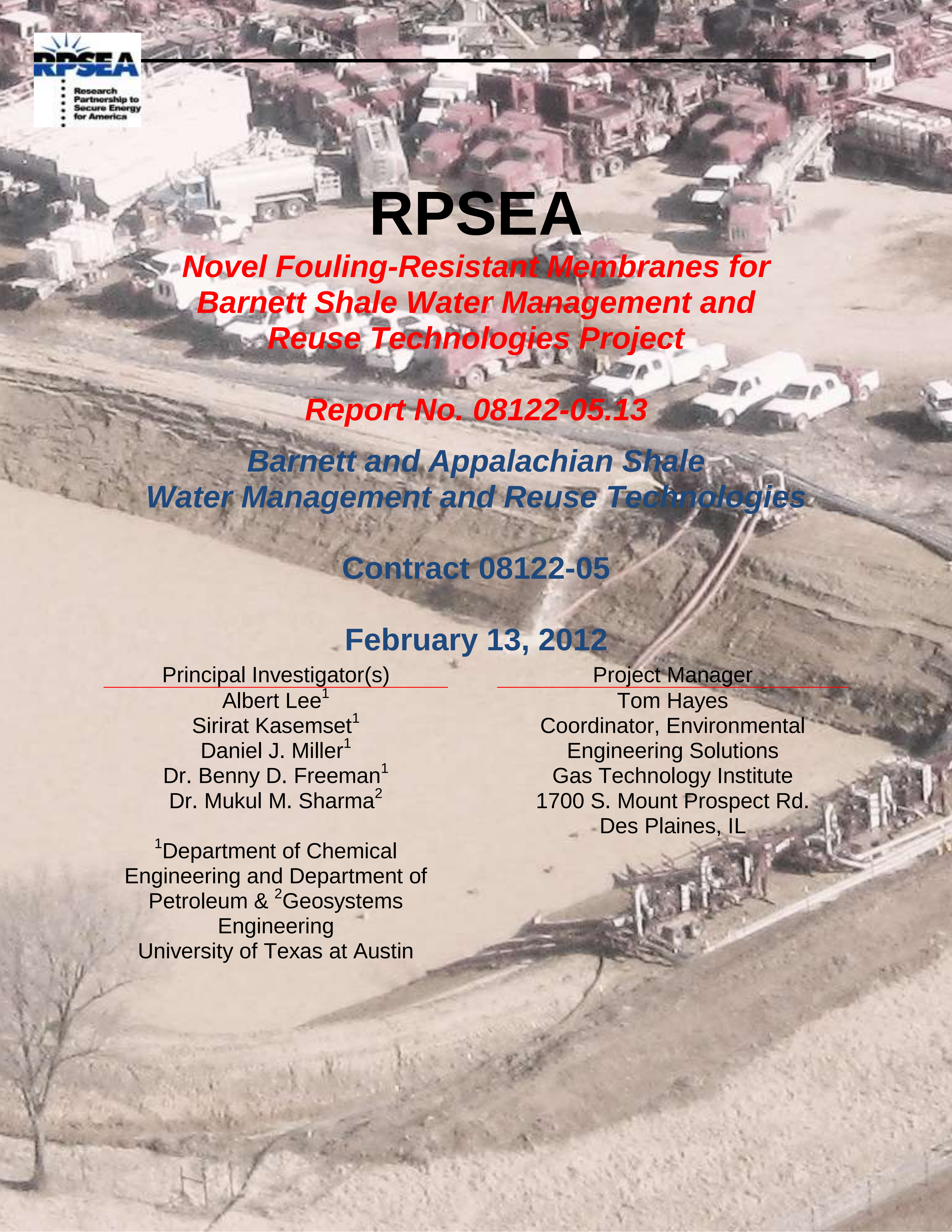

# RPSEA

## *Novel Fouling-Resistant Membranes for Barnett Shale Water Management and Reuse Technologies Project*

## *Report No. 08122-05.13*

## *Barnett and Appalachian Shale Water Management and Reuse Technologies*

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# Executive Summary

The reuse of produced and flowback water from oil and gas production is an expensive process, and often this water is reinjected into the ground at significant cost. Water purification via membrane technology offers an inexpensive, energy efficient alternative to reinjection. A key challenge in using membrane technology for produced water purification lies in fouling. Fouling is the build-up of materials (foulants) on the membrane, either externally or internally, which eventually inhibits the water transport. Unlike regular seawater or brackish water, produced water contains emulsified oils and organics, which aggressively foul the membranes.

As a result of this research program, polydopamine (PDOPA) was found to be an effective anti-fouling surface coating for UF, NF, and RO membranes for produced water purification. The deposition of PDOPA improved the permeate flux for all types of membranes studied during simulated oil/water emulsion filtration. For UF membranes, additional grafting using poly(ethylene glycol) (PEG) further enhanced the fouling resistance. Energy savings were estimated for the PDOPA-modified UF and RO membranes in oil/water emulsion filtration by comparing the power required per unit of permeate volume generated. With the same amount of energy provided by the pump during one hour of oil/water emulsion filtration, the modified RO membranes produced 1.27 times more volume than unmodified RO membranes. The modified UF membranes' permeate volume increased by a factor of 2.35 after 1 hour of oil/water emulsion filtration. Translating these benefits into industrial savings, PDOPA modification of membranes is estimated to reduce the capital costs by 30% and the operating costs by 40-80%. Based upon our two year study, surface modification of membranes by using PDOPA proved effective in enhancing oil fouling resistance, which is a major challenge in produced water treatment that employs membrane technology.

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# Chapter 1: Introduction

### Water Scarcity

Covering over 70% of the Earth's surface, water is an abundant resource. However, with the oceans accounting for 97% of this water and much of the fresh water located far below ground or frozen in icecaps and glaciers, less than 1% of the world's water is readily accessible as fresh water for human consumption[1]. Today, according to the World Health Organization (WHO), more than one billion people around the world lack access to clean water, and this number is expected to grow exponentially[2]. To meet these additional demands for clean water, we must develop an economical treatment method for water sources that are accessible in large quantities around the world, such as seawater, brackish water, and produced water[1],[3].

### Produced Water

With the global growth of the oil and gas industry, one water source has become readily available: produced water. Produced water is a byproduct of oil and gas production that is typically composed of dispersed oil, organics, salts, metals, treatment chemicals such as scale and corrosion inhibitors, coagulants to remove solids, and emulsion breakers[4]. In 2002, over 14 billion barrels of produced water was generated, about 7 times the production of oil[3]. This water is usually considered unfit for municipal use and is reinjected into the ground at significant cost. Moreover, since produced water varies in composition and is difficult to treat, the cost of purification is even higher than the cost of reinjection. Due to its availability in many especially water-stressed areas, the purification and reuse of produced water would be a major step toward addressing water scarcity.

In recent years, natural gas production based on unconventional shale gas reservoirs has tremendously grown in the United States. Hydraulic fracturing treatment used in the production of natural gas from the unconventional gas shales allows the gas to escape in large volume, but requires a large quantity of water, typically between 1 and 4 million gallons of water for each well completion[5]. Challenges for extensively employing the hydraulic fracturing technique are the availability of water, and the management and disposition of produced water and flowback water from the well completion. One approach to mitigate these problems is to reuse the water, where treatment processes can be used to demineralize the water and remove organic contents. Membrane purification technology is a potential way to treat these waters for reuse and reduce concerns regarding water demand and water management/disposition associated with hydraulic fracturing.

