using physical cleaning or high flow rate to strip the layers from the membrane surface along with the chemical cleaning the mineral and organic layers. Mineral and organic fouling has been utilized for cleaning by the industry for oily water fouled ultrafiltration by acidic and basic solutions, respectively [12]. The micelle solutions created using surfactants were utilized in this study as a solution for

cleaning of produced water fouled ultrafiltration membranes. These surface active agents formed micelles that reacted with the mineral and oil droplets to form larger particles that are then removed by the high flow rate. The micelle should improve the effectiveness of dissolving the organic and mineral fouling layer over the acidic and basic solutions currently employed.

This study was testing the feasibility of using such a micelle solution to clean the membrane fouling that was occurring during operation. The specific objective of this research was to examine the feasibility of using micelle chemical solutions with different micro emulsion characteristics for membrane cleaning of produced water fouled ultrafiltration membranes. The research was designed to measure micelle solution cleaning at ambient conditions and compare their performance to commercial acidic and basic solutions or manufacturers recommended cleaning solutions for produced water. The research evaluated the use of the micelle solution on PVDF ultrafiltration membranes from three manufactures, GE, PTI, and Snyder, used in produced water treatment and to determine whether physical conditions of cleaning time, flow rates, and rinse times affect the cleaning performance to optimize the micellar cleaning solution for these ultrafiltration membranes.

4.3. Materials and Methods

4.3.1. Fouling of membrane samples

The membranes are fouled by using random samples of different produced water obtained from a local disposal well with unknown oil and suspended solids concentrations. The produced water sample obtained is then filtered by a 10 μm depth filter to remove large particles. The membranes are fouled by a 6-8 liter filtered produce

water feed sample by batch operating the experimental apparatus for 2 hours with concentrated recycle under different operating conditions provided in *Table 4.*

Table 4 Fouling conditions for ultrafiltration membranes

Fouling Condition	Feed Flow Rate LPM	TMP psi (kPa)
1A	1.9	20 (138)
1B	1.9	30 (207)
1C	1.9	40 (276)
2A	3.8	20 (138)
2B	3.8	30 (207)
2C	3.8	40 (276)

The effect of fouling conditions will be assumed to be negligible on cleaning effectiveness. The effect of the conditions under which the membranes were fouled should have no appreciable effect on cleaning the surface of the membranes since the cleaning solutions were being designed to clean heavily fouled oily membranes. These heavily fouled membranes have a limit on the amount to which they are fouled and can be fouled only to the limiting factor of the cross flow rate or shear rate of the feed across the membrane.

4.3.2. Cleaning of fouled membranes

4.3.2.1. Solution preparation and cleaning procedure

The micelle solutions were prepared using reverse osmosis (RO) water and precise amounts of surfactants and salt concentration to provide the micellar characteristics. The micellar solution consisted of a 1-1.5% surfactant solution of three

components A, B, C in a 2-5% sodium chloride solution. The three components consisted of a nonionic A, a nonionic B, and althyl alcohol C. The surfactants were used to generate Winsor type micro emulsion system with different phase behaviors. *Table 5* below showed the characteristics of the micelle solutions.

Table 5 Micelle solution characteristics

Formula	Surf. Conc., %wa	SL 11, Molar	nC_4OH, %v	NaCl, %w	ME phase	Equilibration
50406A	1.0	0.4M	2.5	2.0	m-phase	2 phase
50406B	1.5	0.4M	2.0	2.0	m-phase	m-phase
50928A	1.0	0.5M	2.0	2.0	2-phase	Slow separation
50928B	1.0	0.1M	2.5	2.0	2-phase	Very slow separation
50928C	1.0	0.5M	2.5	2.0	m-phase	Very slow separation
50928D	1.5	0.1M	2.5	2.0	m-phase	Slow separation
50928E	1.5	0.5M	2.5	2.0	m-phase	Fast separation
50928F	1.5	0.1M	2.5	5.0	m-phase	Fast separation
50928G	1.5	0.5M	2.5	5.0	m-phase	Fast separation

A cleaning experiment test procedure consisted of taking a fouled membrane and using the experimental apparatus diagram in *Figure 1* and running the step by step procedure below:

1. Add RO water to feed tank. Flush membrane system (no recycle) with clean RO water specified rinse flow rate for *t* minutes and minimum pressure (fully open back pressure valve). Record average temperature and pH over specified time.

