

**Process for the Removal of Spent Oil Spill Dispersants
From Test Water at the
National Oil Spill Response Test Facility**



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ABSTRACT

Dispersants are an important tool in the response to oil spills. Proper testing of dispersants and the interpretation of results, however, is complicated by issues such as the weathering of oil (Fingas et al, 2001)(Moles et al, 2001) and by problems associated with scaling bench-top tests to a full response scenario. In order to fulfill the need to test dispersants on a large-scale and gain valuable scientific evidence of their efficacy and behaviour, the use of a large test tank such as the OHMSETT facility is a logical choice. The presence of even trace amounts of dispersants in the test tank, however, can affect the behaviour of standard test oils (Ross et al, 2000). This can influence subsequent dispersant tests or even alter the performance of other response techniques (e.g. booms and skimmers) that are also tested in the tank. As such, it is important to have an effective, reliable, quick and relatively inexpensive method of detecting and removing dispersants following their testing.

This report looks at the development of two analytical techniques to detect trace quantities of dispersant in water, and a method of removing trace quantities of dispersant from the test tank using membrane separation. A suite of different membranes were selected based upon their documented compatibility to this task, and were tested at the bench scale. An additional step involving the use of Advanced Oxidation was also used as a possible polishing step. The testing protocols and results are presented in this report.

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1 INTRODUCTION

Dispersants are an important tool in the response to oil spills. Proper testing of dispersants, however, is complicated by the fact that there are problems associated with scaling bench-top tests to a full response scenario. In order to fulfill the need to test dispersants on a large-scale and gain valuable scientific evidence of their efficacy and behaviour, the use of a large test tank such as the OHMSETT facility is a logical choice. The presence of even trace amounts of dispersants in the test tank, however, can affect the behaviour of standard test oils and alter the performance of other response techniques (e.g., booms and skimmers) that are also tested in the tank. As such, it is important to have an effective, reliable, quick and relatively inexpensive method of removing dispersants following their testing.

2 BACKGROUND

Dispersant testing has been performed at the OHMSETT facility over the past few years. As part of this testing, quantities of dispersant were discharged into the tank to determine their performance. Problems were encountered when the trace amounts of dispersant remaining in the water column proved difficult to remove. The remaining dispersant unfortunately had detrimental effects on subsequent tests by affecting the surface tension of the tank water. Because no simple means of determining the exact concentration of dispersant remaining in the water existed, operators used surface tension as an indicator of residue in water samples. Attempts to employ the in-house filtration system to remove the dissolved dispersant failed. This was not surprising given that the water filtration treatment system is not designed to remove dissolved compounds.

Membrane processes have been used for the removal of surfactants and oil from different types of aqueous streams, primarily industrial wastewaters. In those streams, surfactants and oil can be found in either a dissolved or a dispersed form or in both forms. The latter is represented by droplets of emulsified oil and micelles of surfactants. It was these types of applications which helped with the selection of applicable membranes for further study.

It has been well documented that chemical properties of solution components play a crucial role in membrane separation. It is important therefore to know exactly the chemical nature of dispersants used in spill tests. It is understood, however, that the chemical compositions of many of the commercially available dispersants are proprietary and may not be readily available. A previous literature search revealed that non-ionic and anionic surfactants are those most commonly used in commercial dispersant formulations – this information was used as the basis for developing relatively simple analytical techniques to attempt to identify trace quantities of dispersant in water.

3 ANALYTICAL METHOD DEVELOPMENT

Two possible analytical protocols to determine the concentration of residual dispersants in OHMSETT water were identified. The first may be useful in determining the non-ionic surfactant component of dispersants, while the second may identify the anionic component. The protocols and testing summaries are detailed below.

3.1 Non-ionic Surfactants

This section describes the steps required for the determination of non-ionic surfactants in water samples based titration with a standard solution of sodium tetrakis (4-fluorophenyl) borate ($C_{24}H_{16}F_4BNa$). The indicator is Victoria Blue B.

3.1.1 Glassware

- 25 ml burette
- basic laboratory glassware

3.1.2 Chemicals

- Triton X-100
- Triton X-405
- Sodium tetrakis(4-fluorophenyl)borate, 5×10^{-4} M in water
- Victoria Blue B, 0.04% in ethanol
- KOH, 6M
- 1,2-dichloroethane

3.1.3 Procedure

Follow the steps below to determine non-ionic surfactants in water:

- 1) pipette 10 ml of water sample into 300 mL Erlenmeyer flask
- 2) add 5 ml of 6M KOH
- 3) add 1-2 drops of Victoria Blue B
- 4) add 5 ml of 1,2-dichloromethane
- 5) titrate with 5×10^{-4} M tetrakis(4-fluorobiphenyl) borate
- 6) Shake vigorously after each addition of titrant

3.2 Anionic Surfactants

This section describes the steps required for the analysis of anionic surfactants spectrophotometrically using acridine orange as a derivatization agent.

3.2.1 Glassware

- Basic laboratory glassware

3.2.2 Chemicals

- acridine orange 0.001M in water (or toluene)
- sodium lauryl sulfate 520 ppm in water
- toluene

3.2.3 Instrumentation

- Perkin-Elmer spectrophotometer

3.2.4 Procedure – Calibration

- 1) Prepare a series of standard solutions 0.01, 0.05, 0.010, 0.05, 0.100, 0.500, 1.00, 5.00 ppm in test tubes
- 2) Add 1000 µL acridine orange
- 3) Add 100 µL glacial acetic acid
- 4) Add 5 mL toluene and shake vigorously for 10 sec
- 5) Allow the sample to stand for 1 hr for phase separation; you may centrifuge the sample
- 6) Transfer the toluene layer into a UV cell
- 7) Plot absorbance at 500 nm versus ppm

Note: analyze blank with every batch of samples.

3.2.5 Procedure – Sample Analysis

- 8) Pipette 10 ml of the water sample into a test tube
- 9) Add 1000 µL acridine orange
- 10) Add 100 µL glacial acetic acid
- 11) Add 5 mL toluene and shake vigorously for 10 sec
- 12) Allow the sample to stand for 1 hr for phase separation (organic on top); you may centrifuge the sample
- 13) Transfer the toluene layer to a UV cell
- 14) Measure the absorbance at 500 nm

Calculate the concentration of anionic surfactants as follows:

$$ppm = \frac{A}{RF}$$

where,

A = absorbance

RF = response factor

The concepts on which these two methods can be developed have been proven as demonstrated by the preliminary data generated for the two types of oil dispersants.

3.3 Nonionic Surfactants Summary

The 12-unit ethylene oxide component of the nonionic surfactants combines with one barium regardless of the kind of alkyl or alkylaryl groups in the nonionic surfactants. The nonionic surfactants can also trap potassium ions in its spirals and be extracted into dichloroethane from one 1 to 2 M KOH, as an ion pair with tetrakis(4-fluorophenyl) borate, but any anionic surfactants in the sample is not extracted. The aqueous phase remains colourless throughout the titration, due to the insolubility of the Victoria Blue in alkaline water. The results of titration of reagent blank, Triton mixture, and real field samples are shown in Table 1. As can be seen, the method responded well to nonionic surfactants in difficult to analyze

water samples contaminated with salt and oil. Repeated measurements were made to demonstrate the robustness, selectiveness and sensitivity of the test method. The method was deemed useful to meet project objectives and may be applied under field conditions because it does not require sophisticated equipment or high skills, and uses basic laboratory supplies.

Table 1: Titration of non-ionic surfactants in reagent blank, Triton mixture and real field samples.

Sample ID	Concentration in ppm
Blank	1.6
Spiked sample (4027 ppm initial)	4080
COREXIT 9527	461
COREXIT 9500	230
COREXIT 9527 + 500ppm oil	230
COREXIT 9500 + 500ppm oil	428
COREXIT 9527 + 500ppm oil	263
COREXIT 9500 + 500ppm oil	395

1mL of titrant consumed = 31.34 ppm nonionic surfactants; ND = not detected.

Synthetic samples were prepared from the oil dispersant "COREXIT" by weighing into a flask and making up the volume to the mark. They were analyzed by this method to determine the non-ionic surfactants in COREXIT. Figure 1 delineates the results of analysis indicating that not all COREXIT constituents are non-ionic surfactants.

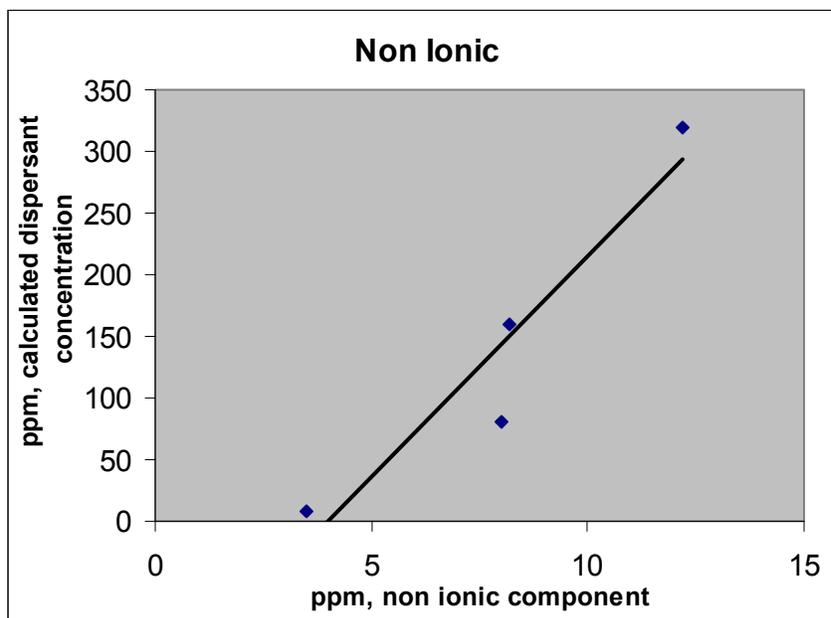


Figure 1: Non-Ionic Linearity Results

3.4 Anionic Surfactants Summary

Anionic surfactants form 1:1 complexes with cationic dyes and depending on the property of the dye the method of determining these dye complexes could be performed either spectrophotometrically or fluorometrically. The former was used in this study. The main criterion of this test method is that the dye should be sufficiently soluble in water so that the excess dye can be disposed off easily and the ion-association complex should have extractability in organic solvents such as toluene. The concentration of anionic surfactants was plotted against absorbance to establish the linear dynamic range of the detection system.