## Water Purification Technologies

In water purification, desalination to treat brackish water and seawater was formerly dominated by thermal techniques: evaporating the water into vapor, thereby separating out the salt[4]. This method consumes a large amount of energy and is expensive. Oil and gas production companies often avoid thermal methods and choose to reinject the water at lower cost. Since the late 1990s, membrane-based desalination, which treats water using a selective membrane layer, has become the most economical choice for conventional desalination of, for example, brackish and seawater. These water purification membranes can separate contaminants according to size, and their relatively low use of energy, around ten percent that of thermal purification, makes them an economical choice[2]. Most desalination plants constructed today employ membrane technology, and membranes membrane are well worth exploring to produce purified water.

## Fouling

A major challenge in purifying produced water with membranes is fouling. Fouling, as shown in Figure 1, is the build-up of particulate matter on the membrane either externally or internally that eventually inhibits its activity. Internal fouling occurs when foulants clog the membrane pores, while external fouling involves the build-up of foulants on the membrane surface. Unlike regular seawater or brackish water, produced water contains many particulates, such as emulsified oils and organics, and the membrane surfaces in contact with such a mixture are readily fouled. The accumulation of foreign material on the membrane hinders the flow of water through the membrane, which in turn drives up the cost of operation[6].

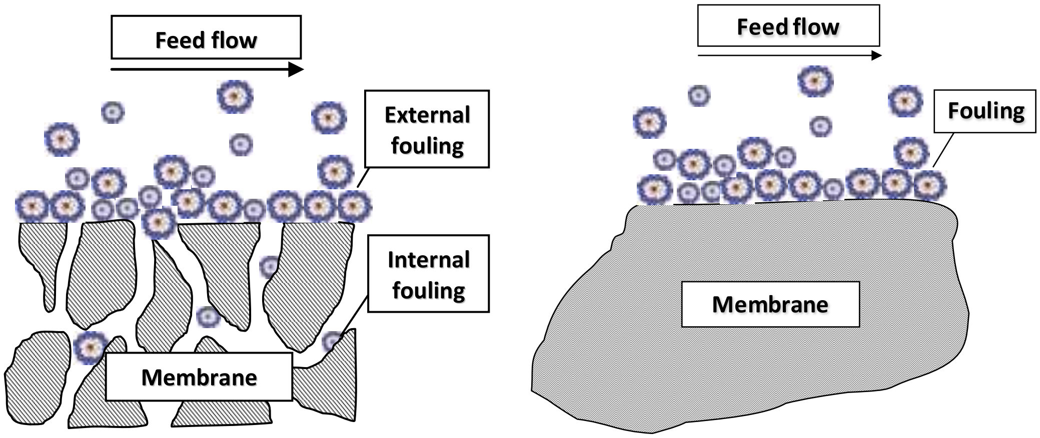

**Figure 1.** Fouling in porous (left) and non-porous (right) water purification membranes.

## Membrane Selection

Liquid purification membranes are often categorized by their ability to separate contaminants of various sizes. As shown in Figure 2, four main categories of water purification are microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), and reverse osmosis (RO).

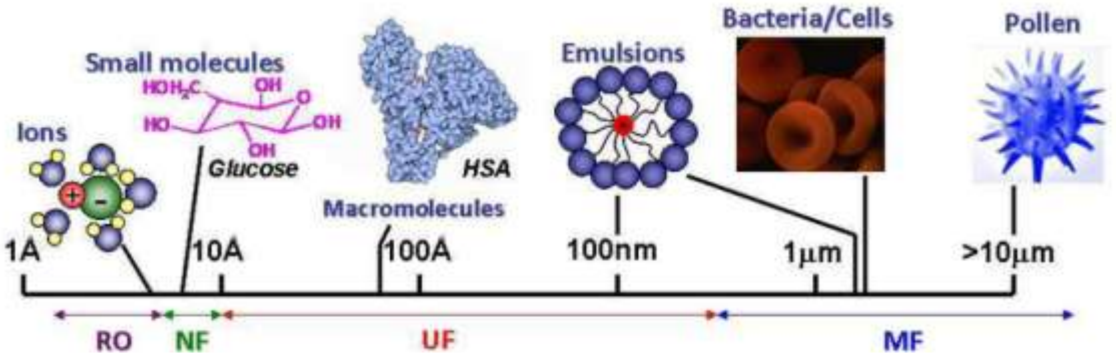

**Figure 2.** Membrane classification according to size-sieving ability.

Since produced water generally has high salt concentration, which requires removal prior to reuse or surface discharge, demineralization can be an important step in treating this water. The primary membrane type used in produced water purification (and in desalination) is the reverse osmosis (RO) membrane. Highly size-sieving RO membranes can remove salts and organics that are present in produced water. Moreover, a pretreatment step that employs UF membranes helps remove oil and grease, suspended solids, and other large molecules prior to RO treatment helps reduce the degree of fouling in RO membranes and may in fact prolong their useful life. Nevertheless, RO and UF membranes suffer from heavy fouling when treating produced water for extended periods of time. Surface modification to improve the fouling characteristics of commercial RO and UF membranes is the major focus of this research.

# Chapter 2: Background

### Polydopamine (PDOPA)

Surface coating with polydopamine (PDOPA) is a novel approach to improve membrane fouling resistance. Polydopamine is formed from dopamine, a naturally-occurring hormone and neurotransmitter. The structure of dopamine is shown in Figure 3. Messersmith et al. reported that dopamine in tris-HCl buffer solution will undergo polymerization under slightly alkaline conditions to form polydopamine, which mimics some properties of mussel adhesive proteins (specifically, *M. edulis* foot protein 5 (Mefp-5))[7]. The mechanism of dopamine polymerization and the exact structure of polydopamine are still currently unknown and are the subject of active investigation in our laboratories.

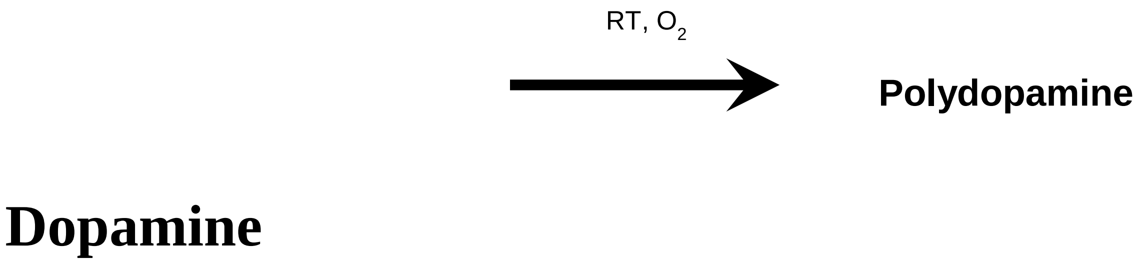

**Figure 3.** Conversion of dopamine to polydopamine (PDOPA).

Polydopamine can non-selectively deposit onto virtually any surface. Deposition is on the order of 1-100 nanometers in thickness, depending on contact time. The polydopamine layer exhibits excellent adhesion properties: it cannot be removed under sonication even at extreme acidic conditions[7].

### Polydopamine Coated Membranes

A PDOPA-coated membrane exhibits two advantages over an uncoated membrane:

1) The polydopamine layer is uncharged and hydrophilic; thus, it helps reduce oil/grease adhesion and alleviate membrane fouling.
2) Polydopamine, under alkaline conditions, rearranges to form a quinone-like structure, providing a mean for further conjugation to other organic compounds.