2. Flush membrane system (concentrate recycle) with clean RO water specified rinse flow rate for *t* minutes and minimum pressure. Record average temperature and pH over specified time.
3. Drain system
4. Add RO water to feed tank. Run system taking clean water flux data over range of pressures at 3.8 LPM flow rate.
5. Record flux data and plot with temperature correction for viscosity.
6. Drain system
7. Add 2L of cleaning solution to feed tank. Run cleaning chemical solution over system (concentrate recycle) for *t* min at specified operating flow rate and minimum pressure. Record average temperature and pH over specified time.
8. Drain system
9. Add RO water to feed tank. Flush system (no recycle) for *t* minutes with clean RO water at specified rinse flow rate and minimum pressure.
10. Flush system (concentrate recycle) for *t* minutes at rinsing flow rate and minimum pressure
11. Drain system.
12. Add RO water to feed tank. Run system taking clean water flux test over range of pressures at 3.8 LPM flow rate.
13. Record flux data and plot with temperature correction and compare to new clean flux data and to Step 4 data.

Step 1 and 9 were performed without any recycling of the RO water to reduce mixing of fouling water or cleaning solution and Step 2 and 10 were performed with concentrate recycle specifying the time and flow rate while monitoring pH and temperature of feed through the instrumentation shown in *Figure 1*. Then, Step 4 and 12 were conducted by using a stopwatch and graduated cylinder for permeate flow rate measurements at the specified TMP and 3.8 LPM flow rate. Permeate flow rate measurements were taken over a range of at least 5 TMP pressures suggested by the membrane manufacturers from 69 to 345 kPa to obtain a pure water flux versus TMP plot. During the permeate flow rate measurements, pH and inlet and outlet temperatures were recorded.

4.3.2.2. Analysis of the cleaning effectiveness

The cleaning effectiveness was determined by comparing the un-cleaned flux to the cleaned flux. The operational conditions during fouling were assumed not a factor due to limited effect these conditions will have on cleaning effectiveness. To calculate the flux the permeate flow rate is divided by the membrane area. After initial flux calculation, the flux was adjusted or corrected to a specified temperature of 298 K by viscosity for baseline comparisons. Simple linear regressions were used to analyze the corrected flux curves. Linear regressions were used to predict pure water flux rate at three specified TMP for the un-cleaned, cleaned, and the new flux curves. The predicated pure water flux rate were used to calculate ratios of cleaned flux to un-cleaned flux, un-cleaned flux to new clean flux, and un-cleaned flux to cleaned flux at the 3 specified TMP. The ratios obtained at each specified TMP were averaged to provide overall flux ratio for cleaned to un-cleaned, cleaned to new, un-cleaned to new, and the cleaning effectiveness calculated according to *Eq. 2.*

$$Cleaning\ \ Effectiveness\ \ (\%) = \left(1 - Avg\left(\frac{uncleaned\ \ flux}{cleaned\ \ flux}\right)\right) * 100 \qquad (2)$$

The cleaning effectiveness percentage showed percentage improvement provided by the cleaning solution and procedure over the un-cleaned flux. The percentage calculated the effect of cleaning the membrane while neglecting the amount of fouling that was obtained by the fouling conditions.

4.3.3. Membrane testing

4.3.3.1. Micelle solution formulation experiments

The first series of cleaning tests, Experiments 1-9, were testing the differences between the micelle micro emulsion solutions. This series is conducted using the above

procedure with each test being conducted on the same membrane under the identical cleaning parameters of flow rates and time as indicated in *Table 6*. The series also included Experiment RC, a recommended cleaning procedure provided by Ecolab using their commercial cleaning chemicals of 2% enzyme solution of Ultrasil 53, 1% acidic solution of Ultrasil MP, and1.5% basic solution of Ultrasil 10 in series to clean the membranes.

Table 6 Micelle solution test conditions

Experiment Test	1	2	3	4	5	6	7	8	9	RC
Micelle formula	50406A	50406B	50928A	50928B	50928C	50928D	50928E	50929F	50929G	Ultrasil 53 Ultrasil MP Ultrasil 10
No recycle Rinse before Cleaning Cycle duration (min)	1	1	1	1	1	1	1	1	1	1 1 1
Recycling Rinse before Cleaning duration (min)	5	5	5	5	5	5	5	5	5	5 5 5
Rinse Solution Flow Rate (LPM)	3.8	3.8	3.8	3.8	3.8	3.8	3.8	3.8	3.8	3.8 3.8 3.8
Cleaning Cycle duration (min)	15	15	15	15	15	15	15	15	15	15 15 15
Cleaning Solution Flow rate (LPM)	3.8	3.8	3.8	3.8	3.8	3.8	3.8	3.8	3.8	3.8 3.8 3.8
No recycle Rinse after Cleaning Cycle duration (min)	1	1	1	1	1	1	1	1	1	1 1 1
Recycling Rinse after Cleaning Cycle duration (min)	5	5	5	5	5	5	5	5	5	5 5 5
Membrane	JW	JW	JW	JW	JW	JW	JW	JW	JW	JW