Figure 2 depicts a typical calibration of anionic surfactants. As can be seen the curve is linear from 0.1 ppm to 2 ppm, demonstrating the usefulness of the test method for the determination of anionic surfactants in water samples. Table 2 presents concentration in absorbance of a series of standard solutions used in construction of calibration curve.

Table 2: Spectrophotometric method for the determination of anionic surfactants

ppm	A
0.1	0.0222
0.3	0.1185
0.6	0.2058
1.8	0.7203
2.3	0.7274
5.9	0.7882

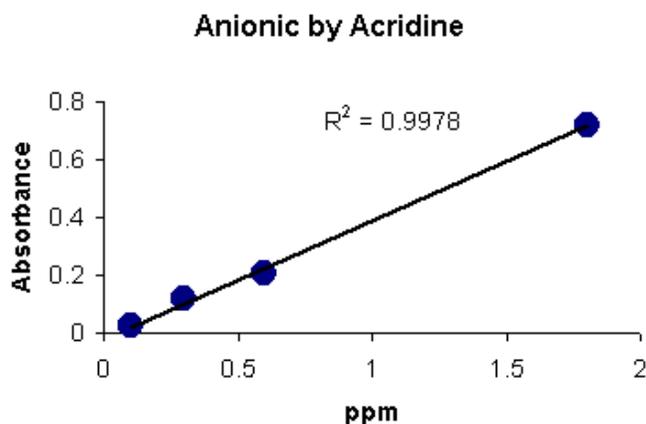


Figure 2: Absorbance Relationship Below 2ppm

Figure 3 delineates the results of analysis of anionic surfactants in the COREXIT samples, mentioned above, suggesting that not all COREXIT components are anionic surfactants. The composition of COREXIT used in this study is unknown but the results of analyses have shown that this oil dispersant material may contain organic solvents, oil dispersants with dual behaviours as ionic and non-ionic. This dual property of COREXIT may have been introduced by the manufacturer to increase its efficacy as oil dispersant. The test method of anionic surfactants was subjected to intensive investigations and found robust, selective and sensitive, and suitable for field applications.

Results generated thus far are preliminary in nature, but are promising. The anionic protocol was able to generate reliable results when measuring concentrations up to 300 ppm. The non-ionic protocol demonstrated some variability when measuring the same concentration range. Further study of both protocols would help identify the variability and level of confidence to be expected from these analyses.

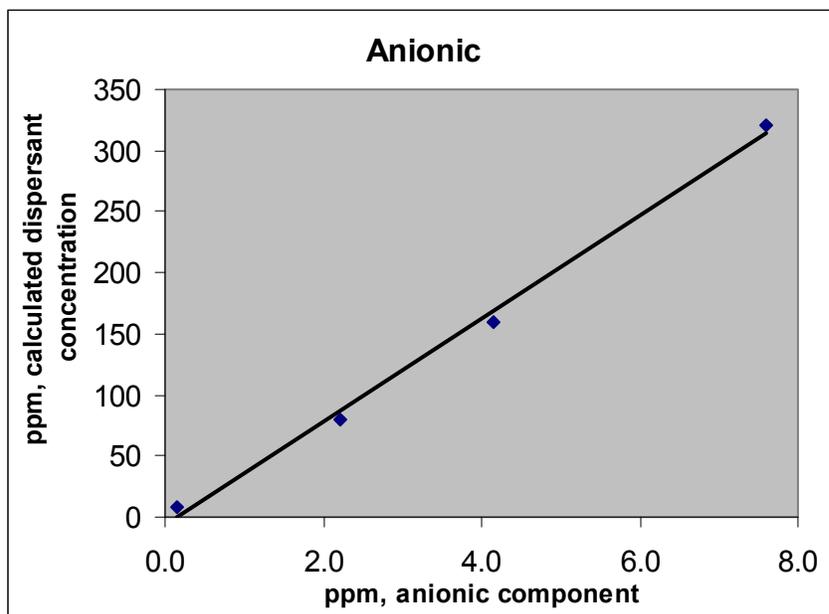


Figure 3: Anionic Linearity Results

This work has shown that two analytical techniques can be useful for the determination of low concentrations of both anionic and non-ionic surfactants in water contaminated with salts. The derivatization with Acridine is combined with spectrometry for the determination of traces of anionic surfactants in difficult to analyze matrices. A titration method based on tetrakis(4-fluorobiphenyl) borate as a titrant and Victoria Blue as indicator has been successfully developed to determine traces of non-ionic surfactants in salty water. Both analytical techniques have been found quick, selective, and sensitive. They require inexpensive equipment and labware with basic worker skills. Although these preliminary results are positive, additional study is recommended to help determine the sensitivity limits of both protocols.

Due to the fact that additional research is recommended for the development of these protocols, the traditional method of inferring dispersant concentration by analyzing surface tension was used for subsequent membrane tests.

4 DISPERSANT REMOVAL MATERIALS AND METHODS

A range of membrane types were used in a suite of experiments to determine key operating parameters. Different types were selected in order to find a membrane that was selective while having a relatively high flux. The types of membranes considered and the dispersants used during testing are detailed in the following sections.

4.1 Nanofiltration Membranes

Three different commercial polymeric flat sheet membranes were initially selected for use in this study: Desal 5, NF45 and NF90. They were selected based on their reported effectiveness in separating surfactants/dispersants and oil from various aqueous streams. Their main characteristics are presented in Table 3.

Table 3: Nanofiltration Membranes

Membrane	Desal 5	NF 45	NF 90
Manufacturer	Osmonics/Desal	Dow Chemical	Dow Chemical
Material	proprietary thin film composite	proprietary thin film composite	proprietary thin film composite
Salt rejection (%)*	96**	95***	95***
Permeate flux****	45 L/m ² ·hr (26.5 gal/ft ² ·day)	44 L/m ² ·hr (25.9 gal/ft ² ·day)	12 L/m ² ·hr (7.1 gal/ft ² ·day)
Operating pH range	4 - 11	3 - 9	3 - 9
Cleaning pH range	2 - 11.5	1 - 11	1 - 11

- * NF membranes have specific rejection of divalent salts, such as Ca²⁺ and Mg²⁺. The majority make up of the seawater, sodium chloride, will not be rejected by NF membranes.
- ** Based on the following test conditions: 2,000 ppm MgSO₄, 4.8 bar (70 psi), 25°C.
- *** Based on the following test conditions: 1,000 ppm MgSO₄, 6.9 bar (100 psi), 25°C.
- **** SAIC Canada test data at 5.2 bar (75 psi) and 25°C.

4.2 Ultrafiltration Membranes

Three ultrafiltration polymeric membranes were selected for this study. Table 4 below shows the main characteristics of these membranes.

Table 4: Ultrafiltration membranes

Membrane	G5	G10	G20	G50
Manufacturer	Osmonics/ Desal	Osmonics/ Desal	Osmonics/ Desal	Osmonics/ Desal
Material	Proprietary thin film composite	proprietary thin film composite	proprietary thin film composite	proprietary thin film composite
Molecular Weight cutoff (Daltons)	1000	2500	3500	8000
Operating pH range	2-11	2-11	2-11	2-11
Cleaning pH range	2-11.5	2-11.5	2-11.5	2-11.5

4.3 Microfiltration Membranes

MEMBRALOX membranes are tubular ceramic membranes. The manufacturer reports excellent thermal stability, a wide pH range of 0 to 14, sterilizability, a bursting pressure > 50 bar and a complete range of modules. The characteristics of the membrane are listed in Table 5

Table 5: Microfiltration membrane

Membrane	MEMBRALOX
Manufacturer	Pall Corp.
Material	α -alumina
Membrane configuration	Tubular
Outside diameter, cm	4.24
Length, cm	28.5
Filter area, cm²	450
Pore size, μm	0.2
Operating pH range	0-14

4.4 Membrane Separation Parameters

The following parameters of the membrane separation were determined in experiments and subsequently used to evaluate the effectiveness of membrane filtration:

Rejection (%) Rejection (R) is a fraction of the total contaminant mass/concentration rejected by the membrane. It is determined by the following ratio:

$R = (C_F - C_P) / C_F$, where C_F and C_P are contaminant concentrations in the feed/concentrate and the permeate, respectively.

Permeate flux (L/m²/hr) Permeate flux (J) is the volume (V) of the permeate generated from a membrane surface area (F) within a given time (t): $J = V / (F \cdot t)$

Volume recovery (%) Volume recovery (R_v) is a fraction of the total volume of the wastewater that can be recovered as the clean permeate:

$R_v = V_P / V_F$, where V_F and V_P are volumes of the feed and the permeate, respectively.

4.5 Dispersants

Two dispersants were used during this study, specifically Corexit 9527 and Corexit 9500. These dispersants have been used in numerous studies, and currently represent most commonly stocked dispersants in North America.

4.6 Bench-scale Membrane Testing System

4.6.1 Flat Sheet Membrane Tests

All the flat sheet membrane tests in this study were performed using a bench-scale three-cell membrane system. A picture of the experimental set-up is shown in Figure 4 and Figure 5. The system included a feed/concentrate tank, a high-pressure piston pump, three stainless steel plate-and-frame membrane elements, a pressure gauge, a pressure control valve, a safety bypass valve, a pressure relief valve, a heat exchanger (stainless steel cooling coil), a flowmeter, a pH meter, an electrode (pH probe), a thermometer, and three permeate collection beakers.

The feed solution was pumped at a rate of 11 L/min through three parallel cells from the feed tank by a high-pressure piston pump. A portion of the feed stream permeated through the membranes and formed the permeate stream. The remainder was rejected by the membranes and formed the concentrate stream. The permeate was collected into beakers while the concentrate returned into the feed/concentrate tank.

The trans-membrane pressure (TMP) in the test system, which was the "driving force" of separation, was controlled by the pressure control valve and monitored by the pressure

gauge. A pressure relief valve was incorporated into the system to avoid damage due to possible pressure fluctuations, while a water-cooled heat exchanger was employed to remove heat generated by the pump. The system was operated in a batch mode with a maximum feed solution volume of approximately 20.5 L, and a minimum achievable concentrate volume of approximately 2 L.

