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# Effect of polydopamine deposition conditions on fouling resistance, physical properties, and permeation properties of reverse osmosis membranes in oil/water separation

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## ABSTRACT

A commercial polyamide reverse osmosis (RO) membrane was surface-modified with polydopamine deposited from buffered, aqueous dopamine solution at ambient conditions. The influence of various modification conditions (i.e., dopamine solution concentration, polydopamine deposition time, and initial pH of Tris–HCl buffer) on pure water flux, flux during filtration of an oil/water emulsion, and NaCl rejection was investigated. Dead-end filtration results showed decreased pure water flux with increasing dopamine solution concentration and polydopamine deposition time. Membranes modified at a pH of 5 exhibited no change in pure water flux or flux during fouling experiments compared to the native membranes, suggesting that polydopamine was not deposited under such acidic coating conditions. All polydopamine-modified membranes, except those coated at a pH of 5, had higher fluxes when filtering an oil/water emulsion than that of unmodified membranes. NaCl rejection values in all membranes were within the manufacturer's specification. The increased flux when filtering an oil/water emulsion was not sensitive to dopamine concentration, coating time greater than 60 min, or alkaline buffer pH value. Short deposition times slightly reduced the fouling resistance of coated membranes, and membranes modified at acidic pH values showed no improvement in fouling.

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## 1. Introduction

Freshwater scarcity is a severe problem in many regions of the world; the number of people living in highly water-stressed areas is predicted to increase throughout the 21st century [1,2]. Alternative water sources available in large quantities, such as seawater, brackish water, and produced water, may be used to an even greater extent than they are presently by developing economical water purification methods [3,4]. With the growth of the oil and gas industry, produced water has emerged as a potential alternative water source in many areas. Produced water is a byproduct of oil and gas production and typically contains dispersed oils, soluble organics, salts, metals, and treatment chemicals [5,6]. In 2007, nearly 21 billion barrels of produced water were generated in the U.S.; to put this enormous volume of produced water in perspective, it is almost eight times the volume of crude oil produced by onshore production in the same year [7]. Moreover, hydraulic fracturing, a necessary step in natural gas production from unconventional gas shales and certain types of

oil production, requires large amounts of water, typically between 1 and 4 million gallons of water for each well completion [8]. Rehabilitation of produced water for reuse in hydraulic fracturing could potentially contribute to addressing issues regarding water availability and management in this application. This water is usually considered unfit for beneficial uses and is reinjected into the ground at significant cost [9,10]. To employ produced water for hydraulic fracturing applications or municipal, agricultural, and industrial purposes, many contaminants in the water such as organics (e.g., emulsified oil) and salts must be removed [5,6,9].

Polymer membranes are increasingly used to purify water [11,12]. For example, membrane-based desalination has become the dominant desalination technology in terms of capacity [13] and is often the most economical choice for brackish and seawater desalination [3,11,12]. These membranes can reject very small contaminants, such as hydrated ions, while allowing a high flux of water through them. Their separation ability and relatively low use of energy – around ten percent that of some thermal methods – typically makes reverse osmosis (RO) membranes an economical choice over thermal desalination [3].

However, fouling remains a major barrier to widespread implementation of membrane-based produced water filtration despite feed water pretreatment [14–17]. Fouling is the build-up of

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particulate and colloidal matter, including organics such as oil, on the surface and in the pores of the membrane [17,18]. Produced water contains many particulates and dispersed contaminants not typically found in seawater or brackish water such as emulsified oil; the membrane surfaces in contact with such a mixture can become severely fouled. This fouling hinders the flow of water through the membranes which, in turn, increases operational costs [18].

Surface modification is one approach to improving membrane fouling resistance. Surface characteristics such as hydrophilicity, roughness, and charge have been reported to influence fouling [19]. For hydrophobic foulants (e.g., oil), increased membrane hydrophilicity has been reported to help reduce membrane fouling by limiting surface-foulant hydrophobic interactions [20,21]. Additionally, smooth membranes are reported to be less susceptible to fouling than rough membranes [22,23]. Charge–charge interactions with ionic foulants are minimized on membranes with reduced (or neutral) surface charge, a feature that has also been linked to improved fouling behavior [24].