A commercial cleaning process was performed to use as a baseline comparison. Experiment RC was performed under the same flow rate and rinse flow rate and duration as Experiments 1-9 but with corresponding rinse and cleaning cycle for each additional cleaning solution as shown in *Table 6.*

4.3.3.2. Flow rate experiments

The next series of experiments, Experiments 10-18, consisted of using the best two micelle solutions from the first test series and performing threes sets of three flow experiment tests. The first set of three experiments was performed on the JW membrane and used the 50928A formula where three flow rates for the cleaning solution were tested within the set. The second set consisted of the utilization of the same three flow rates and the 50928A formula but were performed on the 5k membrane. The last set was conducted on the 5k membrane and the three flow rates but utilized a different formula 50406B. All three sets were conducted using the same specified cleaning parameters for rinse flow rate, rinse time, and cleaning time as shown in *Table 7*. These sets of experiments tested the effect shear stress or cross flow rate for the cleaning solution effectiveness. This series of tests also considered whether the different formulas had different or corresponding effect on cleaning performance and flow rate effect and whether the different membranes showed similar performance trends.

Table 7 Flow rate test series parameters

Experiment Test	10	11	12	13	14	15	16	17	18
Micelle formula	50928A	50928A	50928A	50928A	50928A	50928A	50406B	50406B	50406B
No recycle Rinse before Cleaning Cycle duration (min)	1	1	1	1	1	1	1	1	1
Recycling Rinse before Cleaning Cycle duration (min)	5	5	5	5	5	5	5	5	5
Rinse Solution Flow Rate (LPM)	3.8	3.8	3.8	3.8	3.8	3.8	3.8	3.8	3.8
Cleaning Cycle duration (min)	15	15	15	15	15	15	15	15	15
Cleaning Solution Flow rate (LPM)	1.9	3.8	7.6	1.9	3.8	7.6	1.9	3.8	7.6
No recycle Rinse after Cleaning Cycle duration (min)	1	1	1	1	1	1	1	1	1
Recycling Rinse after Cleaning Cycle duration (min)	5	5	5	5	5	5	5	5	5
Membrane	JW	JW	JW	5k	5k	5k	5k	5k	5k

4.3.3.3. Contact time experiments

The next series of tests consisted of two additional cleaning experiments, Experiment 19 and 20. This series tested the cleaning solution contact time or duration. The tests were to evaluate whether time of cleaning solution contact was a factor and can improve performance. The tests were performed following the cleaning procedure and under the baseline cleaning parameters for rinse flow rate, rinse time, cleaning flow rate shown for Experiments 2 shown in *Table 6.* The only test condition that was changed was the cleaning time was doubled to 30 minutes and that the test was repeated. The contact time could cause an increase in effectiveness by increasing the chemical solubilization of the fouling layers.

4.3.3.4. Water rinsing experiments

The last series of cleaning tests conducted evaluated the changing of the rinse duration and flow rates to see if any effect was seen of the micro emulsion solution being maintained on the membrane and reducing the actual effectiveness of the cleaning cycle. The tests were conducted to form sets of experiments to coincide with previous tests, Experiment 17 and 18 shown in *Table 7,* to test the rinse flow rate effect with similar conditions for comparison. The experiments in *Table 8* along with Experiment 17 and 18 tested whether doubling the rinse time and flow rate before and after the cleaning cycle added any notable effect on performance.

Table 8 Water rinsing test series parameters

Experiment Test	21	22	23	24	25	26	27	28
Micelle formula	50406B	50406B	50406B	50406B	50928C	50928C	50928C	50928C
No recycle Rinse before Cleaning Cycle duration (min)	1	1	1	2	1	1	2	2
Recycling Rinse before Cleaning Cycle duration (min)	5	5	5	10	5	5	10	10
Rinse Solution Flow Rate (LPM)	7.6	7.6	3.8	3.8	3.8	7.6	3.8	7.6
Cleaning Cycle duration (min)	15	15	15	15	15	15	15	15
Cleaning Solution Flow rate (LPM) Reynolds Number	3.8	7.6	3.8	3.8	3.8	3.8	3.8	3.8
No recycle Rinse after Cleaning Cycle duration (min)	1	1	1	2	1	1	2	2
Recycling Rinse after Cleaning Cycle duration (min)	5	5	5	10	5	5	10	10
Membrane	5k	5k	BN	BN	BN	BN	BN	BN

The different sets consists of changing one other variable along rinse flow rate or time to make direct comparisons on performance changes and to notice any trends or slight variation on the rinse effect to the other parameters.