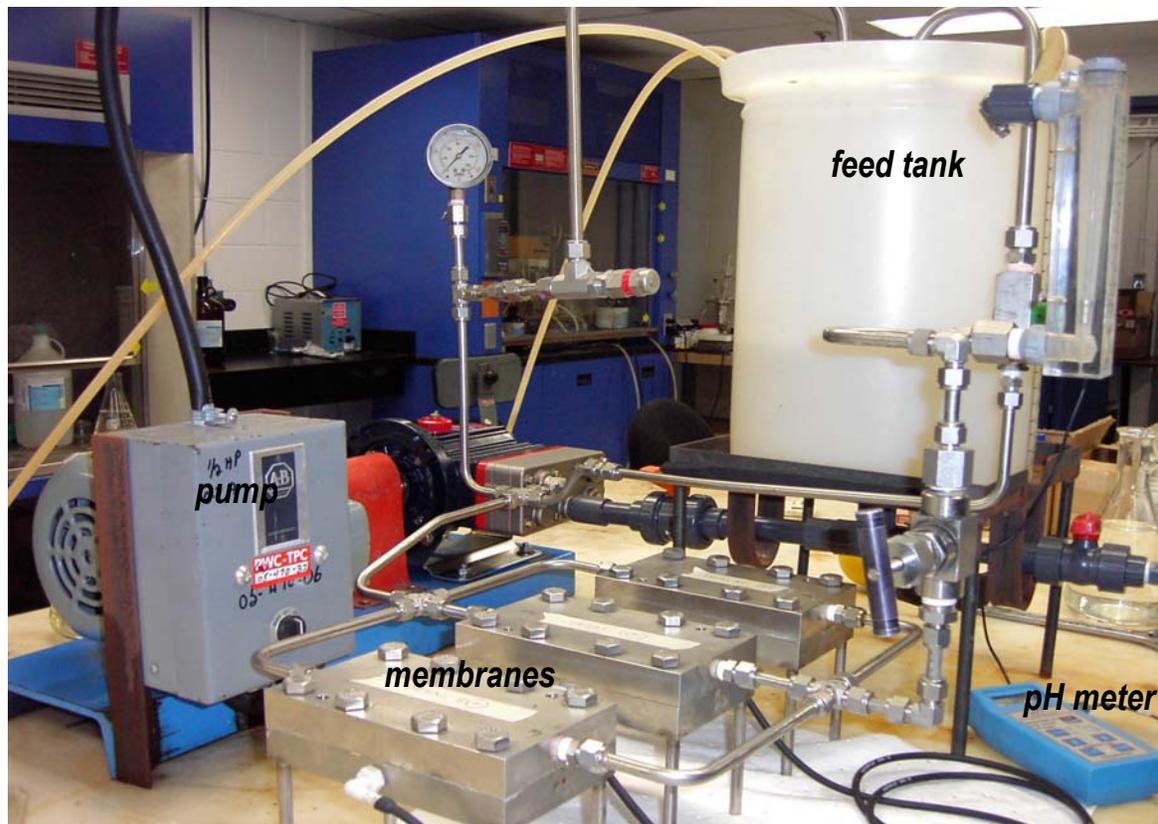


Figure 4: Bench-scale flat sheet membrane system

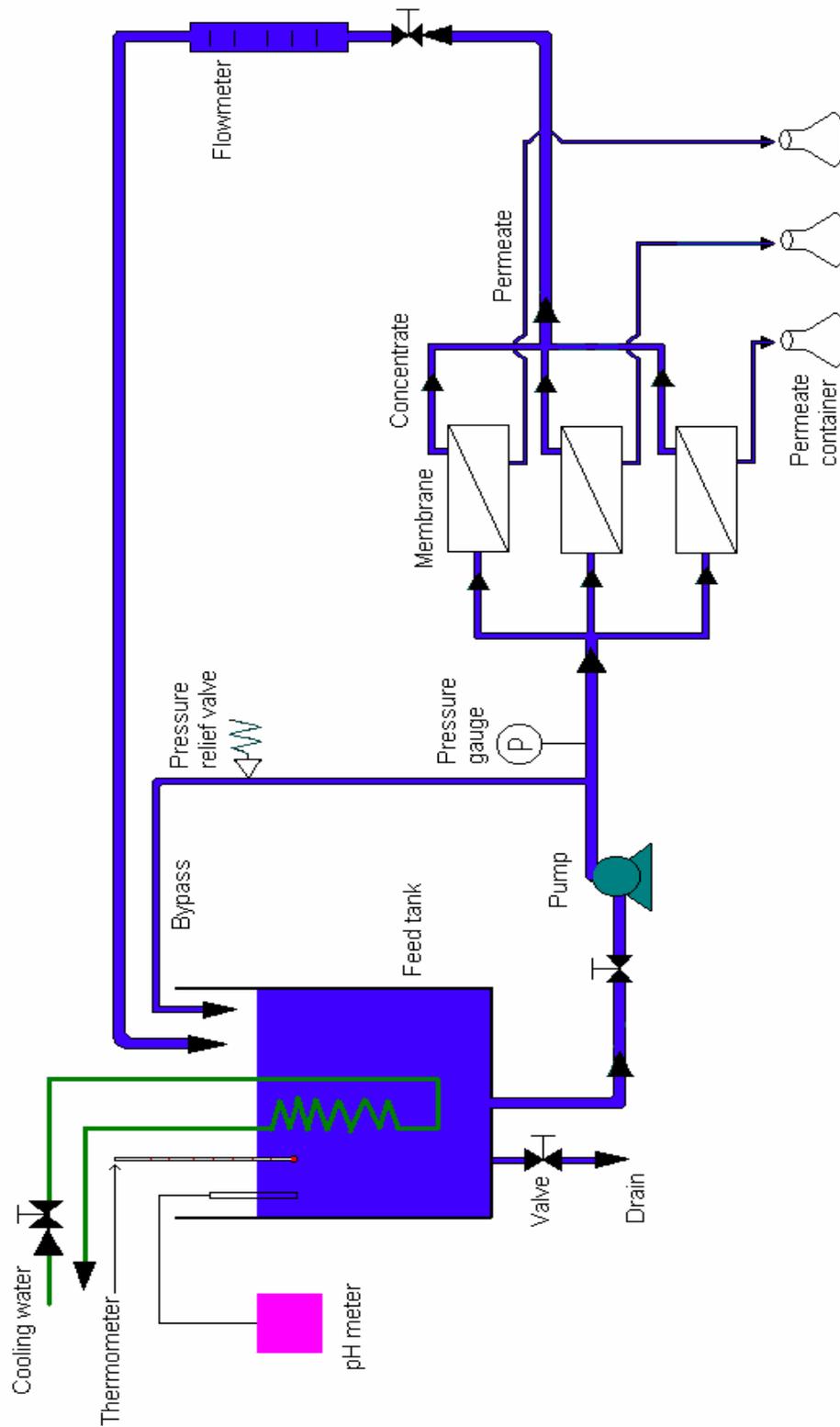


Figure 5: Flow diagram of Bench-scale three-cell flat sheet membrane system

4.6.2 Tubular Membrane Tests

Tubular membrane tests were performed using the experimental set-up shown in Figure 6 and Figure 7. It is similar to the flat sheet set-up shown in Figure 4 and Figure 5 with a few notable differences:

- The three cells were replaced by the MEMBRALOX tubular membrane module described previously in Table 3.
- The pump used in this system was a 0.187 kW ($\frac{1}{4}$ horsepower) dual diaphragm pump (Dayton Pumps) that provided a pressure up to 6.9 bar (100 psi) at 11.4 l/min (3 gal/min).
- There was no cooling coil in the new system because the diaphragm pump generated much less heat compared to the piston pump used in the first system. This system was constructed out of PVC piping.