The free hydroxyl groups on polydopamine can be used to covalently bind other molecules to the PDOPA-coated surface. McCloskey *et al.* reported that amine-terminated poly(ethylene glycol) (PEG-$NH_2$) can be grafted to the PDOPA-modified surface to improve the surface hydrophilicity without drastically altering surface charge[8]. Many other molecules could be grafted to the surface using a similar technique.

Coating membranes with a thin layer of polydopamine should improve their resistance to fouling and, due to polydopamine's nonspecific properties, provide a versatile starting point for further surface modification to a wide variety of membranes. Because the deposited polydopamine layer is so thin, the effect of the coating on membrane flux should be minimal.

## Effect of Surface Properties on Fouling

Membrane surface modification is an effective way to improve fouling resistance of membranes[9]. This method can help prevent irreversible internal membrane fouling, which cannot be eliminated via cleaning processes or by optimization of operating conditions (*e.g.*, adjusting fluid dynamics on the membrane surface). Factors previously identified that influence surface fouling are hydrophilicity, surface charge, and roughness of the membrane surface[9].

Generally, the effect of membrane hydrophilicity on fouling depends on the specific characteristics of the foulants. For hydrophobic foulants (*e.g.,* oil), an increase in membrane hydrophilicity helps reduce membrane fouling by limiting hydrophobic interactions on the surface. In addition, the surface hydrophilicity helps increase the affinity of water for the membrane and results in the higher water flux.

The surface roughness represents the peaks-and-valleys morphology of the membrane surface. Membranes with higher roughness tend to foul because the foulants easily accumulate in the valleys of the rough membrane. This valley clogging reduces the surface area of the membrane, creates mass transfer resistance, and reduces the permeate flux.

# Chapter 3: Materials and Experimental Methods

## 3.1 Membrane Pretreatment and Modification

### Membrane Pretreatment

The UF membranes were prepared for PDOPA modification by immersion in isopropyl alcohol (IPA) for 10 minutes to wet the membrane pores. After that, the membranes were immersed in deionized water for at least 30 minutes to completely replace the alcohol in the pores. Similarly, RO membranes were prepared by soaking in 25% (v/v) aqueous isopropyl alcohol (IPA) solution for 20 minutes to remove any extractable components (*e.g.*, glycerin) and wet the membrane. Then the membranes were soaked in deionized water, which was changed three times. Finally, they were stored overnight (16-24 hours) in deionized water prior to PDOPA modification.

### Membrane Modification

The membranes were coated with PDOPA by exposing their active layers to an aqueous buffer solution of dopamine in tris-HCl, as shown in Figure 4. The coating process involved placing the membrane (with its active surface face up) on a glass plate and securing the membrane to a glass ring by applying vacuum grease on the outer edge. Then the dopamine solution was poured into the glass ring (in contact with the membrane surface) and the glass plate was placed on a rocking platform shaker to uniformly coat the membrane. The dopamine solution was prepared from dopamine hydrochloride in 15 mM tris-HCl buffer. Unless otherwise stated, a dopamine concentration of 2 mg/mL was used with a tris-HCl buffer solution at pH 8.8, and the deposition time was 60 minutes. After that, the membrane was soaked in ethyl alcohol (for UF) or 25% (v/v) IPA (for RO) for 10 minutes to remove any weakly-bonded polydopamine. Then the membranes were rinsed thoroughly with deionized water 8-10 times to remove the ethyl alcohol. They were stored in deionized water until needed.

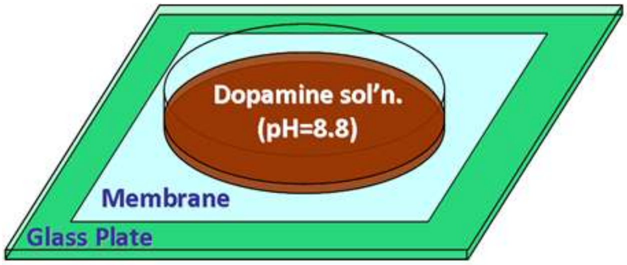

**Figure 4.** Polydopamine deposition technique.

To further enhance the hydrophilicity of the PDOPA-coated surface, a common fouling-resistant polymer, poly(ethylene glycol) was grafted to polydopamine by using methyl-terminated poly(ethylene glycol) amine (mPEG-$NH_2$, MW = 5 kDa). As shown in Figures 5 and 6, grafting was achieved by immersing the PDOPA-coated membrane in 1 mg/mL solution of PEG-$NH_2$ at 60°C for 60 minutes. The PEG-$NH_2$ solution was prepared from PEG-$NH_2$ in 15 mM tris-HCl buffer at pH 8.8. The PDOPA-g-PEG-modified membrane was then rinsed with deionized water and stored in deionized water until use.

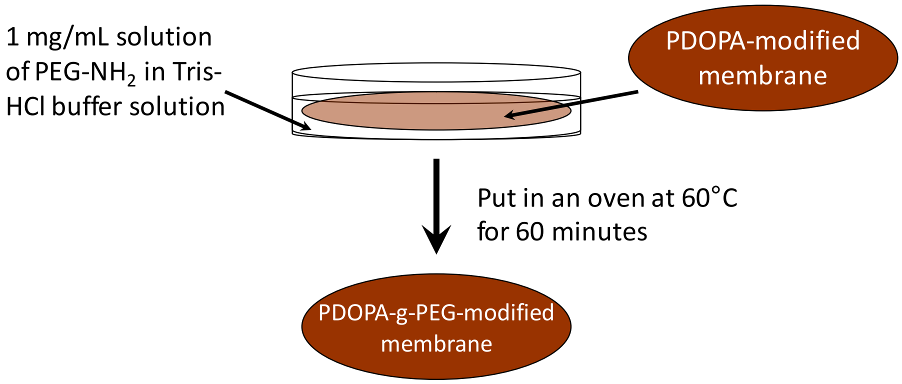

**Figure 5.** PEG-$NH_2$ grafting technique on PDOPA-modified membrane.

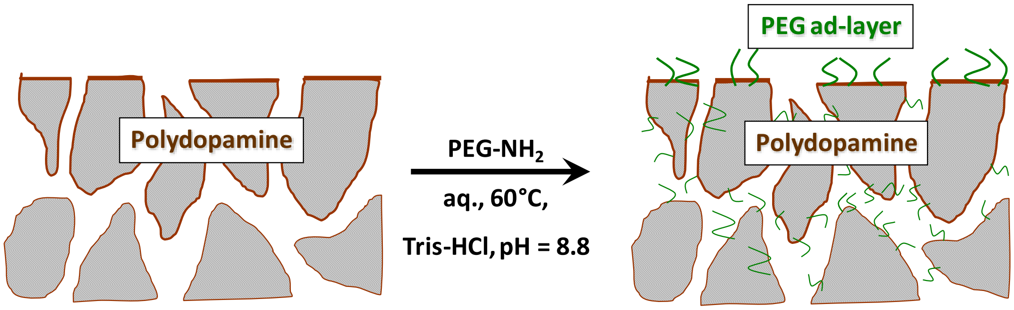

**Figure 6.** Conjugation of PEG-$NH_2$ to polydopamine coating on porous membrane.

## 3.2 Membrane Characterization

### Constant Transmembrane Pressure (TMP) Crossflow Filtration

The fouling study utilized a constant transmembrane pressure (TMP), variable flux crossflow filtration system, as shown in Figure 7. The model feed foulant solution was 1500 ppm soybean oil/DC193 in deionized water emulsion (with an oil:DC193 ratio of 9:1); DC193 is a non-ionic surfactant. To study salt rejection of RO membranes, 2000 ppm NaCl was added to the feed solution 30 minutes prior to adding the foulant solution. The permeate flux was measured as a function of time to determine the fouling characteristics of the membranes. The average and standard deviation of true salt rejections of at least three membrane samples were reported.