4.3.3.5. Comparison of type of membrane on cleaning effectiveness

The last set of experiments and analysis consists of analyzing the data to make a comparison on which membrane type was cleaned more effectively. The set of experiments consisted of the baseline test conditions of Experiments 1-9 with changing only the membrane type and utilizing the same micelle solution. The analysis also included whether different membranes showed different effects for rinsing effects or cleaning flow rates. This analysis tested the suitability of the micelle solution for wide varieties of PVDF ultrafiltration membranes. The analysis also examines the cleaning solution temperature provided by ambient conditions.

4.4. Results

4.4.1. Micelle solution test series

The flux measurement results from Experiment 1 are shown in *Figure7.*

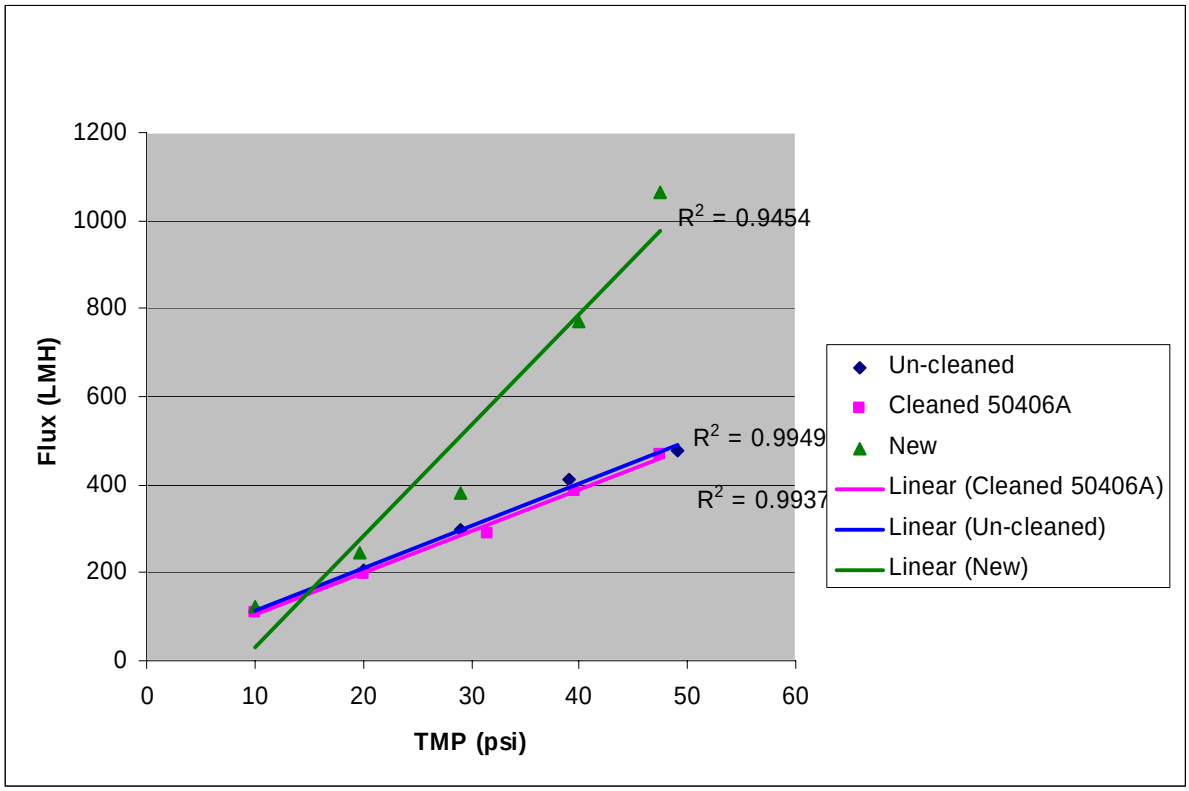


Figure 7 Experiment 1 Pure water flux curves. The flux measurements were measured and adjusted to 298K.

Graphs similar to *Figure 7* were utilized to compare and analyze each individual experiment and to calculate the average ratios of cleaned to used, cleaned to new, used to new, and cleaning effectiveness as percentage of unclean to clean. The ratios are averaged over the 3 different points on the flux curve and provided in *Table 9*. The data in *Table 9* also includes the baseline commercial cleaning process from Experiment RC with a cleaning effectiveness of 14.2%.