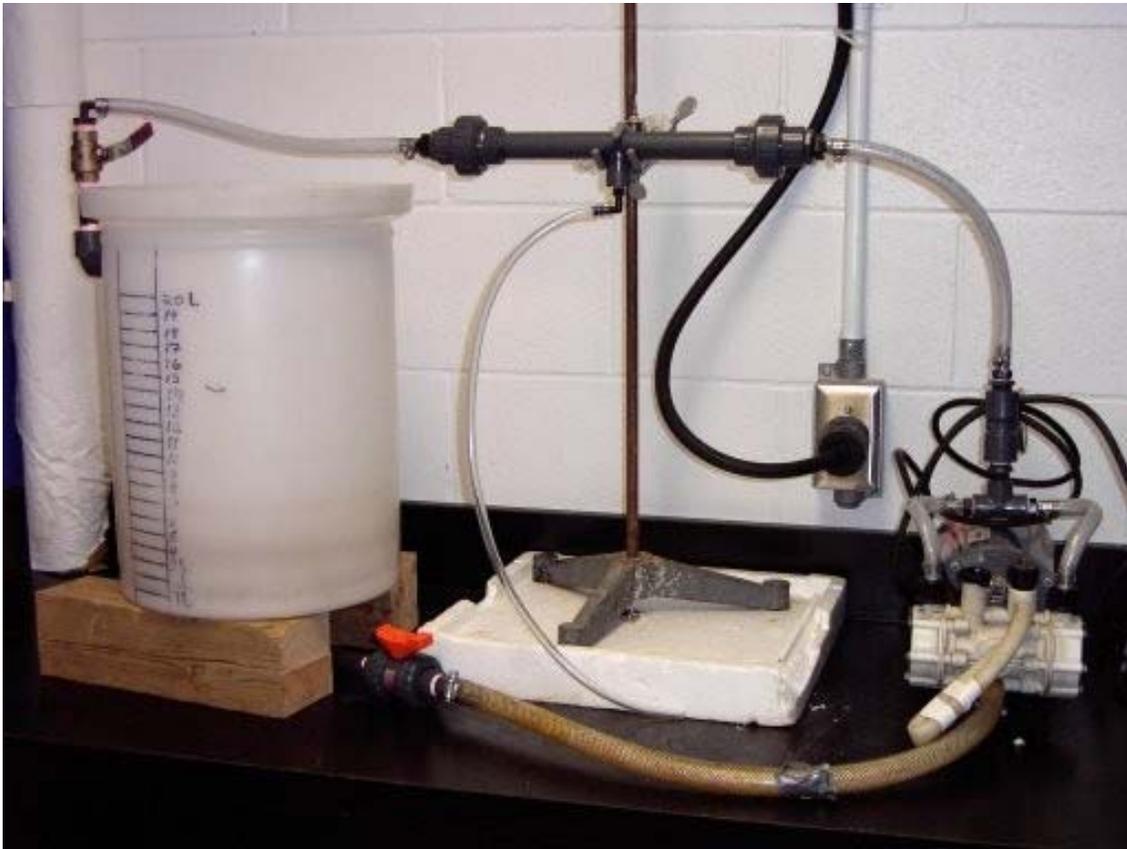


Figure 6: Bench-scale tubular membrane system

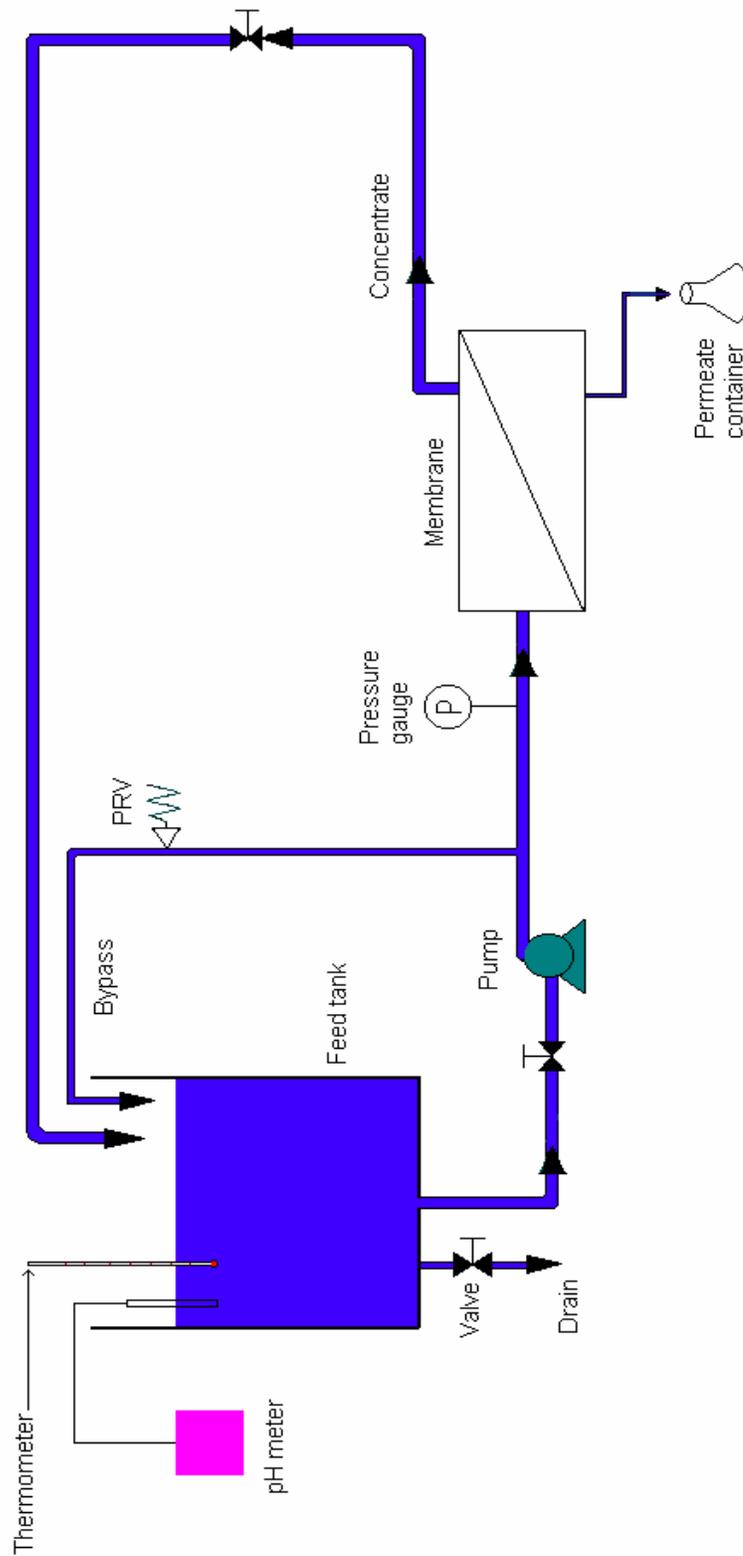


Figure 7: Flow diagram of the tubular MF membrane experimental set-up

4.7 Experimental Procedures

4.7.1 Preparation of water samples

The actual water samples (OHMSETT water) used in this work were obtained from the OHMSETT test tank. These samples were spiked with dispersant as indicated in the test descriptions. Synthetic water samples were prepared by adding dispersant and oil to tap water or deionized (DI) water to prepare a similar makeup as the OHMSETT test tank water. A dispersant concentration in the range of 500ppm was selected as the initial concentration – which would enable the effect of dispersants to be easily measured and be representative of residual concentrations in OHMSETT water following dispersant tests.

Water samples were prepared using the following procedures:

1. Place 10 litres of water into a clean pail,
2. Add 5 mL of dispersant to the water,
3. Start mixing using the drill press, while mixing add 10 mL of oil,
4. Mix for 10 minutes,
5. Settle for 5 minutes,
6. Skim the small layer of oil from the top and side with a piece of oil sorbent.

4.7.2 Flat sheet membrane filtration tests

For each run, one type of membrane was put in the three cells while 10 litres of feed solution was tested. The runs were usually carried out over a period of several hours.

The feed tank was cleaned before each run. The cleaning was conducted by circulating 20 litres of tap water (four times) and DI water (two times) in the system. During the tests, the trans-membrane pressure was controlled at 10.3 bar (150 psi).

For most of the runs, the following procedure was used:

1. Put 10 L of feed solution into the feed tank;
2. Take the initial feed sample;
3. Take feed and permeate samples as the remaining concentrate in feed tank drops to 9 L, 7 L, 5 L and 1.5 L;
4. Take permeate readings from each cell every half an hour;
5. Record temperature and pH readings every half an hour.

4.7.3 Tubular membranes filtration tests

The test procedure was the same as the flat sheet membrane tests except that the trans-membrane pressure was maintained at 4.1 bar (60 psi).

4.8 Analyses

Analyses of test samples were performed in-house by SAIC Canada. Surface tension was determined as a function of dispersant concentration. Analyses of surface tension were performed using surface tensiometer (Model 20, Fisher Scientific).

For most of the membrane filtration tests, the temperature of the feed solutions ranged from 22 to 24°C. The permeate flux data present in this report were normalized to 20°C based on the viscosity of the solution being used.

5 RESULTS AND DISCUSSION

The following section presents the results and discussions generated from the above experiments.

5.1 Membrane Selection

The objective of the tests in this section was to study the selection of membrane. This was based on the ability of the membrane to reject dispersants and permeate flux.

5.1.1 Surface tension vs. dispersant concentration

Experiments were performed to study the relationship between surface tension and dispersant concentration in different solutions. This was performed as an indirect means of determining trace concentrations of dispersant in the subsequent membrane test samples. Two dispersants were studied: Corexit 9500 and Corexit 9527. Test samples with different dispersant concentrations were prepared and the surface tensions were measured. Three calibration curves of surface tension vs. dispersant concentration were produced using DI water, tap water (with natural background salts) and OHMSETT water (with natural and added salts). Results have been plotted in Figure 8 to Figure 10. These results show that the surface tension increased when the dispersant concentration decreased as expected. In Figure 8, the surface tension was 36.0 dynes/cm when the concentration of Corexit 9500 was 10,000 ppm. Reducing concentration of Corexit 9500 to 10 ppm (which means 99.9% reduction of concentration) resulted in increase of surface tension to 57.0 dynes/cm. Similar trend can be found for Corexit 9527.