A relatively new approach to improving membrane fouling resistance is surface coating with polydopamine [25–27]. Lee et al. [28] reported that in aerobic, alkaline aqueous solution, dopamine will form very thin layers of a material known in the literature as polydopamine. Thin polydopamine coatings deposit non-selectively from solution onto virtually any surface, including polymers used for water purification membranes [28]. The polydopamine layer is hydrophilic [25,29,30] and its application decreases surface charge on some polymers [31]. Additionally, a slight reduction in surface roughness on membranes coated with polydopamine has been reported [31]. Therefore, polydopamine is of interest as a fouling resistant membrane surface modification material [25–27]. Prior publications report changes in surface characteristics (e.g., contact angle, coating thickness, roughness, etc.) of polymers modified with polydopamine applied at various dopamine concentrations, polydopamine deposition times, and dopamine solution pH values [25,29–35]. Recently, Azari and Zou have reported that deposition of a compound structurally related to dopamine, L-dopa, onto reverse osmosis desalination membranes reduced the static adhesion of bovine serum albumin (BSA) to the membrane surface and improved the fouling resistance of these desalination membranes when filtering water containing foulants such as BSA, alginate sodium salt, or dodecyltrimethyl ammonium bromide (DTAB) surfactant [36]. Additionally, Arena et al. reported that when the polysulfone support membranes of desalination membranes are treated with polydopamine, the performance of the resulting membranes in pressure retarded osmosis experiments is improved [37]. These studies motivate our interest to further understand the ability of polydopamine-treated desalination membranes to improve fouling resistance in oil/water filtration.

In this study, flat-sheet commercial polyamide reverse osmosis membranes were surface-modified with polydopamine from an aqueous solution of dopamine in Tris–HCl buffer. The influence of dopamine concentration, polydopamine deposition time, and initial pH of the Tris–HCl buffer on membrane performance and properties (i.e., contact angle, pure water flux, and NaCl rejection) are presented. The fouling characteristics of the polydopamine-modified membranes are compared to those coated at different conditions and to those of the unmodified membranes by monitoring permeate flux decline during oil/water emulsion crossflow filtration.

## 2. Experimental

### 2.1. Materials

Flat-sheet polyamide reverse osmosis (XLE RO) membranes were kindly provided by DOW Water & Process Solutions (Edina, MN).

Dopamine hydrochloride (3-hydroxytyramine hydrochloride), Trizma hydrochloride (Tris–HCl), and sodium bicarbonate ( $\text{NaHCO}_3$ ) were purchased from Sigma Aldrich (St. Louis, MO). Sodium hydroxide (NaOH), hydrochloric acid (HCl), and sodium chloride (NaCl) were purchased from Fisher Scientific (Pittsburgh, PA). Isopropyl alcohol (IPA, BDH Chemicals) was purchased from VWR International (Radnor, PA). Wesson vegetable (soybean) oil was purchased from a local supermarket, and DC193C non-ionic surfactant was obtained from Dow Corning (Midland, MI). All chemicals were used as received. All ultrapure water was obtained from a Millipore Milli-Q Advantage A10 water purification system (18.2 M $\Omega$ -cm at 25 °C, 1.2 ppb TOC) (Billerica, MA).

### 2.2. Membrane storage, handling, and pretreatment

The XLE RO membranes were received as rolls of dry, flat-sheet membranes. The membrane rolls were stored vertically in a dark, cool container to limit possible oxidation of the membrane surfaces [38]. According to the manufacturer's pretreatment procedures, the XLE RO membrane samples were soaked in 25% (v/v) aqueous IPA solution for 20 min to wet the membrane pores and to remove glycerin, which had been applied by the manufacturer to maintain the porous structure of the polysulfone support [38]. The membrane coupons were then soaked in ultrapure water to remove the alcohol and residual glycerin. The soaking water was changed three times, and the membranes were stored for approximately 16–24 h in ultrapure water prior to surface modification or further experiments.