Table 9 Micelle solution testing results

Experiment Test		1	2	3	4	5	6	7	8	9	RC
Micelle formula		50406A	50406B	50928A	50928B	50928C	50928D	50928E	50929F	50929G	Ultrasil 53 Ultrasil MP Ultrasil 10
Membrane		JW	JW	JW	JW	JW	JW	JW	JW	JW	JW
Cleaning Solution	Flow Rate (LPM)	3.8	3.8	3.8	3.8	3.8	3.8	3.8	3.8	3.8	3.8 3.8 3.8
	Reynolds Number	931	907	954	895	900	932	825	803	792	966 1026 1038
	Temperature (K)	299	298	300	297	298	299	294	293	292	311 314 314
	pH	6.0	5.9	6.0	6.4	5.8	7.1	6.0	7.0	6.5	8.6 2.9 10.7
Clean flux/ Un-cleaned flux		1.15	4.86	7.53	2.16	2.78	1.32	2.16	1.34	1.3	1.17
Clean flux/ New flux		0.81	0.94	0.93	0.84	0.57	0.54	0.29	0.17	0.35	0.53
Un-cleaned flux/ New flux		0.71	0.20	0.12	0.38	0.21	0.45	0.15	0.15	0.27	0.49
Cleaning Effectiveness (%)		12.9	79.3	86.7	53.6	63.8	20.6	52.5	19.4	23.2	14.2

Note: All experiments were conducted under rinse flow rate, before and after cleaning total rinse time, cleaning time of 3.8 LPM, 12 minutes, and 15 minutes, respectively

4.4.2. Cleaning solution flow rate test series

The results of the cleaning flow rates tests for formula 50406B and 50928A are summarized in *Table 10* based on linear regression flux curves and averaged ratios as done previously. *Table 10* also shows the effect of different membrane types on the micelle solution performance.

Table 10 Cleaning flow rate test sets

Experiment Test		10	11	12	13	14	15	16	17	18
Micelle formula		50928A	50928A	50928A	50928A	50928A	50928A	50406B	50406B	50406B
Membrane		JW	JW	JW	5k	5k	5k	5k	5k	5k
Cleaning Solution	Flow Rate (LPM)	1.9	3.8	7.6	1.9	3.8	7.6	1.9	3.8	7.6
	Reynolds Number	396	825	1562	418	825	1766	407	770	1606
	Temp. (K)	292	294	292	295	294	297	294	291	293
	pH	6.5	6.5	6.3	6.5	6.5	6.5	6.5	6.4	6.5
Clean flux/ Used flux		1.26	1.64	1.72	1.13	1.00	1.00	1.10	1.33	0.92
Clean flux/ New flux		0.36	0.33	0.40	0.30	0.46	0.28	0.34	0.39	0.35
Used flux/ New flux		0.29	0.21	0.24	0.27	0.46	0.28	0.32	0.30	0.38
Cleaning Effectiveness (%)		20.6	38.9	41.7	11.3	0.0	-0.4	7.8	24.1	-9.1

Note: All experiments were conducted under rinse flow rate, before and after cleaning total rinse time, cleaning time of 3.8 LPM, 12 minutes, and 15 minutes, respectively

4.4.3. Contact time test series

The test series consisted of repeated tests, Experiments 19 and 20, and the results of Experiment 2 to investigate the effect of doubling the contact time for the cleaning micelle solution. The repeated experiments were conducted under Experiment 2 cleaning

parameters for rinse flow rate, rinse time, and for cleaning flow rate. The experiments resulted in cleaning effectiveness for Experiment 19 and 20 of 82.7% and 77.2 %, respectively. The clean flux to un-cleaned flux ratios were 5.77 and 4.40, respectively. The clean to new flux ratios for set were 0.78 and 1.60. The unclean to new flux ratios for Experiment 19 and 20 were 0.14 and 0.37, respectively.

4.4.4. Water rinse test series

Water rinse effects on cleaning results are shown in *Table 11*. The results are for doubling the rinse flow rate, rinse duration, or both.

4.4.5. Membrane type and ambient temperature effect

The general effectiveness of the micelle cleaning solution for each membrane type, see *Table 2*, was shown under the same test conditions in Experiments 2, 17, and 23. The cleaning effectiveness for this set of experiments was 79.3%, 24.1%, and 71.7%, respectively. Also, Experiments 10-15 indicated that the membrane type was a factor on how changing cleaning flow rates affected cleaning solution effectiveness. The membrane type effect was indicated by the difference in the effect of the cleaning flow rate for Experiments 10-12 on the JW membrane and the effect shown for Experiments 13-15 for the 5k membrane.