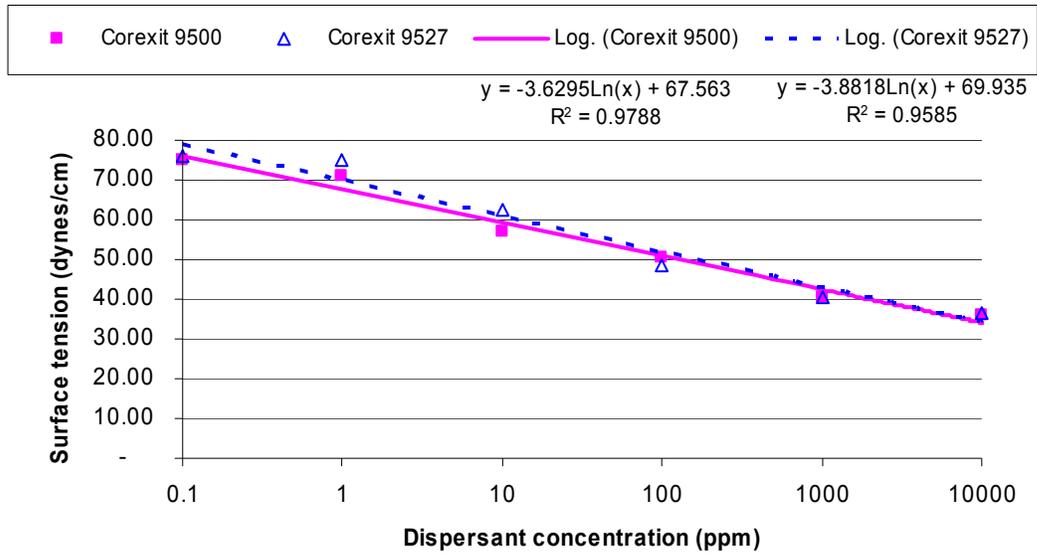


Figure 8: Plot of surface tension vs. dispersant concentration using DI water

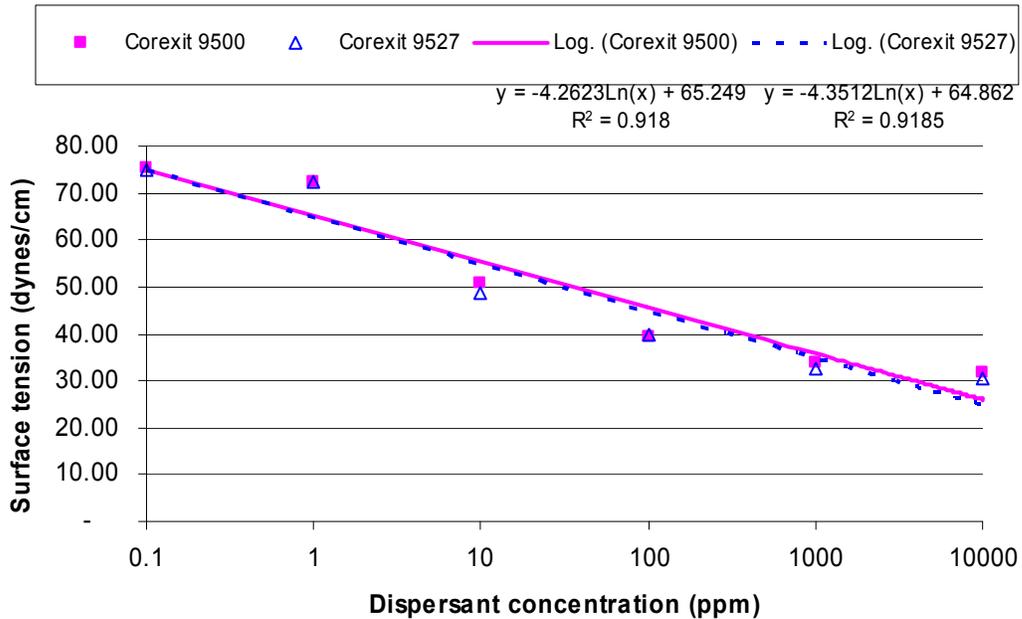


Figure 9: Plot of surface tension vs. dispersant concentration using tap water

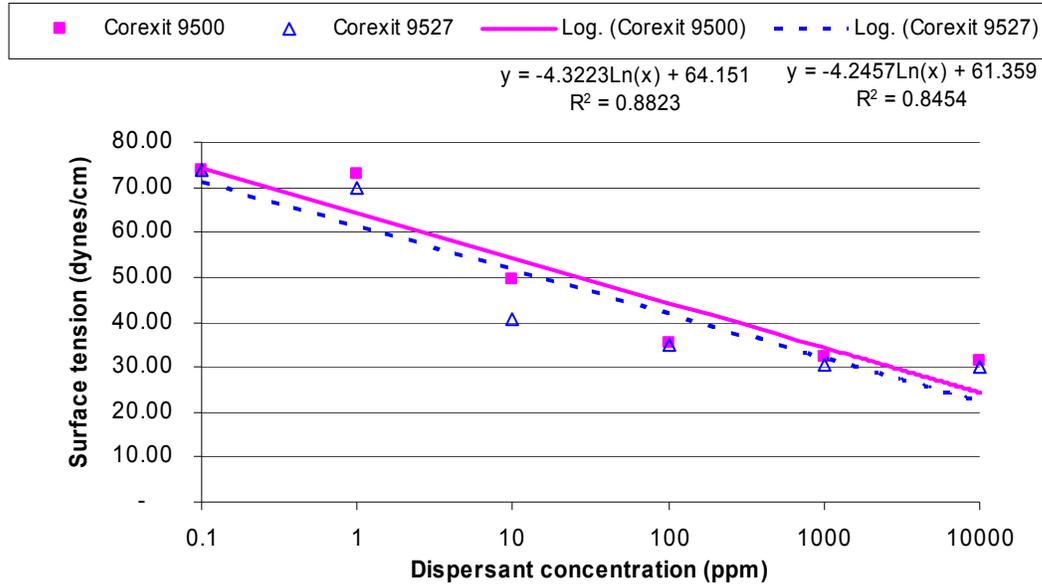


Figure 10: Plot of surface tension vs. dispersant concentration using OHMSETT water

5.1.2 Preliminary membrane tests

In order to study membrane rejection of dispersant, filtration tests were performed using synthetic water samples (tap water + Corexit 9500 + oil). Initial water samples and permeate samples after one hour of filtration were collected and analyzed. Permeate fluxes after one hour of filtration were measured. Results are given in Table 6 below. These results show that all the NF and UF membranes tested have excellent rejection of dispersant. The surface tension of the initial samples was around 37 dynes/cm. The surface tension of the one hour permeate samples ranged from 56 to 70 dynes/cm. Based on the plot shown in Figure 9 it was estimated that more than 99% of dispersant was rejected by these NF and UF membranes. The rejection of dispersant for the MF ceramic membrane was found to be poor. The surface tensions of the initial feed and the permeate were 36.5 dynes/cm and 37.3 dynes/cm, respectively.

The permeate fluxes of G5 (7.2 L/m²/h) and MEMBRALOX (6.6 L/m²/h) were found to be unacceptably low. The fluxes of the other membranes ranged from 17 to 36 L/m²/h, which were considered to be acceptable in this study.

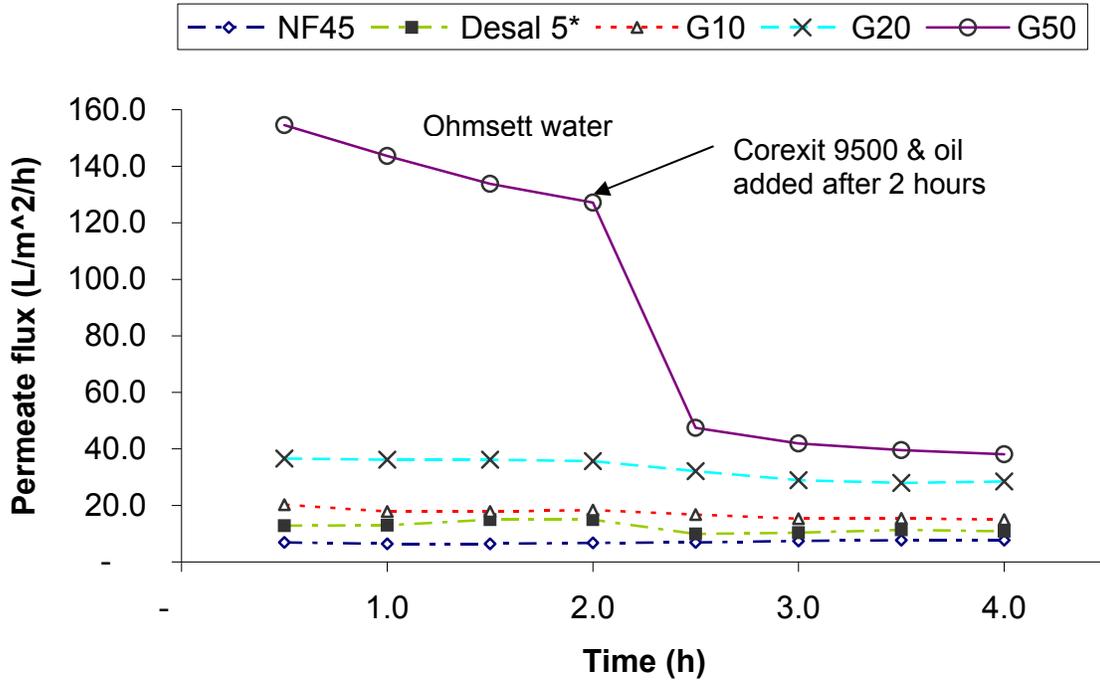
Table 6: Preliminary membrane filtration test results (tap water)

Membrane	Surface tension (dynes/cm)		Corresponding dispersant concentration (ppm)*		Permeate flux (L/m ² /h)
	Initial feed	Permeate	Initial feed	Permeate	
Desal 5	35.5	64.7	1074	1.1	32.3
NF 45	37.1	70.7	738	0.3	36.0
NF 90	37.2	62.5	721	1.9	23.7
G 5	37.3	63.3	704	1.6	7.2
G 10	36.8	63.3	792	1.6	17.5
G 20	37.3	56.7	704	7.4	23.5
MEMBRALOX	36.5	37.3	850	704.3	6.6

5.1.3 Permeate flux

To further investigate the effect of dispersant and oil in permeate flux decline, a series of tests were performed using five types of flat sheet membranes: NF45, Desal 5, G10, G20, plus an additional membrane from the same series, the G50. These membranes were tested with a solution of OHMSETT water and a mixture of dispersant and oil. The OHMSETT water was tested for two hours to obtain a "baseline", then a mixture of dispersant and oil was added to the feed tank. Tests continued for another two hours.

Experimental results are shown in Figure 11 below. These five runs were performed at similar operating conditions. The permeate fluxes were normalized to 20°C. It was found that the G50 membrane had the highest permeate flux while the NF45 membrane had the lowest flux when treating the actual OHMSETT water plus dispersant and oil. For the G50 membrane, permeate flux decreased significantly after adding dispersant and oil to the OHMSETT water. For the other four membranes, permeate fluxes did not decline significantly after adding dispersant and oil to the initial feed solution. This indicates that for these smaller pore size membranes, the addition of dispersant and/or oil did not play a major role in membrane flux decline.



* Desal 5 membranes were replaced by new membranes after first two hours for visual inspection.

Figure 11: Plot of permeate flux vs. time for the NF45, Desal 5, G10, G20 and G50 membranes (TMP=150psi, 20°C)

5.1.4 Membrane rejection

Feed and permeate samples for different membrane filtration tests described in section 4.1.3 were collected and surface tensions of these samples were measured. Results have been plotted in Figure 12 and Figure 13. It can be found that the G50 membrane had poorest dispersant and oil rejection although it had highest permeate flux. The surface tension of the feed and permeate samples for the G50 membrane was 32.2 and 36.8 dyne/cm, respectively. The other four membranes showed excellent dispersant and oil rejection. For these membranes, the surface tension of the feed samples was about 30 dynes/cm. However, the surface tension of the permeate samples was higher than 71 dynes/cm. These indicate more than 99.9% rejection of dispersant and oil.

In view of these facts, the G20 membrane was considered to be the best performing membrane in this application.