Different crossflow rates, TMP, and filtration times were used for different types of membranes, as shown in Table 1.

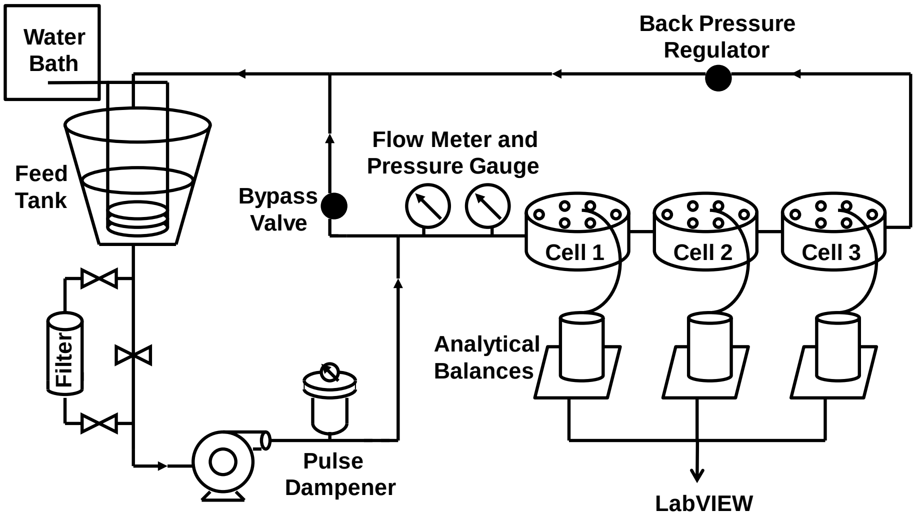

**Figure 7.** Constant TMP crossflow filtration system.

**Table 1.** Crossflow rates, Reynolds number, TMP, and filtration time for each membrane type

| Membrane Type | Crossflow Rate (L/min) | Reynolds Number | TMP (psi) | Filtration Time (hours) |
|---|---|---|---|---|
| UF | 0.8 | 1000 | 30 | 1 |
| RO | 3.8 | 4900 | 150 | 24 |

### Pure Water Flux Dead-End Filtration

Pure water flux of RO membranes was measured by using dead-end filtration cells (HP4750, Sterlitech Corp., Kent, WA). The effective filtration area was 14.6 cm$^2$, and the applied pressure difference was 150 psi. Figure 8 is a schematic of the pure water flux dead-end filtration test. The slope of the linear plot of permeate volume versus time was used to calculate the pure water flux of each membrane. At least three membrane samples were tested, and the average and standard deviation were reported.

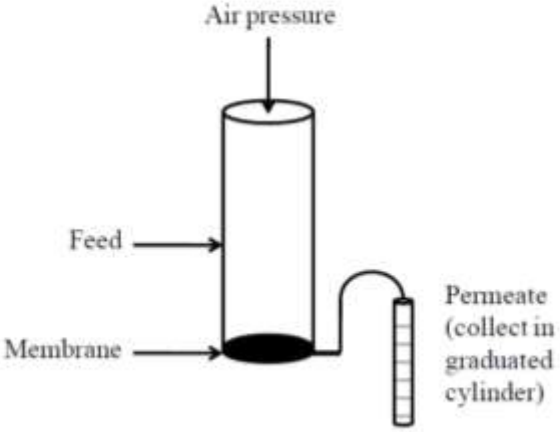

**Figure 8.** Schematic of pure water flux dead-end filtration test[10].

### Contact Angle Measurement

Contact angle was measured with a goniometer (Ramé-Hart, Model 200), using a captive-bubble technique. Figure 9 illustrates the experimental set up for the (*n*-decane)-in-water contact angle measurement. A strip of membrane sample (3-4 mm wide) was mounted face down on the sample holder and immersed in the environmental chamber filled with deionized water. The *n*-decane droplet (~5 μm) was dispensed underneath the membrane sample by using a microliter syringe (Gilmont Instruments, 0.2 ml) with a J-hooked needle and the contact angle was measured. At least three samples from each membrane modification were tested, and the average and standard deviation were reported.

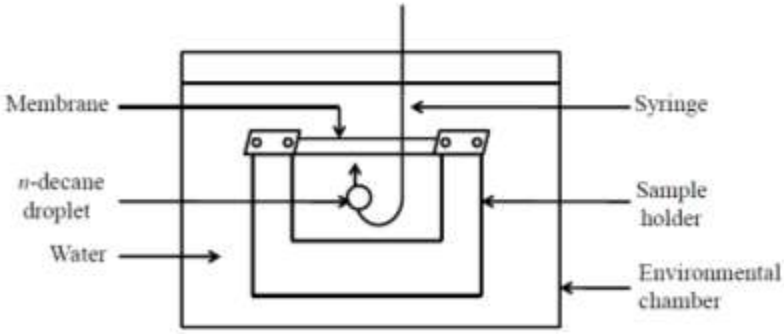

**Figure 9.** Experimental set up of (*n*-decane)-in-water contact angle measurement[10].

# Chapter 4: Results and Discussion

### Emulsified Oil Fouling Tests

Two classifications of membrane with different polymer types (chosen for their industrial relevance) were selected in this experimental set, as listed in Table 2. McCloskey *et al.* completed a number of constant TMP crossflow experiments to investigate the anti-fouling behavior of PDOPA-modified membranes and PDOPA-g-PEG-modified membranes[8]. The experimental results are shown in Figure 10.

**Table 2.** Commercial membranes used in the fouling tests

| Classification | Membrane Polymer | Manufacturer | Pore Size | Flux (LMH/bar) | Study ID |
|---|---|---|---|---|---|
| UF | Polysulfone | Sepro (PS-20) | ~20 kDa MWCO | 1000 | PS-20 UF |
| UF | Polyethersulfone | Sepro (PES-30) | ~20 kDa MWCO | 300 | PES UF |
| NF | Polyamide | Dow (NF-90) | N/A | 12.3 | PA NF-90 |
| RO | Polyamide | Dow (XLE RO) | N/A | 7.7 | PA XLERO |