### 2.3. Membrane modification with polydopamine

Each XLE RO membrane sample was coated with polydopamine by exposing its selective top layer to aqueous dopamine solution at room temperature, as shown in Fig. 1. The membrane sample, with its selective side up, was anchored to a glass plate, and a glass ring was secured atop the membrane with vacuum grease. Dopamine solution (50 mL) was poured into the glass ring and the glass plate was rocked on a rocking platform shaker (VWR International, Radnor, PA) for a desired coating time. The dopamine solutions were prepared from dopamine hydrochloride at several concentrations (i.e., 0.1, 0.5, 2, 4, and 8 mg/mL) in 15 mM Tris–HCl buffer. The pH of Tris–HCl buffer solutions was adjusted to three different values (i.e., 5, 8.8, and 11) by adding HCl or NaOH prior to use. Polydopamine deposition time was varied (i.e., 30, 60, and 120 min). After the polydopamine deposition step was complete, the membrane was rinsed with ultrapure water once and soaked in 25% (v/v) IPA solution for 10 min to remove unattached or weakly-bound polydopamine from the membrane surface. Finally, the membrane was rinsed thoroughly under running ultrapure water to remove the alcohol and stored in ultrapure water before testing.

### 2.4. Contact angle measurements

Contact angle measurements were performed using a contact angle goniometer (Ramé–Hart Model 200) with DROPImage Standard software version 2.4 (Ramé–Hart Instrument Co., Netcong, NJ). Fig. 2 illustrates the experimental apparatus. A captive-bubble method was

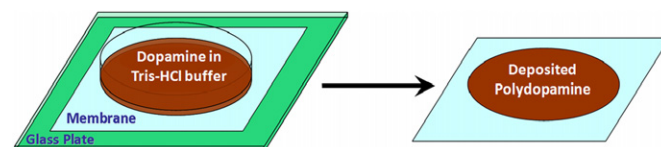


Fig. 1. Polydopamine membrane modification technique.

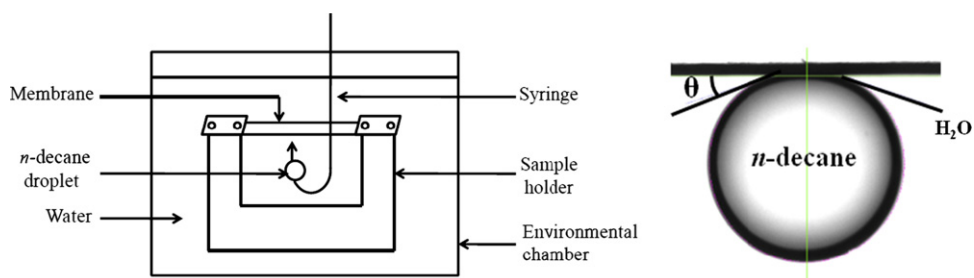


Fig. 2. Experimental set up of (*n*-decane)-in-water contact angle measurement (left) [39], and contact angle ( $\theta$ ) from captive-bubble method (right) [40].