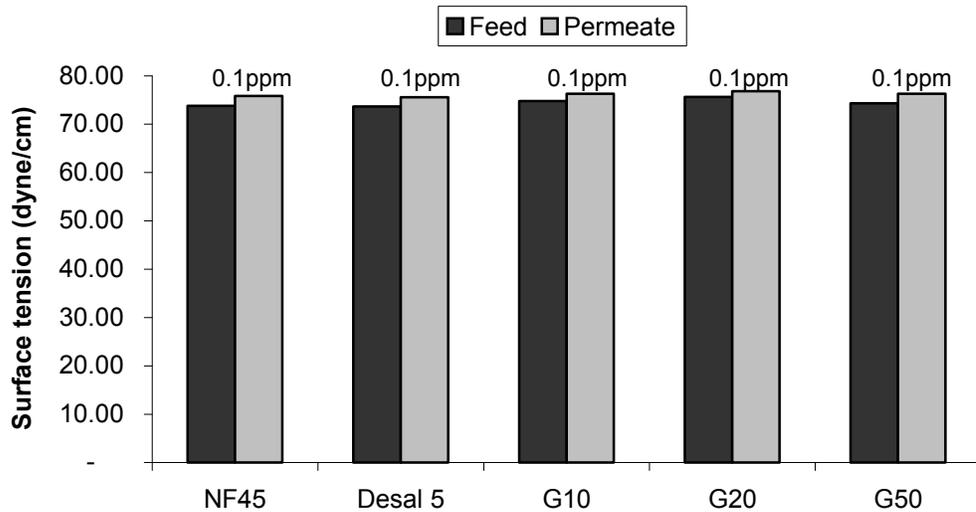


Figure 12: Surface tension measurement for different membrane filtration tests using only OHMSETT water (TMP=150psi, 20°C)

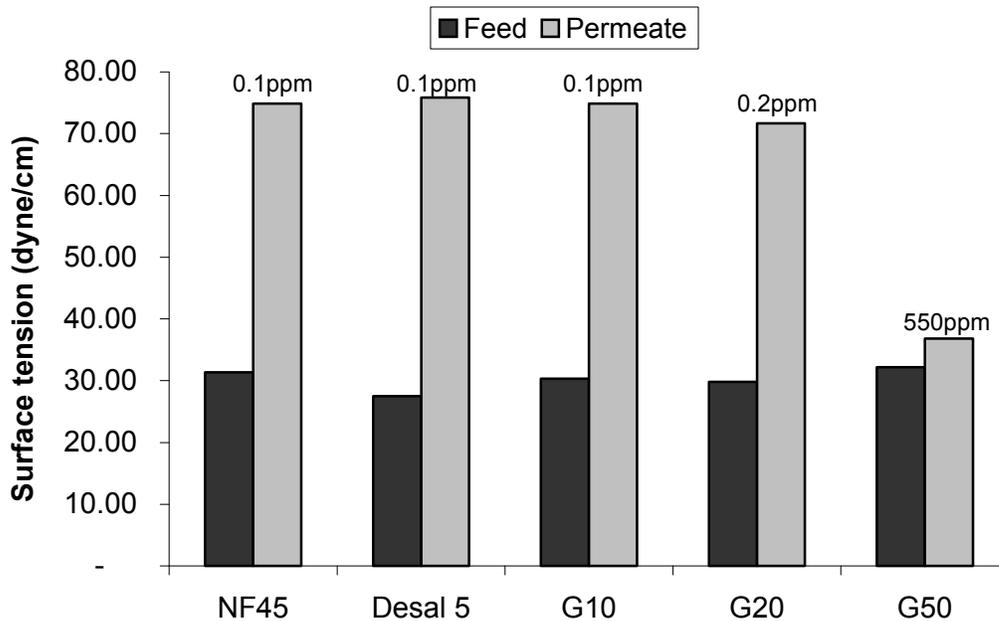


Figure 13: Surface tension measurement for different membrane filtration tests using a mixture of OHMSETT water, Corexit 9500 and oil (TMP=150psi, 20°C)

5.2 Volume Reduction

Several volume reduction runs were performed by concentrating 10 L of spiked water samples to 1.5 L. The objective of the volume reduction runs was to study the membrane rejection and permeate flux as the feed became more concentrated during each run. Table 7 below summarizes the experimental results.

Table 7: Volume reduction test results for the Desal 5, NF 45 and G 20 membranes using a mixture of tap water, Corexit 9500 and oil (TMP=150psi, 20°C)

Membrane	Remaining Feed Volume (L)	Surface tension (dynes/cm)		Corresponding dispersant concentration (ppm)*	
		Feed	Permeate	Feed	Permeate
Desal 5	10	37		760	
	9	37.4	68.3	690	0.5
	5	35	69.7	1210	0.4
	1.5	34	67.8	1530	0.5
NF 45	10	38		600	
	9	38.7	63	510	2
	5	37.3	54	700	14
	3	35.3	56	1130	9
G 20	10	36		960	
	9	35.7	52.3	1020	21
	5	32.3	45	2280	116
	1.5	30.3	41.2	3640	282

*calculated value $x = \exp((y-65.249)/-4.2623)$

These results illustrate that these membranes retained a high rejection efficiency of dispersant even when the feed volume was reduced by 85%. For the Desal 5 membrane, the reduction of feed volume did not affect the surface tensions of the permeate samples. For the other two membranes, the surface tensions of the permeate samples decreased while the feed volume was reduced. But they still showed excellent rejection ability. Figure 14 shows the change of surface tension of permeate samples as the volume of the system was reduced. Based on Figure 9 discussed in section 5.1.1, it was estimated that 99 % dispersant in the feed solutions was rejected by these membranes while the feed volume was reduced by 85%.

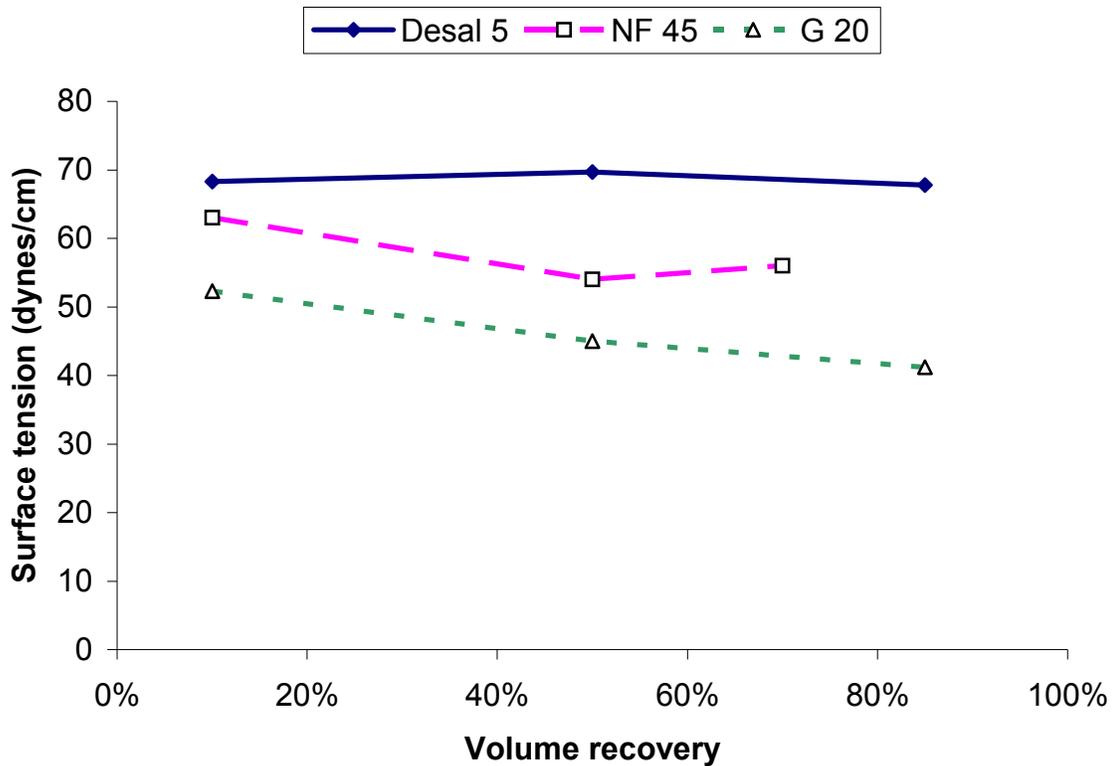


Figure 14: Plot of permeate surface tension vs. volume recovery for the Desal 5, NF 45 and G 20 membranes using a mixture of tap water, Corexit 9500 and oil (TMP=150psi, 20°C)

5.3 Advanced Oxidation Process treatment of dispersant-contaminated water

The objective of the tests in this section was to determine the impact of Advanced Oxidation Process (AOP) treatment on trace dispersant-contaminated water. This was done by applying ultraviolet (UV) light radiation on a mixture of water and trace quantity of dispersant with and in the absence of peroxide. Two types of dispersants were employed: Corexit 9500 and Corexit 9527. Two type of stock solutions were used in this study: DI water + dispersant and OHMSETT water permeate + dispersant. The concentration of dispersant in the water was 2 ppm. The peroxide being dosed into the solution mixture was ten times the quantity of dispersant (20 ppm). Each of the stock solutions was “treated” using ultraviolet (UV) light for half an hour. For each run, four samples were taken: 0 minute, 5 minutes, 15 minutes and 30 minutes samples. Surface tension of the test samples was measured. Results are as follows:

Table 8: Surface tension results of AOP treatment

Time (min.)	Surface tension (dynes/cm) (with Corexit 9500)				Surface tension (dynes/cm) (with Corexit 9527)			
	DI water		OHMSETT water		DI water		OHMSETT water	
		•OH		•OH		•OH		•OH
0	76.33				74.00			
5	71.33				73.33			
15	75.5				72.67			
30	72.33				74.17			
0		73.17				74.83		
5		76.33				73.83		
15		73.17				75.83		
30		76.33				73.67		
0			67.67				71.50	
5			70.83				72.50	
15			73.83				73.17	
30			72.33				75.17	
0				69.33				75.67
5				73.83				73.00
15				75.83				76.17
30				73.67				75.83

As shown by these results the lightly spiked samples started with a fairly high surface tension did not show a dramatic change. Based upon the effectiveness of the membranes in this study, however, advanced oxidation would not be warranted as a polishing step due to the high capital cost and negligible impact in this scenario.

6 CONCLUSIONS

A number of membranes looked promising until their results using spiked tap water were validated using Ohmsett water. Base Ohmsett water had enough impurities to affect the performance (flux rates) of membranes even before the water was spiked with dispersant and oil which narrowed the selection.

It was found that the G50 membrane had poorest dispersant and oil rejection although it had highest permeate flux. The NF45, Desal 5, G10, and G20 had very good rejection, with the G20 having the highest flux rate of the four. Because of these facts, the G20 was selected as the recommended membrane for the Ohmsett application.

The results of the membrane testing indicate that it is possible to separate surfactants from water using membrane technology. Problems with relatively low flux rates, however, indicate that a relatively large membrane system would be required to clean the Ohmsett tank.