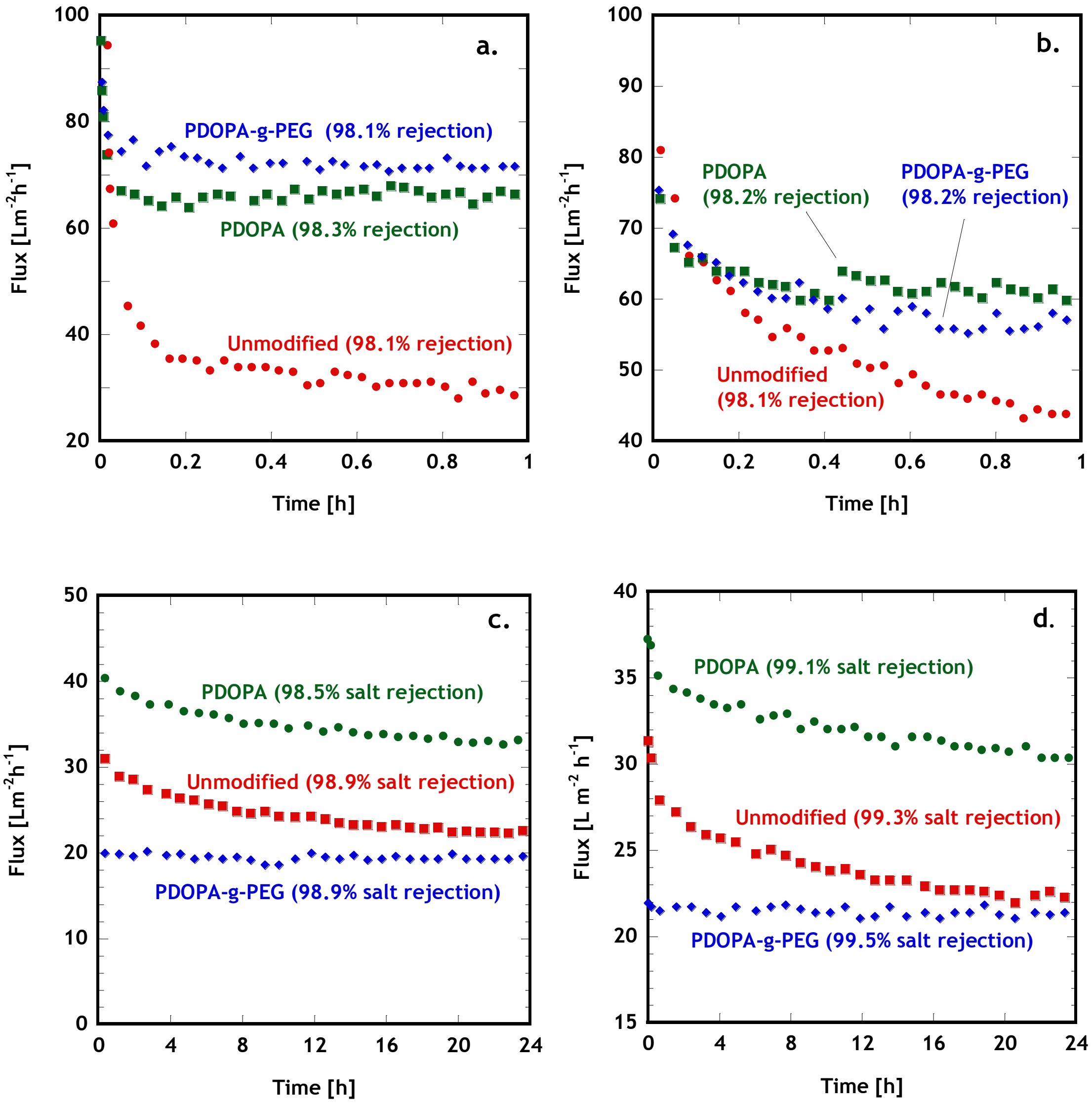

**Figure 10.** Permeate flux as a function of time in soybean oil/water emulsion filtration using unmodified, PDOPA-modified, and PDOPA-g-PEG-modified membranes: a. PS-20 UF, b. PES UF, c. NF-90, and d. PA XLERO membranes. Rejection values (organic rejection for UF membranes, salt rejection for NF and RO membranes) were measured at the end of the filtration.

During the oil/water emulsion fouling experiments, the permeate flux of the unmodified membranes decreased. In all cases, the PDOPA-modified membranes performed significantly better in the permeate flux (at 24 hours filtration) than did the unmodified membranes.

Grafting PEG-$NH_2$ onto the PDOPA coating slightly enhanced the permeate flux of the PS-20 UF and maintained the permeate flux of the PES UF from those for the PDOPA-modified (ungrafted) samples. On the other hand, the RO and NF membranes yielded lower permeate flux after they had been grafted with PEG-$NH_2$. PEG-$NH_2$ coating generally adds another layer with mass transfer resistance to the water transport. For membranes with pores, such as UF membranes, the added mass transfer resistance is small compared to the increase in hydrophilicity which could enhance the permeate flux. However, membranes with very small or no pores, such as NF or RO membranes, suffer from large additional mass transfer resistance introduced by the PEG-$NH_2$ grafting.

## Effect of Polydopamine Surface Modification Conditions

As described in the previous section, membrane fouling resistance was improved by PDOPA coating. This experimental set examined the effect of PDOPA modification conditions on the anti-fouling behavior of the modified membranes. Dopamine concentration, PDOPA deposition time, and initial pH of tris-HCl buffer solution were the parameters varied in this study.

Following a standard protocol, we coated membranes with PDOPA using a dopamine concentration of 2 mg/mL, deposition time of 60 minutes, and tris-HCl buffer solution at initial pH 8.8. Various modification conditions were investigated, as listed in Table 3.

The experiments were conducted with PA XLERO membranes from Dow Filmtec. The membrane pretreatment and modification, pure water flux experiments, and oil/water emulsion fouling crossflow tests were conducted using the same protocol as described earlier.

**Table 3.** Summary of PDOPA modification conditions variation*

| | |
|---|---|
| Dopamine concentration (mg/mL) | 0, 0.1, 0.5, 2, 4, 8 |
| Deposition time (min) | 30, 60, 120 |
| Initial pH of tris-HCl buffer | 5, 8.8, 11 |

*Underline indicates the standard conditions used in other study.

### *Dopamine Concentration Variation*

PA XLERO membranes were modified at five different dopamine concentrations in tris-HCl buffer solution at initial pH 8.8 and with deposition time of 60 minutes. The dopamine concentration was varied from 0 (control) to 0.1, 0.5, 2, 4, and 8 mg/mL.

Figure 11a shows the pure water flux as a function of dopamine concentration used in the modification. Higher dopamine concentrations in the modification yield thicker PDOPA layers on the membrane surface[12]-[14]. This layer creates additional mass transfer resistance, which reduces the pure water flux.

Corresponding to the previous results, all PDOPA-modified membranes exhibited higher permeate flux than did the unmodified membranes. Figure 11b shows that membranes modified with different dopamine concentrations display little variation in the permeate flux during oil/water emulsion filtration, while an increase in dopamine concentration reduced the pure water flux of the membranes. During oil/water emulsion filtration, because the mass transfer resistance due to the additional layer of PDOPA was insignificant compared to the resistance from the foulant layer introduced by oil emulsion, no variation was observed in permeate flux of membranes modified at different dopamine concentrations.