Table 11 Rinse water test series results

Experiment Test		17	18	21	22	23	24	25	26	27	28
Micelle formula		50406B	50406B	50406B	50406B	50406B	50406B	50928C	50928C	50928C	50928C
Membrane		5k	5k	5k	5k	BN	BN	BN	BN	BN	BN
Cleaning Solution	Flow Rate (LPM)	3.8	7.6	3.8	7.6	3.8	3.8	3.8	3.8	3.8	3.8
	Reynolds Number	770	1606	848	1529	848	792	792	825	770	814
	Temp, (K)	291	293	295	291	295	292	292	294	291	294
	pH	6.4	6.5	6.5	6.5	6.5	6.0	6.0	6.5	6.5	6.0
Rinse Solution	Flow Rate (LPM)	3.8	3.8	7.6	7.6	3.8	3.8	3.8	7.6	3.8	7.6
	Reynolds Number	765	797	1711	1626	842	765	762	1657	775	1663
Rinse solution Total Contact time (min)		12	12	12	12	12	24	12	12	24	24
Clean flux/ Used flux		1.33	0.92	0.98	1.24	3.62	2.10	2.71	1.95	3.02	2.87
Clean flux/ New flux		0.39	0.35	0.34	0.31	0.87	0.47	0.61	0.87	0.58	0.58
Used flux/ New flux		0.30	0.38	0.35	0.25	0.24	0.23	0.23	0.45	0.19	0.25
Cleaning Effectiveness (%)		24.1	-9.1	-2.2	18.4	71.7	50.5	62.5	48.6	65.9	58.2

Note: All experiments conducted under a cleaning time of 15 minutes.

4.5. Discussion

4.5.1. Micelle solution test series

The results from the first series of tests were shown in *Table 9* and indicate that Experiments 2 and 3 showed the best results with highest cleaning effectiveness percentage and cleaned to un-cleaned flux ratios. In 1994, Lindau and Jonsson reported acid and basic cleaning of oily water membranes cleaned to un-cleaned flux ratio of 1.3 and 1.4, respectively [11].The data in *Table 9* indicates that the performance of the micelle solution in Experiments 2, 3, and 5 were significantly better than for the commercial cleaning process (Experiment RC). The data indicated that the micelle solution generally provided a cleaned to un-cleaned flux ratio greater than the commercial cleaning process value of 1.17.

Micelle formulas 50406B, 50928A, and 50928C chemically reacted to the oilfield brine fouled membrane, achieving better cleaning effectiveness by dissolving the oil particulates on the surface of the fouled membrane into the micelle solution. The data shows that cleaning of produced water fouled ultrafiltration membranes with micelle is feasible and more effective than reported in the literature for standard acid and basic cleaning of such fouled membranes. The results also indicate the micelle solution can be optimized to obtain the desired oil and water properties to enhance the performance of the solution.

4.5.2. Cleaning solution flow rate test series

The results of Experiments 10-18 indicated that there might be a maximum or optimum effective cleaning flow rate for the micelle solution for produced water fouled membranes. The change in cleaning effectiveness indicated that increasing cleaning flow

rate improves performance for Experiments 10-12 but only to a point shown by Experiments 13-15 for micelle solution 50928A. Solution 50406B and Experiments 16-18 also showed that increased flow rate improves performance to a point that then reduced performance. These experiments indicated the point at which cleaning flow maximizes cleaning effectiveness is dependent on the specific membrane and the micelle solution formula. The membranes affected the cleaning flow rate effect by how tight the membrane was and whether the micelle solution penetrates within the membrane by the increased flow rate.

Experiment 11 and 12 for the micelle solution also indicated that increasing the cleaning flow rate above the rates of the fouling solution flow rates (see *Table 6*) show only marginal cleaning effectiveness improvement from 38.9% to 41.7%. This result along with Experiments 15 and 18 indicates that increasing micelle solution cleaning above the operation flow is not necessary or significantly beneficial to cleaning effectiveness. Cleaning flow rates above the operational flow rates for Experiment 15 and 18 yielded cleaning effectiveness of- 0.4% and -9.1% respectively or a flux reduction due to the cleaning cycle.

4.5.3. Micelle solution contact time test series

Experiment 2 and repeated experiments for doubling the contact time of the micelle solution Experiments 19 and 20 indicated that no significant effect on the cleaning performance was achieved by the increased contact time. The three experiments, Experiments 2, 19-20, resulted in cleaning effectiveness of 79.3%, 82.7%, and 77.2%, respectively. The three experiments showed little if any change in effectiveness between the repeated longer contact time tests and Experiment 2 that

would not be expected for repeated experiments. The set of three experiments show the reaction time of the micelle solution is not the limiting factor on the cleaning effectiveness. The experiments indicated the cleaning flow rate described earlier has a greater effect on performance than contact time.

4.5.4. Water rinse test series

Comparison of results obtained between Experiments 17 and 21, 18 and 22, and between Experiment 25 and 26 indicates the effect of doubling the rinse water flow rates from 3.8 LPM to 7.6 LPM. The data indicates that doubling the water rinse flow rate for the cleaning cycle greatly reduces the effectiveness of the cleaning solution unless the micelle solution flow rate was also doubled. Previous experimental series data indicated that increasing the cleaning solution flow rate above the operational condition of fouling was not beneficial. The combined effect of these facts indicate that for the micelle solution, the cleaning flow rate and the rinse flow rate should be the same for the most effective cleaning cycle. These results in the conclusion that turbulent flow effects of higher cross flows had no significant advantage on cleaning effectiveness for the micelle solution. The micelle solution cleaning cycle flow rate should be determined by the membrane specification on size or by the separation flow rate used during operation of the membrane.