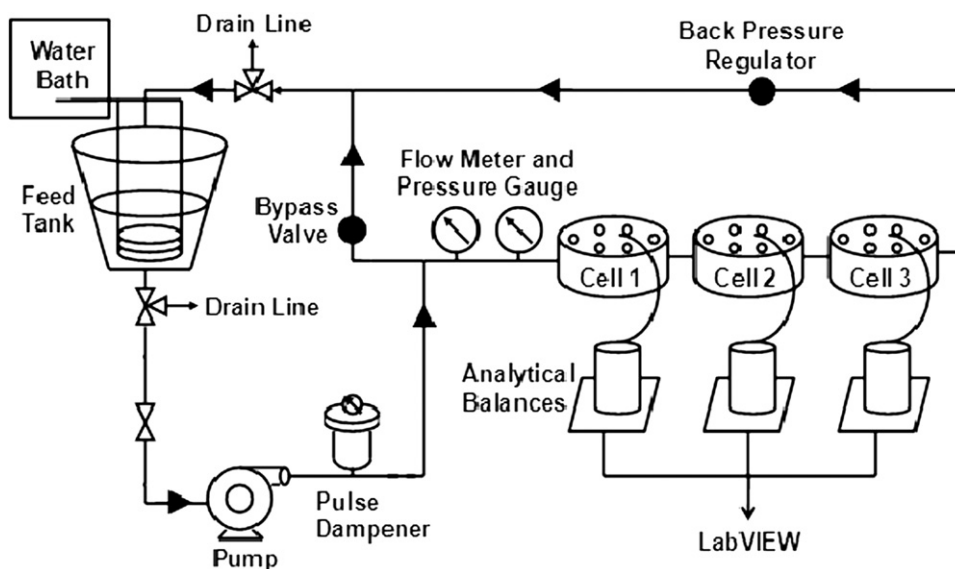


Fig. 3. Constant TMP crossflow filtration system [38].

used. Membrane samples (3–4 mm wide) were mounted in a sample holder with the membrane selective side facing down; the sample holder was immersed in a transparent environmental chamber filled with ultrapure water. *n*-Decane droplets were deposited beneath the membrane surface using a Gilmont Instruments microliter syringe (Cole-Parmer, Vernon Hills, IL) equipped with a J-hook needle to dispense *n*-decane droplets underneath the membrane surface. Static contact angles were measured as shown in Fig. 2. The reported average and standard deviation were calculated from the mean values (of left and right contact angles) obtained for at least five oil droplets placed on each membrane coupon.

### 2.5. Pure water flux dead-end filtration

The pure water flux of unmodified and polydopamine-modified membranes was measured using dead-end filtration cells (Sterlitech Corp., Kent, WA). The effective filtration area was 14.6 cm<sup>2</sup>, and the applied transmembrane pressure difference (TMP) was 150 psi (10.3 bar). During the experiments, 25 mL of permeate was collected, and permeate volume data were recorded as a function of filtration time. The pure water flux of each membrane was calculated from the membrane surface area and the slope of a plot of permeate volume produced as a function of time [24]. The average pure water flux values from measurements on at least three separate membrane samples are reported. The uncertainty in pure water flux is reported as  $\pm 1$  standard deviation of the measured flux values.

### 2.6. Oil/water emulsion preparation

To be consistent with earlier studies from our laboratories on the topic of oil/water fouling [41,42], the model foulant used in this study was a 1500 ppm emulsion of soybean oil/DC193C surfactant in water (9:1 ratio of oil to surfactant). The emulsion was prepared by blending 40.5 g of soybean oil with 4.5 g of DC193C non-ionic surfactant in 3 L of 2000 ppm NaCl solution. To prepare a stable emulsion, the mixture was blended in a high-speed blender (Waring Laboratory, Torrington, CT) at  $\sim 20,000$  rpm (highest rotational speed) for 3 min. The emulsion was then cooled to  $\sim 25$  °C before dilution in the crossflow system feed tank containing 27 L of 2000 ppm NaCl solution to achieve a 1500 ppm soybean oil emulsion.

### 2.7. Constant transmembrane pressure difference (TMP) crossflow filtration

Fouling studies were conducted using a constant TMP (i.e., variable permeate flux) crossflow filtration system (Separation Systems Technology, San Diego, CA) shown in Fig. 3. The details of the apparatus are presented elsewhere [38]. The system was cleaned prior to each filtration experiment by circulating 0.3% (v/v) of bleach (Clorox<sup>®</sup>) solution for 30 min to disinfect the system and 0.2% (v/v) aqueous solution of Nalgene L900 liquid detergent (Fisher Scientific, Pittsburgh, PA) for another 30 min to remove residual organics (e.g., oil and surfactant). The system was then rinsed for at least three cycles with tap water and one cycle with ultrapure water. For each rinse cycle, the feed tank was filled

with 30 L of water, and the water was run through the system in a single pass (i.e., without recirculation). All filtration experiments were conducted at a feed pressure of 150 psig (10.3 barg), permeate pressure of atmospheric (i.e., the TMP was 150 psi (10.3 bar)) and feed flow rate of 1 gallon per minute (3.8 L per minute), which corresponded to a Reynolds number of 4900 inside our crossflow cells. The Reynolds number was calculated based on a calculation for turbulent flow in noncircular tubes by employing a mean hydraulic radius ( $R_h$ ) as shown in Eqs. (1) and (2) [43]. The geometry of the flow channels was 3 in. long  $\times$  1 in. wide  $\times$  0.125 in. deep (or approximately 76 mm long  $\times$  25 mm wide  $\times$  3 mm deep).