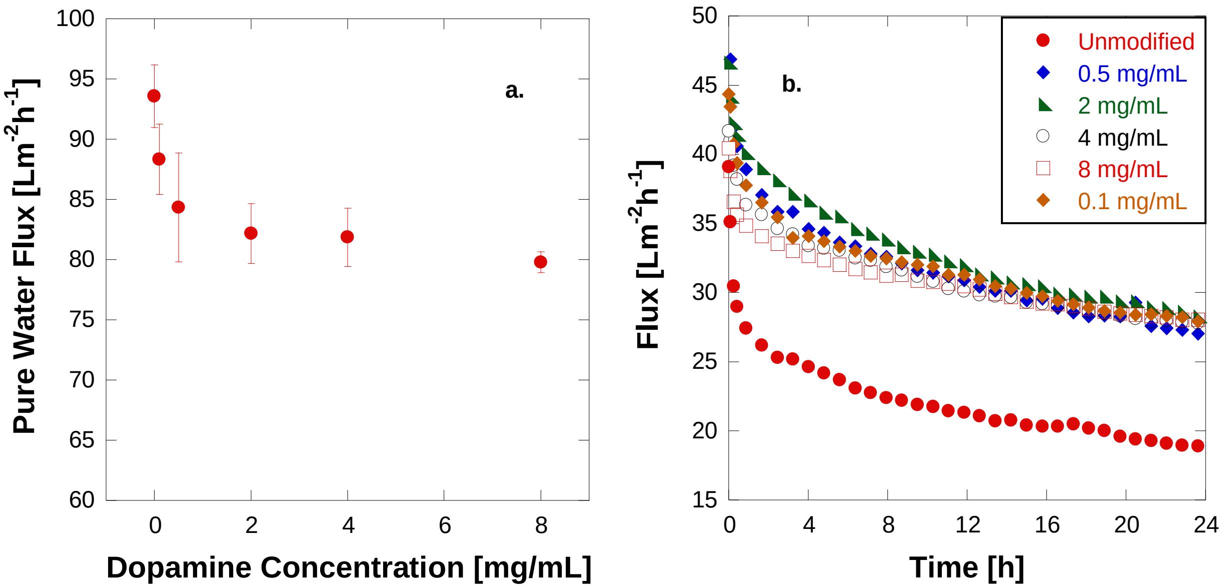

**Figure 11.** a. Pure water flux as a function of dopamine concentration used during PA XLERO membrane modification, b. Permeate flux as a function of time in soybean oil/water emulsion filtration using PA XLERO membranes unmodified and PDOPA-mcodified at different dopamine concentrations (with 60 minutes deposition time and tris-HCl buffer initial pH at 8.8).

### *Polydopamine Deposition Time Variation*

PA XLERO membranes were modified at three different deposition times, from 0 to 30, 60 (control), and 120 minutes. These samples were exposed to 2 mg/mL dopamine solution in tris-HCl buffer solution at pH 8.8.

Figure 12a shows the pure water flux as a function of PDOPA deposition time. As the deposition time increased, the pure water flux of the membranes decreased. Longer coating times create thicker PDOPA coating layers[7], [12]-[16], which resist water transport and reduce the pure water flux.

The fouling test result in Figure 12b shows that all PDOPA-modified membranes outperformed the unmodified membranes. The membranes modified with 30 minutes deposition time had slightly lower permeate flux than those modified for 60 and 120 minutes. The difference between deposition times of 60 and 120 minutes had an insignificant effect on the permeate flux throughout the oil/water emulsion fouling experiments.

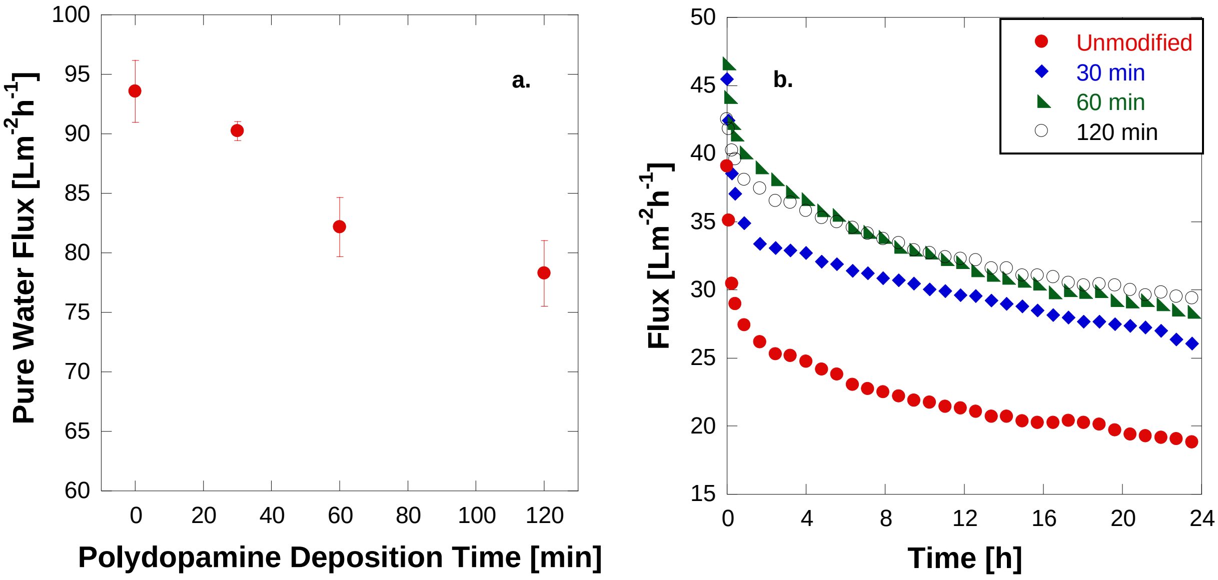

**Figure 12.** a. Pure water flux as a function of deposition time used during PA XLERO membrane modification**,** b. Permeate flux as a function of time in soybean oil/water emulsion filtration using PA XLERO membranes unmodified and PDOPA-modified at different deposition times (with 2 mg/mL dopamine concentration and tris-HCl buffer initial pH at 8.8).

### *Initial pH of Tris-HCl Buffer Variation*

PA XLERO membranes were modified at two pH values (8.8 and 11) of tris-HCl buffer using dopamine concentration of 2 mg/mL and a deposition time of 60 minutes. Typically, the polymerization reaction of dopamine can be detected visually from the development of a brown color in the buffer solution. As seen in Figure 13, our preliminary study of the reaction of dopamine in tris-HCl buffer at pH 5 showed no visual sign of dopamine polymerization reaction; however, for the reaction at pH 8.8, a brown color was observed, indicating that polymerization occurred. Moreover, with our coating protocol at acidic pH, no visible brown coating layer formed on the membrane surface.

**Figure 13.** Polydopamine reaction from dopamine in tris-HCl buffer solution at pH 5 (right) and 8.8 (left).

Figure 14a shows the pure water flux as a function of initial pH of tris-HCl buffer solution used in the modification. Membranes modified at pH 5 had pure water flux similar to that of the unmodified membranes. The membranes modified at alkaline conditions (i.e. pH 8.8 and 11) showed a decrease in pure water flux from the unmodified membranes. These results suggest that when membranes were coated in acidic conditions, no additional mass transfer resistance was introduced by the coating, while the coating was successful in alkaline conditions.

Figure 14b shows that the PDOPA-modified membranes at pH 5 exhibited no improvement in permeate flux compared to the unmodified membranes; there was no effective coating to provide membrane fouling resistance under these coating conditions. On the other hand, the membranes modified with PDOPA in alkaline conditions showed improved permeate flux relative to the unmodified membranes. These results indicate that membrane fouling resistance improved when samples were coated with PDOPA in alkaline conditions. Very little difference in permeate flux was observed between the membranes modified at pH 8.8 and 11.