A preliminary cost estimate was obtained for a system with the following parameters: Membrane: G20 (Osmonics, Inc.; MWCO: 3500 Daltons), permeate flux of 20L/m²/hr, with a volume recovery of 90%. Initial estimated capital costs (excluding operating cost) for a system capable of handling 1200 usgpm would be approximately \$1,000,000 US. If the flow was reduced to 360 usgpm the capital cost would still be approximately \$375,000 US. It must be noted that these capacity figures are based on results of bench scale testing. Pilot scale testing would be strongly recommended in order to provide more accurate estimates due to scaling factors.

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APPENDIX A – SUMMARY LITERATURE REVIEW

Review of Analytical Methods For Surfactants / Dispersants

Overview

The overall objective is to develop a method for removing dispersants from the test tank following their testing. SAIC Canada believes that the use of membrane technologies would be the solution. Prior to the membrane evaluation, an intensive literature survey is conducted to collect background information on analytical methods that can be used to monitor the effectiveness of the membrane technology. Those methods most suited to the process evaluation will be selected, and where necessary, modified for this study.

This subtask of the project (analytical method review) is focused on:

- ✓ Review of test methods of anionic and nonionic dispersants and hydroxylated organic solvents.

- ✓ Selection of the most suited ones for the study based on:
 - Applicability to water and wastewater matrixes

 - Sensitivity to ppm levels

 - Workability at our facility or others

Dispersants

Dispersants are a group of chemicals to be sprayed onto oil slicks, to accelerate the process of natural dispersion. Dispersants have two main components, a surfactant and an organic solvent. Surfactants are surface-active agents that are usually organic chemicals. In fact, the term surfactants is derived from “Surface active agent.” When added to liquid, surfactants change the interfacial properties of that liquid, thereby rendering it into miscible or emulsion. These properties are the direct result of surfactants having both hydrophilic and hydrophobic properties in their molecular structures. For example, when surfactants are added to a mixture of water and oil, one end of the surfactant molecule is attracted to oil (oleophilic) while the other end is attracted to water (hydrophilic).

The surfactants, which are synonymous to soap in industrial terminology, are classified as (Morelle and Szajer, 2000):

- ✓ Anionic. Examples are those used in oil spills such as sodium dioctyl sulfosuccinate, sodium ditridecanoyl sulfosuccinate and those used in laundry such as benzene sulfonate (LAS), alkyl ether sulfate, alkyl sulfate, fatty acid salts (soaps), sulfonated fatty esters, tetrapropylene benzene sulfonate (TPBS), and super surfactants (fluorinated surfactants). The focus will be on the above oil spill anionic surfactants.

- ✓ Nonionic. Examples are sorbitan esters of oleic or lauric acid, polyethylene glycol esters of oleic acid, ethoxylated propoxylated fatty alcohols, and ethoxylated octylphenol.
- ✓ Cationic. This group includes mainly quaternary ammonium compounds and will not be addressed in this work.
- ✓ Hydroxy-compound solvents commonly used to dissolve surfactants, e.g., ethylene glycol monobutyl ether, diethylene glycol monomethyl ether, diethylene glycol monobutyl ether.

Applications of Surfactants to Oil Spills

There are three main types of surfactants formulations (ITOPF, 2002):

- Type 1: Surfactants are mixed with hydrocarbon solvents between 15 and 25% surfactants. They are sprayed neat onto the oil as pre-dilution with seawater renders them ineffective.
- Type 2: Surfactants are dilutable concentrate surfactants which are alcohol or glycol (i.e. oxygenated) solvent based with a higher surfactant concentration.
- Type 3: Surfactants are also concentrate surfactants with a similar formulation to type 2 products. However, they are used neat.

The review of analytical methods is confined to the following groups of surfactants:

- ✓ Nonionic
- ✓ Anionic
- ✓ Hydroxy-compound solvents including:
 - Eethylene glycol monobutyl ether (EGBE)
 - Diethylene glycol monomethyl ether (DGME)
 - Diethylene glycol monobutyl ether (DGBE)

Literature Search

This section describes the literature survey of the available analytical methods currently used for the determination of surfactants in water and wastewater. The analytical techniques used for the analysis of surfactants in general are classified into: (a) gas chromatography, (b) liquid chromatography and (c) other techniques such as spectrometric and volumetric techniques. The focus of this review centered on these last techniques which are considered to be comparatively simple, rapid, direct and inexpensive.

This section describes briefly some of the analytical methods currently available in the literature for the determination of selected hydroxy-compounds surfactants.

Uphues 1998 demonstrated a method for amphoteric surfactants. Amphoteric surfactants play an important role for the formulation of cosmetical shampoos. In recent years they find also increasing interest as for the development of dishwashing agents or household cleaners. The following article intends to demonstrate as simply as possible the chemical background of the mainly used substance types. Also technological properties as well as ecological and toxicological properties will be described in a general form. Numerous references are cited for special information like manufacturing conditions or numerical quotation of evaluation results.

Bergh et al (1998) analyzed ethoxylated alcohols - non-ionic surfactants. The majority is used in household cleaners, laundry products, toiletries and in industrial and institutional cleaners. In previous studies, an ethoxylated non-ionic surfactant of technical quality showed allergenic activity in guinea pig experiments. Chemical analysis revealed a content of formaldehyde, a well-known contact allergen, and peroxides in the surfactant. Most cases of occupational contact dermatitis are considered to be of irritant origin, caused by contact with water and surfactants, but if allergenic autoxidation products can be formed, allergic contact dermatitis cannot be excluded. The sensitizing potential of a chemically defined high purity ethoxylated alcohol was investigated and oxidation under various storage and handling conditions was studied for this and a homologous product. The pure surfactant showed no significant allergenic activity on predictive testing in guinea pigs. When ethoxylated alcohols were stored in the refrigerator, their deterioration was limited. At room temperature, their content of peroxides and formaldehyde increased with time. Levels of formaldehyde above those capable of causing positive patch test reactions were found. Since such surfactants have wide applications, resulting exposure to formaldehyde could be more frequent than is generally realized, contributing to persistence of dermatitis in individuals allergic to formaldehyde.

Selection of Analytical Methods

The analytical test methods have been selected to meet project objectives with the criteria of simplicity, selectivity, cost effectiveness and field applicability have been applied. The proposed analytical methods have been extracted from the literature (Pal and Bandyopadhyay, 2000 and Tsubouchi et, 1985) to meet these requirements. Every effort has been made to make the propose methods easy to setup and generate large volumes of data with a reasonable turn around time.

Determination of Non-ionic Surfactants

A two-phase volumetric method has been developed for the determination of non-ionic surfactants (alkyl phenol polyethoxylates). It is based on the reaction of sodium tetrakis-(4-fluorophenyl) borate with the surfactants in the presence of chlorinated organic solvent. Victoria Blue B is used to mark the end point of the titration. The method is selective, reproducible and free of matrix interference. The method detection limit is initially estimated to be approximately 3 ppm. This may be too high for the application at Ohmsett in terms of

interference with other types of testing as well as New Jersey discharge permit standards for tank water. It may, however, be possible to reduce this limit using dilution techniques.

Determination of Anionic Surfactants

A spectrophotometric method has been selected for the determination of anionic surfactants in the sample. Acridine has been identified to complex anionic surfactants in the sample, which is then extracted with toluene. Only the anionic surfactants – Acridine complex is extracted into the organic solvent. The organic phase is withdrawn into a UV/Vis cell for measuring the absorbance. The method is easy to use, selective and free from matrix interference and can be used at the field. The method detection limit is estimated to be 0.3 ppm.

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APPENDIX B – SUMMARY LITERATURE REVIEW

MEMBRANE SEPARATION OF AQUEOUS SOLUTIONS OF SURFACTANTS/DISPERSANTS

Over the last 30 years, membrane filtration has become one of the most commonly used technological processes. Its applications range from seawater desalination to food processing to wastewater treatment. Depending on chemical structure and pore size, membranes are capable of selectively removing a variety of components of different aqueous streams, such as heavy metals, organic molecules, polymers, suspended particles, etc.

Treatment of oily wastewaters and removal of surfactants are the areas where the use of membranes has been reportedly successful. Both of those applications are directly related to the main objectives of the present study. The focus of this literature search is therefore to identify, analyze and summarize data on the applicability and performance of membranes in oil and surfactant removal operations.

Basics of Membrane Separation

A simplified diagram of membrane separation is shown in Figure 1. The aqueous stream is filtered under the pressure through a membrane. Acting as a selective barrier, the membrane separates the components that can permeate through it from the components that are rejected. The rejected stream forms the concentrate while the passed components form the permeate.

Pressure-driven processes are usually classified into four categories according to the pore size of the membrane (3): reverse osmosis (RO), nanofiltration (NF), ultrafiltration (UF), and microfiltration (MF). Reverse osmosis and nanofiltration membranes have very small pores that can reject ions and smaller molecules. These membranes require higher pressures to drive solution components through the pores than other membranes. Ultrafiltration and microfiltration membranes have larger pores. They cannot block ions but are effective in rejecting macromolecules (ultrafiltration) and particles (microfiltration). Membranes for pressure-driven processes are typically made of polymeric films having various chemical structures. The shape of the membranes can be flat, or tubular, or even fiber-like. A relatively new but rapidly growing group of membranes are those made of inorganic materials such as porous ceramic, carbon or stainless steel (1).

Figure 1. Simplified Diagram of Pressure-Driven Membrane Filtration

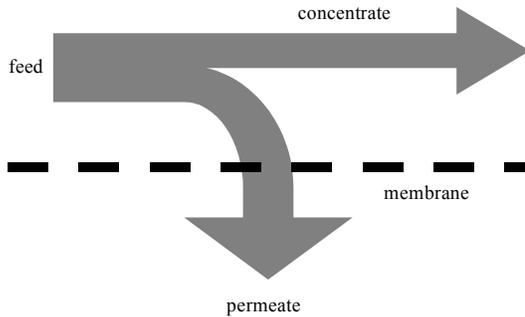


Figure 2 categorizes each of the pressure-driven processes: RO, NF, UF, and MF according to the size of common species (ions, molecules, particles) that can be rejected by respective membranes (2, 4). This diagram can only be used for a general estimation of the process applicability. Specific process characteristics, such as component rejection, vary significantly depending on the material of membranes, conditions of separation (e.g. temperature and pH), and other factors.