$$R_h = \frac{S}{Z} \quad (1)$$

In Eq. (1),  $R_h$  is the mean hydraulic radius,  $S$  is the cross section of the flow channel ( $\sim 25$  mm  $\times$  3 mm), and  $Z$  is the wetted perimeter ( $\sim 57$  mm). The Reynolds number ( $Re_h$ ) is defined as [43]

$$Re_h = \frac{4R_h \langle v_z \rangle \rho}{\mu} \quad (2)$$

where  $\langle v_z \rangle$  is the average velocity in the flow channel ( $\sim 0.78$  m/s),  $\rho$  is the density of oil emulsion at 25 °C ( $\sim 997$  kg/m<sup>3</sup>), and  $\mu$  is the viscosity of oil emulsion at 25 °C ( $\sim 9 \times 10^{-4}$  kg/m s) [44]. The properties of the oil emulsion (i.e.,  $\rho$  and  $\mu$ ) were approximated as the properties of water in this calculation.

Throughout the experiments, the feed temperature was maintained at  $\sim 25$  °C, and the pH of the feed solution was controlled at  $\sim 8$  (which was the membrane manufacturer's suggested value) by adding NaHCO<sub>3</sub> to the feed tank at the beginning of the experiments [38]. The permeate flux,  $J_w$  was calculated as follows:

$$J_w = \frac{\Delta M}{\Delta t} \frac{1}{\rho_w A} \quad (3)$$

where  $J_w$  is the permeate water flux,  $\Delta M$  is the mass of permeate collected during a filtration time of  $\Delta t$ ,  $\rho_w$  is the density of water, and  $A$  is the effective filtration area of the membrane sample (19 cm<sup>2</sup>). The mass of permeate was measured using an analytical balance connected to a computer. Labview software (National Instruments, Austin, TX) was used to record the permeate mass every 60 s during an experiment.

Each filtration experiment consisted of three steps as illustrated in Fig. 4. For the first 30 min of the experiment, ultrapure water was the feed solution. After 30 min of pure water filtration, NaCl was added to the feed solution in an amount that brought the feed solution NaCl concentration to approximately 2000 mg/L. Then, the permeate flux, as well as bulk feed and permeate salt concentrations, were measured. Salt concentrations were measured using a conductivity meter (Oakton CON 11, Oakton Instruments, Vernon Hills, IL) that had been previously calibrated using salt solutions of known composition. The reported apparent NaCl rejection values were calculated from bulk feed and

permeate salt concentrations according to Eq. (4) [18,38,45]. The reported true NaCl rejections were corrected for concentration polarization using the apparent NaCl rejections, pure water flux, and permeate flux from NaCl solution filtration as suggested in the literature [38,45]. The reported average apparent and true NaCl rejection values were calculated from results on at least three membrane coupons; the reported uncertainty values (denoted by error bars) represent one standard deviation. After 30 min of NaCl solution filtration, the oil/water emulsion was introduced to the feed stream, and the fouling test was run for 24 h. The reported permeate flux as a function of time during the fouling test was averaged from flux values measured using at least three membrane samples. At the beginning and the end of the fouling experiments, feed and permeate samples of unmodified membranes and polydopamine-modified membranes (prepared by using a 2 mg/mL dopamine concentration, 60 min deposition time, and Tris-HCl buffer at a pH of 8.8) were collected and organic carbon concentrations were determined using a Total Organic Carbon Analyzer (TOC-Vcsh, Shimadzu Corp., Japan). The organic rejection values were calculated according to Eq. (4) [27], and the average values and uncertainty values (one standard deviation) of at least three membrane samples were reported:

$$R = \left(1 - \frac{C_p}{C_f}\right) \times 100\% \quad (4)$$

where  $R$  is the apparent NaCl rejection or organic rejection,  $C_p$  is NaCl concentration (for NaCl rejection) or organic concentration (for organic rejection) in the permeate, and  $C_f$  is NaCl concentration (for NaCl rejection) or organic concentration (for organic rejection) in the bulk feed.