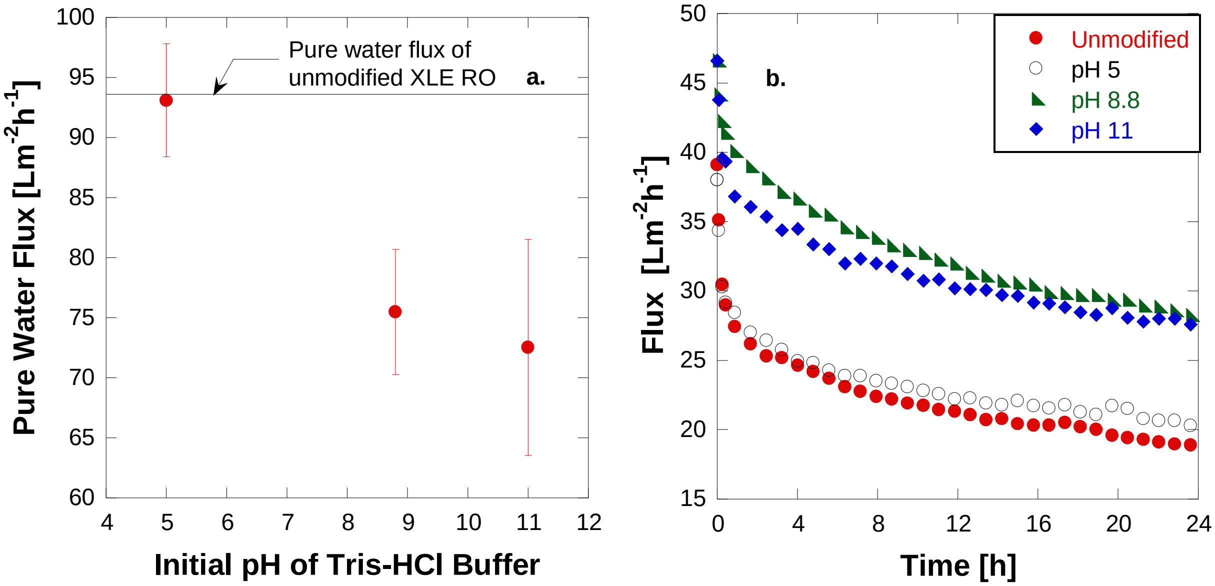

**Figure 14.** a. Pure water flux as a function of tris-HCl buffer initial pH used during PA XLERO membrane modification, b. Permeate flux as a function of time in soybean oil/water emulsion filtration using PA XLERO membranes unmodified and PDOPA-modified at different initial pH of tris-HCl buffer (with 2 mg/mL dopamine concentration and 60 minutes deposition time).

### *Salt Rejection Measurement*

We also measured salt rejection of PA XLERO, modified with PDOPA at different modification conditions, during the constant TMP crossflow filtration experiments. The reported true salt rejections were corrected for concentration polarization by using the method introduced by Van Wagner *et al.*[11]. Figure 15a, b, and c show the true salt rejection as a function of dopamine concentration, PDOPA deposition time, and initial pH of tris-HCl buffer solution, respectively. The data suggest that all modified membranes maintained the same true salt rejection as the unmodified membranes.

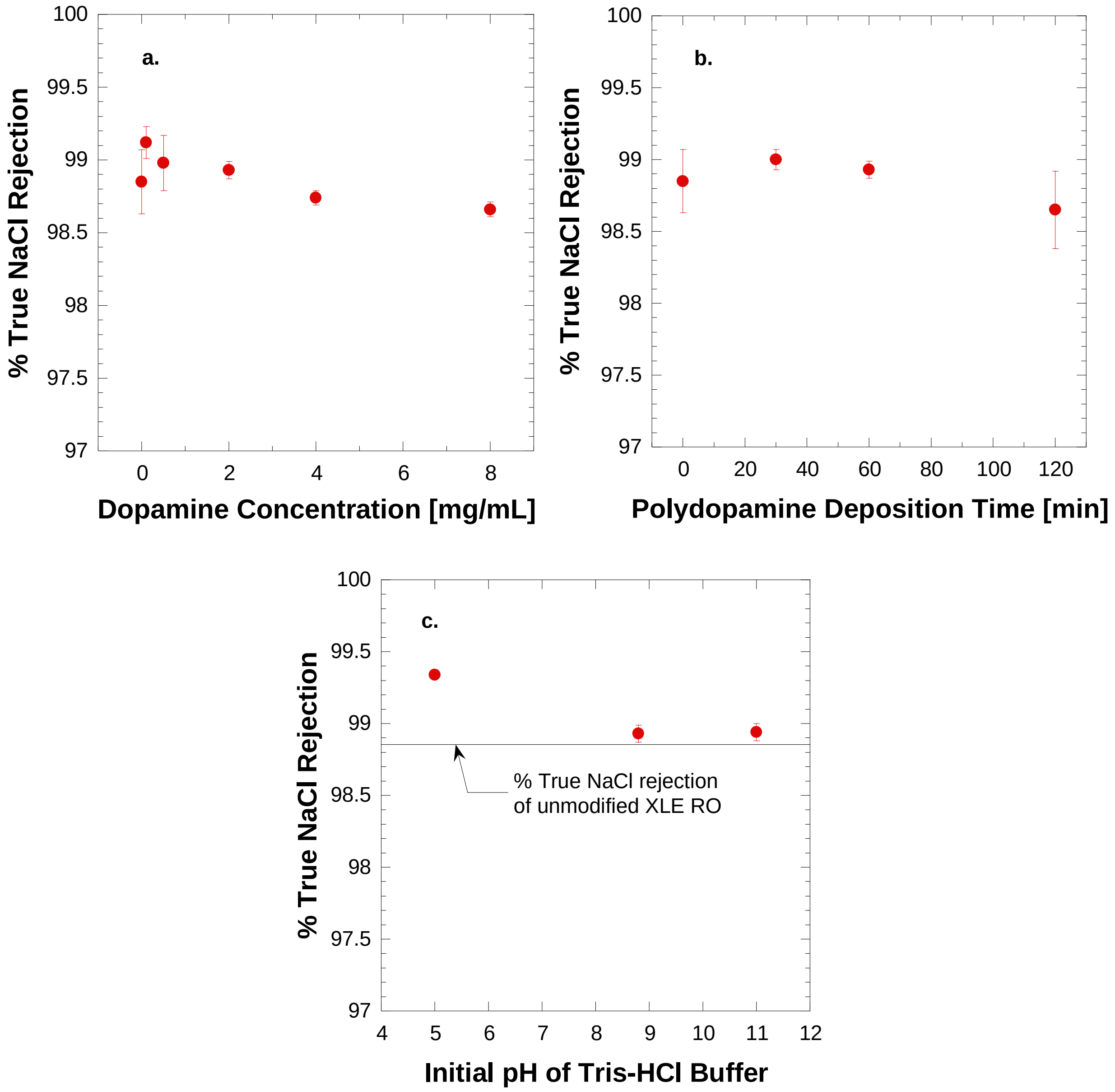

**Figure 15.** True NaCl rejections from 2000 ppm NaCl feed of unmodified and PDOPA-modified PA XLERO membranes as a function of PDOPA modification conditions: a. dopamine concentration, b. PDOPA deposition time, and c. initial pH of Tris-HCl buffer.