Membrane processes have been used for the removal of surfactants and oil from different types of aqueous streams, primarily industrial wastewaters. In those streams, surfactants and oil can be found in either a dissolved or a dispersed form or in both forms. The latter is represented by droplets of emulsified oil and micelles of surfactants. In pressure-driven membrane processes, oil and surfactants can be rejected via one or more of the following mechanisms: filtration, electric repulsion, and adsorption on the membrane (1, 3). Filtration is the predominant mechanism in ultra- and microfiltration while surface interactions such as electric repulsion play the most prominent role in nanofiltration and reverse osmosis. Adsorption of surfactants and oil can take place in all of the processes.

Figure 2. Pressure-Driven Membrane Processes

Membrane Separation Process	Nanofiltration				Microfiltration						
	Reverse Osmosis		Ultrafiltration								
Size of Common Materials	Salts		Carbon Black		Paint Pigments		Human Hair				
	Metal Ions		Pyrogens		Bacteria		Sand				
	Sugars		DNA, Viruses		Coal Dust		Mist				
	Atoms		Smoke Particles		Dust		Red Blood Cells				
			Colloids		Flour		Pollens				
			Albumin Proteins								
Molecular Weight of Poly-saccharide Molecules	100	200	1000	10,000	20,000	100,000	500,000				
Particle Type	Ions		Molecules		Macromolecules		Micro Particles		Macro Particles		
Micrometres (Log Scale)	0.001		0.01		0.1		1.0		10	100	1000

Characteristics and Factors of the Membrane Performance

Like any separation process, membrane filtration is characterized by two main parameters: throughput and selectivity of separation. Membrane throughput is normally defined as filtrate (permeate) flux *J* and expressed in units of the permeate volume *V* generated from a unit of the membrane surface area *F* over a period of time *t*:

$$J = V/(F t)$$

Using different units *J* can be measured for example in L/m²/hour or gal/ft²/day. In pressure-driven processes MF membranes usually have the highest permeate flux and RO membranes have the lowest flux.

Selectivity of separation is normally expressed in terms of rejection *R*, or the percentage of the target component (in this case, arsenic) that is rejected by the membrane:

$$R = (C_f - C_p)/C_f \cdot 100\%$$

where C_f and C_p are concentrations of the target component in the feed solution and in the permeate, respectively. UF membranes are often characterized by the molecular weight cut-off (MWCO), i.e., the molecular weight of the largest macromolecules (polyethylene glycol polymers are usually used) that can pass through the membrane pores.

Another important indicator of the membrane performance is volume recovery Φ , or the percentage of volume of the product water (permeate) V_p that can be produced from the feed V_f :

$$\Phi = V_p/V_f \bullet 100\%.$$

The volume recovery is an indication of how concentrated the concentrate stream can become and, since this is typically the stream that require further treatment, the lower its resulting volume the better from an economic point of view. Typically microfiltration has the highest achievable volume recovery and reverse osmosis has the lowest one. Table 1 summarizes typical membrane pore sizes, permeate fluxes, operating pressures and volume recoveries for the pressure-driven processes: RO, NF, UF, and MF (1, 2, 3).

There are many factors that influence membrane performance including the shape of a membrane, hydrodynamic conditions of separation, solution pH, temperature, hardness, presence of suspended particles, etc. For example, hollow fiber membranes have very high specific membrane surface area (and the permeate flux) per volume of a membrane unit; however, they are also very sensitive to the presence of suspended particles. Other types of membranes such as tubular or flat ones can handle those particles more easily. Therefore pre-filtration for suspended solids removal is usually required prior to membrane filtration when hollow fiber membranes are used. The flow rate of the feed solution across the membrane unit is also important. The lower the velocity, which is proportional to the flow rate, the greater are the chances that membrane will become fouled. For this reason the feed flow is usually maintained at the highest rate that is economically feasible.

Table 1. Typical parameter ranges for pressure-driven membrane processes.

Process	Pore size (micron)	Pressure (bar)	Permeate flux (L/m ² /hr)	Volume recovery
Reverse osmosis	10 ⁻⁴ - 10 ⁻³	15 – 60	5-40	30 - 85%
Nanofiltration	10 ⁻³ - 5 x 10 ⁻³	7 – 20	10-50	up to 85%
Ultrafiltration	0.002 - 0.2	2- 10	50-200	up to 95%
Microfiltration	0.05 - 3	0.3 – 4	100-2000	up to 99%

The pH of the feed solution can affect the speciation and charge of arsenic compounds (4). This may change their interaction with the membrane and reduce or increase the rejection of surfactants and /or oil. In addition, high pH may cause the precipitation of some metals such as calcium and magnesium and this will foul the membrane. Temperature affects the viscosity of water and this changes the permeate flux rate. Consequently, the throughput of membrane systems is lower at lower water temperatures. Higher temperatures however may, however, negatively affect the rejection and even damage the membrane material.

It is important to maintain proper process parameters to achieve a satisfactory separation performance of the membrane and extend its lifetime. Information on membrane maintenance can be obtained from membrane manufacturers and suppliers.

Membrane Separation of Aqueous Streams Containing Surfactants/Dispersants

It has been well documented that chemical properties of solution components play a crucial role in membrane separation. It is important therefore to know exactly the chemical nature of dispersants used in spill tests. It is understood, however, that the chemical compositions of many of the commercial dispersants is proprietary and may not be disclosed. A brief literature search revealed that nonionic surfactants are those most commonly used in commercial dispersant formulations (5). Examples are sorbitan esters of oleic or lauric acid, ethoxylated sorbitan esters of oleic or lauric acid, polyethylene glycol esters of oleic acid, ethoxylated and propoxylated esters of fatty alcohols, and ethoxylated octylphenol. Examples of anionic surfactants are sodium dioctyl sulfosuccinate and sodium ditridecanonyl sulfosuccinate. Anionic surfactants are apparently used on a smaller scale. Finally, there is a class of cationic surfactants but their use as commercial dispersants has not been reported, likely due to their high toxicity.

Dispersant formulations also contain a solvent to dissolve solid surfactant and reduce viscosity so that the dispersant can be sprayed uniformly. The three main classes of solvents are: water, water-miscible hydroxy compounds, and hydrocarbons. For example, a popular dispersant Corexit 9527 is hydrocarbon solvent-based.

An analysis of available literature revealed that membrane filtration been used in the treatment of spent cleaning solutions (4, 7). Spent solutions, such as those from degreasing baths, that contain surfactants along with oil, suspended particles and other impurities are filtered through semi-permeable membranes that reject oil droplets, solids and other contaminants. The water along with surfactants passes through the membrane and the resulting filtrate is virtually free of impurities. The filtrate can then be returned to the batch to be reused as a cleaning solution. The objective of study (4) was to remove the oil from the water of degreasing baths without removing the surfactants that should be reused. Concentration of surfactants was high (6.9% to 11.6%) – likely, surfactants form micelles. Those micelles could be rejected by UF membranes. The rejection of anionic surfactants was low suggesting that they easily passed through the membranes. The rejection of non-ionic surfactants was relatively high. Rejection of anionic surfactants was 3% and the rejection of nonionic was 78%.

At the same time, there is a relatively little data available on the use of membranes to reject surfactants. It is acknowledged, however, that large amounts of wastewater containing surfactants are produced nowadays that require cleanup prior to their discharge (8, 9). If treated by a membrane process, process streams can be recycled. The focus of studies dealing with this issue is on adsorption of surfactants (fouling), which can, in addition to flux decline, alter the selectivity of membrane.

It should be noted that when contaminants such as emulsified oil or suspended solids have to be removed, it is normally achieved using ultra- and microfiltration membranes. The size of the particulates is large enough to be rejected by those membranes. Those two types of membranes can also be used to concentrate surfactants that are already present in high concentrations. In those concentrations, surfactants are predominantly present in a form of micelles that are effectively rejected by the membranes.

As far as the removal of surfactants from diluted solutions is concerned (which is the case in this study), microfiltration membranes are not expected to be effective. Surfactants will likely be present in a dissolved form that can be rejected by either nanofiltration or low molecular-weight ultrafiltration membranes.

9 -Negatively charged membranes (“B” type) effectively reject anions. Try discriminate between chloride and sulfate. They are also resistant to fouling.

Selection of Membranes and Operating Conditions for Bench-Scale Testing

The analysis of published technical data on surfactants and their membrane separation leads to a conclusion that nanofiltration and low-molecular-weight (“tight”) ultrafiltration membranes should be evaluated in this study. It is obvious that reverse osmosis membranes will show a high rejection of surfactants. Evaluation of those membranes does not seem to be feasible as because of a high energy consumption and low fluxes associated

with their use. In addition, reverse osmosis membranes rejected all components of the water, including salts, which is not required in the proposed application.

It is known that membrane surface charge plays a prominent role in rejection. For example, negatively charged membranes reject anionic species (9) and are therefore expected to be effective in separating anionic surfactants. In case of non-ionic surfactants, the role of the membrane surface charge will likely be not as strong, although some effects should be expected.

Based on the above considerations, it was suggested to use ultrafiltration and nanofiltration membranes, preferable with a negative surface charge.

Polymeric membranes have been used in a majority of applications dealing with solutions of surfactants. Based on this fact, it was suggested to use them in the study. At the same, there is a rapidly growing interest to inorganic membranes that are highly chemically resistant and can be cleaned using aggressive cleaners. Keeping in mind that surfactants and oil may potentially cause a significant fouling that requires rigorous cleaning, inorganic membranes were also suggested for the study.

As far as the membrane configuration is concerned, tubular membranes are least susceptible to the presence or particulate matter in the feed stream; however, the equipment that uses those membranes is larger in size than similar equipment that uses spiral-wound membranes. On the other hand, spiral-wound membranes usually require a pretreatment to remove suspended particles.

Finally, the following commercial membranes were selected for studies:

Table 2. Membranes selected for the study

Membrane	Material	MWCO/NaCl Rejection/Pore Size	Shape	Manufacturer
Nanofiltration				
Desal-5	polymer	MWCO = 150-300	flat/spiral wound	Osmonics Corp.
NF-45	polymer	Rejection = 40-60%	flat/spiral wound	Dow Chemical
NF-90	polymer	Rejection = 85-95%	flat/spiral wound	Dow Chemical

Ultrafiltration				
G-5	polymer	MWCO = 1,000	flat/spiral wound	Osmonics Corp.
G-10	polymer	MWCO = 2,500	flat/spiral wound	Osmonics Corp.
G-20	polymer	MWCO = 3,500	flat/spiral wound	Osmonics Corp.
Membralox	ceramic	Pore Size = 50 nm	tubular	Vivendi Water

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