Experimental data comparison shows that rinse cycle flow rate does have an effect on the cleaning effectiveness shown in *Figure 8*.

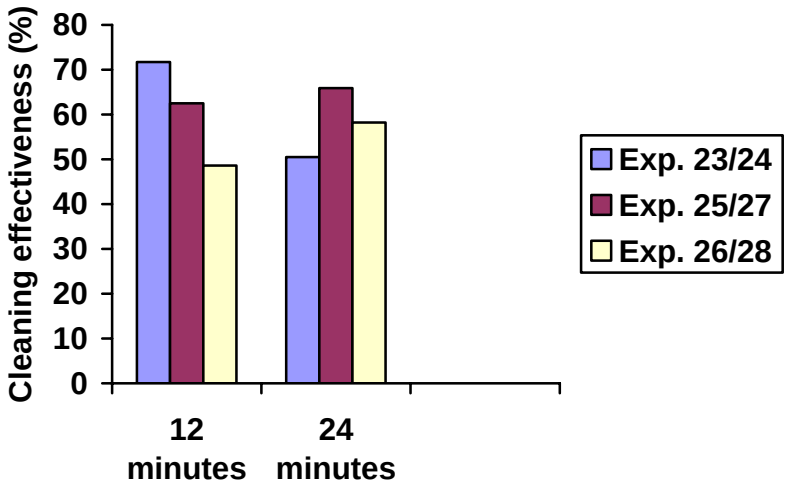


Figure 8 Rinse time comparisons.

Figure 8 shows that for the micelle solution the rinse contact time effect depends on the specific micelle formulation and on the actual rinse flow rate. The comparison indicates that for higher rinse flow rates the effect of doubling the duration of the rinse increases the improvement on the cleaning effectiveness. The data indicated that the longer rinse times provided better cleaning effectiveness through improving removal of residual left by the brine and cleaning solutions on the membrane surface.

4.5.5. Comparison of micelle solution general effectiveness on different membranes

Micellar solution cleaning was effective for all membranes tested. The general cleaning performance was better than the standard cleaning with heated acidic and basic solutions. Micellar systems showed better performance on higher molecular weight cutoff (MWCO) ultrafiltration membranes. The systems worked the best on the BN and JW membranes with an approximately 30,000 MWCO. The data showed that micelle solution generally behaved the same for each membrane type. The only effect that was

indicated by the different membranes was the limit on cleaning flow rate for the tighter membranes tested.

The average temperature of the micelle solution during cleaning for all experiments was monitored. The temperature of the cleaning solution, a factor in cleaning performance, was not controlled and dictated by ambient test conditions and heat added due to the pump and line friction was within range 10K for all tests conducted.

The commercial cleaning process recommended by Ecolab required higher cleaning temperatures than the ambient conditions utilized for the micelle solutions. The commercial cleaning process included three different chemical solutions. The first solution (Ultrasil 53) was an enzymatic cleaning solution developed for organic or biological fouling by proteins, lipids and other biological components. The solution was developed for other organic applications and not specifically for oily water applications. The other two solutions (Ultrasil MP and Ultrasil 10) were buffered acidic and basic cleaning solutions to provide low and high pH solutions that were within membrane pH specifications. These solutions were developed for mineral fouling that would require a non-neutral pH to facilitate membrane cleaning. The micellar cleaning solution was developed to specifically react with oily water deposits from produced water to improve membrane cleaning. The micellar cleaning generally provided better performance than enzyme cleaning for oily water fouled membranes and was achieved at lower temperature (*see Table 9*). The better performance would be due to the specific design of the micelle solution for oily water organics when compared to organics left by biological components. The micellar cleaning would also be able to provide improved cleaning

when compared to higher temperature acidic and basic solution for oily water fouled membranes of literature and commercial cleaning process.

4.6. Conclusions

Micellar solutions were effective in cleaning the produced water fouled membranes. The results indicated that the micelle solution can be optimized to perform better on the produced water fouled membranes according to micro emulsion properties. The results showed that the micelle solution performed better on 30,000 MWCO ultrafiltration membranes than with the tighter 5,000 MWCO membrane. The study showed that the four cleaning cycle parameters affected the micellar system performance. The four parameters for optimization of the micelle system were the micelle formula, the cleaning flow rate influenced by the MWCO, rinse duration, and the membrane type. The micelle solution formula had the most effect on performance, followed by the membrane type or size, then the cleaning flow rate, and last the duration of the water rinses. Cleaning flow rate and water rinse duration showed significant improvement on the base level of cleaning effectiveness of the solution on a membrane type.