## Energy Savings

One benchmark of improved membrane performance is reduced energy use. Most of the energy consumed in a membrane-based process is the power required for the feed pumps. Feed flow rate and transmembrane pressure are used to estimate the power per unit permeate volume using Equations (1), (2) and (3)[17].

$$\dot{P}_{\text{output}} = Q_F \left( p_F - p_{ATM} \right) = Q_F \Delta p \tag{1}$$

$$\dot{P}_{\text{input}} = \frac{\dot{P}_{\text{output}}}{\eta} = \frac{Q_F \Delta p}{\eta} \tag{2}$$

$$\frac{\dot{P}_{\text{input}}}{Q_P} = \frac{Q_F}{\eta Q_P} \Delta p = \frac{E}{\eta V_P} \tag{3}$$

Where $\dot{P}_{\text{input}}$ = Pump power input required to operate the membrane system

$\dot{P}_{\text{output}}$ = Pump power output ; $\eta$ = Pump efficiency

$Q_F$ = Feed flow rate ; $Q_P$ = Permeate flow rate

$p_F$ = Feed pressure ; $p_{ATM}$ = Atmospheric pressure

$\Delta p$ = Pressure drop across membrane ( $\approx$ total pump dynamic head)

$E$ = Energy required for membrane operation

$V_P$ = Permeate volume

We used Equation 4 to compare the performance of PDOPA-treated membranes (defined with subscript 2 in Equation (4)) with unmodified membranes (defined with subscript 1 in Equation (4)), calculating the ratio of energy used per unit volume of permeate of both membranes. We assumed that the pump efficiency and feed flow rates in both cases were the same.

$$\frac{\left( \frac{\dot{P}_{\text{input}}}{Q_P} \right)_1}{\left( \frac{\dot{P}_{\text{output}}}{Q_P} \right)_2} = \frac{\frac{Q_{F1}}{\eta Q_{P1}} \Delta p}{\frac{Q_{F2}}{\eta Q_{P2}} \Delta p} = \frac{Q_{P2}}{Q_{P1}} \tag{4}$$

Figure 16 shows the flux ratio of PDOPA-modified to unmodified membranes during oil/water emulsion filtration. All membranes were modified with 2 mg/mL of dopamine, 60 minutes of deposition time, and tris-HCl buffer solution initial pH at 8.8.

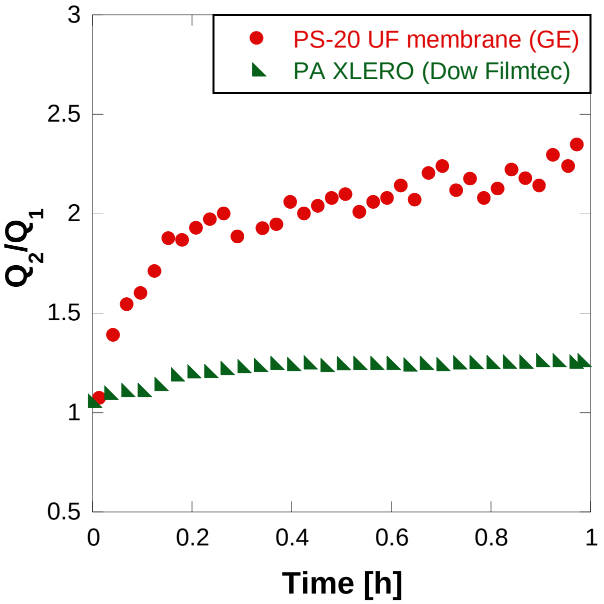

**Figure 16.** Flux ratio of PDOPA-modified to unmodified membranes during oil/water filtration.

**Table 4.** Comparison of flux ratio of PDOPA-modified to unmodified membranes after 1 hour oil/water filtration

| **Membrane Type** | **Flux Ratio ($Q_{p2}/Q_{p1}$)** |
|---|---|
| PS-20 UF (GE) | 2.35 |
| PA XLERO (Dow Filmtec) | 1.26 |

Comparison of the final flux ratios after 1 hour clearly shows the energy advantages of PDOPA-modified membranes. At the same transmembrane pressure difference, the modified membranes yielded much larger amounts of permeate than the unmodified membranes. The modified PA XLERO permeate volume increased by a factor of 1.26, and the modified PS-20 UF membrane permeate volume increased by a factor of 2.35 during 1 hour of oil/water filtration. This increase in permeate flux can translate directly into industrial energy savings.

**Table 5.** Typical capital and operating cost breakdown for membrane plants[18]

| **Capital Costs** | % |
|---|---|
| Pumps | 30 |
| Membrane Modules | 20 |
| Module Housings | 10 |
| Pipes, Valves, Frame | 20 |
| Controls/Other | 20 |
| Total | 100 |
| **Operating Cost** | % |
| Membrane Replacement | 30-50 |
| Cleaning Costs | 10-30 |
| Energy | 20-30 |
| Labor | 15 |
| Total | 100 |

Table 5 shows a typical breakdown of membrane plant capital and operating costs. By utilizing the fouling-resistant PDOPA modification, many of these costs can be significantly reduced. The enhanced permeate flux that the PDOPA-modified membranes provide in oil/water emulsion filtration provides two distinct benefits: First, the membrane modules and housings used in the plant can be smaller in size while maintaining high water purification capability, and second, in operation, the energy devoted to operating the membranes (*i.e.*, providing power to the pumps) can be reduced. The improved anti-fouling properties of the PDOPA-modified membranes provide additional benefits in operating costs. With the decrease in fouling, cleaning cycles can be run less frequently while maintaining a high permeate flux. Higher fouling resistance leads to longer membrane lifetime and results in less frequent need for membrane replacement. Overall, the factors influenced by PDOPA modification account for about 30% of the capital and 40-80% of the operating costs, which could be significantly reduced. We estimate that with this cost reduction in both capital and operating costs, produced water treatment with PDOPA-surface modified UF and RO membranes will be economically feasible for the oil/gas industry in the near future.

# Chapter 5: Conclusions

Polydopamine (PDOPA) is an effective anti-fouling surface coating for UF, NF, and RO membranes. The deposition of PDOPA improved the permeate flux for all types of membranes studied during oil/water emulsion filtration. For UF membranes, additional grafting by using poly(ethylene glycol) (PEG) further enhanced the fouling resistance. To study the effects of PDOPA polymerization, three condition parameters were investigated during modification: dopamine concentration, PDOPA deposition time, and initial pH of tris-HCl buffer. The experimental results showed that differences in dopamine concentration and deposition time did not cause significant variation in permeate flux during oil/water emulsion filtration for PA XLERO membranes. PDOPA was not effectively coated onto the membranes under acidic conditions. The membranes modified at alkaline pH of tris-HCl buffer did not show significant variation in the permeate flux (i.e. pH 8.8 versus pH 11). In addition, with the modification of PDOPA, PA XLERO membranes can retain salt rejection values as good as those of the native membranes.

Energy savings were estimated for the PDOPA-modified UF and RO membranes in oil/water emulsion filtration by comparing power required per permeate volume. With the same amount of energy provided by the pump, modified RO membranes produced 1.27 times more permeate volume than did unmodified RO membranes after 1 hour oil/water emulsion filtration. The modified UF membranes' permeate volume increased by a factor of 2.35 after 1 hour of oil/water emulsion filtration. For industrial membrane applications, PDOPA modification is estimated to yield significant savings, roughly 30% of the capital and 40-80% of the operating costs.

Based upon the two most recent years of research, PDOPA modification has proven to be a simple and effective method of improving the anti-fouling properties of UF, NF, and RO membranes. This novel approach is a promising membrane surface modification technique to enhance fouling resistance, which is a key factor in produced water treatment that employs membrane technology.

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