The micelle solution does provide greatly improved cleaning performance for produced water or oily water fouled membranes over the standard cleaning solution of acid and basic solution typically employed by the membrane industry. The cleaning temperature utilized yielded that a micelle solution can be formulated to operate at ambient conditions and to eliminate the requirement of a heat source for an onsite membrane unit. With optimization, a micelle cleaning solution can provide a very cost effective solution to cleaning oily water fouled membranes at ambient temperature.

5. SUMMARY AND CONCLUSIONS

The first objective of the study was to evaluate the use of three commercial membranes, JW, 5k, and BN, for the pretreatment of produced water. The study conducted showed that PVDF ultrafiltration membranes could provide treatment to less than 5 NTU for subsequent desalination for an onsite produced water treatment system. The results showed that the turbidity removal ranges for JW, 5k, and BN ultrafiltration membranes were 99.27% to 99.87%, 95.75% to 99.82%, and 99.71% to 99.82%, respectively. The study showed that the oil removal ranged for JW, 5k, and BN ultrafiltration membranes were 59.52% to 90.43%, 47.32% to 87.27%, and 78.20% to 94.31%, respectively. BN membrane would be the best membrane available for the treatment of the produced water to meet feed specification for desalination. The data also indicated that for the BN membrane no effect was shown for operation parameters of TMP and feed flow rate on water quality. The 5k and the JW membranes showed TMP and feed flow rate affected the water quality performance of the membrane.

The second objective focused on the cleaning of produced water fouled membranes by micelle solution. The study consisted of using linear regression to calculate average flux ratios and cleaning effectiveness. The data showed that the use of a micelle solution to clean the produced water fouled membranes was a feasible and effective method. The study showed that the micelle solution performed better than acidic and basic solutions reported in the literature for this type of foulant. The study also showed that the micelle solution performed better than the recommended commercial cleaning process for produced water fouled membranes. The study showed

with further adjustment of the micelle solution the cleaning effectiveness could be optimized for an ambient temperature cleaning of membranes.

The last objective was to evaluate the micellar solution cleanup under varying operation parameters. The parameters were the membrane type or size, cleaning flow rate, cleaning duration, rinse flow rate, and rinse duration. The studied showed that for the micelle solution the cleaning effectiveness was not affected by cleaning duration or the rinse flow rate. The study did demonstrate that the cleaning flow rate improved performance but was limited by membrane type or MWCO. The results also indicate that increasing the duration of the rinse before and after cleaning improved the overall effectiveness of the micelle solution cleaning of the produced water fouled membranes.

6. RECOMMENDATIONS

Based on the first study, the use of the BN membrane should be field tested on a pilot plant for the pretreatment of produced water. The BN membrane should be field tested for treatment effectiveness over longer periods. Investigation into the mechanism of fouling of the ultrafiltration membrane by the produced water to explore the two rate of fouling decay observed during the study. Additional studies on the water quality obtained by the membranes should be conducted checking for removal of the other contaminants found in produced water sources. Investigation of hollow fiber membranes for the treatment should be studied and compared to the data obtained for spiral membranes. The micelle solution needs to be field tested on pilot equipment. The micelle solution needs further optimization for cleaning produced water fouled membranes. Studies need to be performed how long the cleaning solution will remain effective in cleaning the membranes. Also, tests should be conducted with higher pH micelle solutions for improved membrane cleaning effectiveness. Statistical testing of the cleaning effectiveness of the optimized micelle solution should be formed to validate its effectiveness for cleaning the produced water fouled membranes.

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VITA

Scott Jay Beech

Professional Address:
142 Scoates Hall
Texas A&M University
College Station, TX 77843-2117

Permanent Address:
305 Flagship Dr
May, TX 76857-1813

Education:
Texas A&M University, B.S. Chemical Engineering, May 2004
Texas A&M University, M.S. Biological and Agricultural Engineering, August 2006

Work Experience:

Texas Agricultural Experiment Station, College Station, TX (10/04-present)
Research Assistant
- Designed & Built 1 field desalination unit

Vector Marketing Corporation, Amarillo, TX (6/01-8/01)
Sales Representative
- Sold company product directly

Demand Staff Inc. Brownwood, TX (6/00-8/00)
Day worker
- Built buildings for local contractor

Keith Silman Painting & Remodeling Amarillo, TX (6/99-8/99)
Painter
- Built commercial cabinets
- Painted commercial and residential buildings