### 3. Results and discussion

#### 3.1. Effect of dopamine concentrations used in membrane modification on contact angle

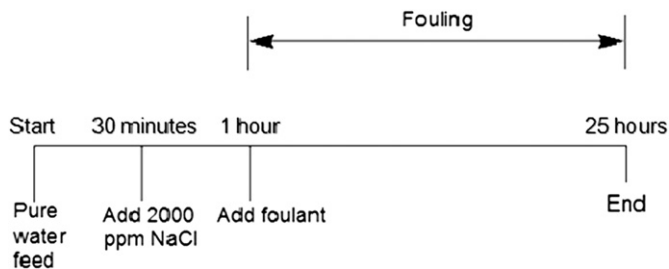
Table 1 presents static contact angles of XLE RO membranes modified using solutions of varying dopamine concentration. The contact angle of an unmodified membrane is included for comparison. The polydopamine deposition time was 60 min, and the initial pH of the Tris-HCl buffer was 8.8 in all cases. Because a hydrophobic oil droplet was suspended from the sample in an aqueous environment, small contact angles are indicative of a hydrophilic surface. All modified membranes and the unmodified membrane exhibited contact angle values of approximately 19°. For many hydrophobic materials, including polymers used for membrane preparation, polydopamine surface treatment increases hydrophilicity of the coated surfaces, which is typically seen as a decrease in contact angle in experiments such as ours [25,28,30,33,36,46]. The hydroxyl, carboxylic acid, and amine functional groups of polydopamine are thought to contribute to the hydrophilicity of coated surfaces [30,46,47]. However, on membranes that are already hydrophilic,

**Table 1**

Captive (*n*-decane)-in-water bubble contact angles of XLE RO membranes modified at different dopamine concentrations.

Dopamine concentration (mg/mL)	Contact angle (deg.)
0 (unmodified)	20.1 $\pm$ 0.8
0.1	19 $\pm$ 2
0.5	20 $\pm$ 2
2	19 $\pm$ 1
4	19 $\pm$ 1
8	19 $\pm$ 2

Note: All samples were prepared using deposition solutions at an initial pH of 8.8 and a deposition time of 60 min.



**Fig. 4.** Timeline of the crossflow filtration experiment [38].

such as XLE RO and hydrophilized PVDF microfiltration membranes, McCloskey et al. [25] observed only minimal changes in contact angle upon polydopamine treatment. The selective polyamide layer of the XLE RO membranes used in this study is synthesized *via* interfacial polymerization of *m*-phenylene diamine with trimesoyl chloride [39]. The polymerization leaves hydrophilic amine and carboxylic acid groups [39] that are likely responsible for the hydrophilic nature of the native membranes. Since the XLE RO membranes were initially hydrophilic prior to polydopamine modification, surface modification with polydopamine did not appreciably change contact angles measured in this experiment.

### 3.2. Effect of polydopamine modification conditions on pure water flux

The pure water flux of membranes modified at varying conditions is presented in Figs. 5–7. These measurements were performed in dead-end test cells as described in the Section 2. The average water permeance ( $A$ ) of unmodified membranes was  $9.0 \pm 0.3$  LMH/bar at a transmembrane pressure difference of 150 psi (10.3 bar), which is within the manufacturer's specified water permeance of 6.5–9.6 LMH/bar reported by Van Wagner et al. [38].

Fig. 5 presents pure water flux of unmodified membranes and membranes modified with dopamine concentrations of 0.1, 0.5, 2, 4, and 8 mg/mL (in Tris–HCl buffer at a pH of 8.8 for 60 min). As dopamine coating solution concentration increased, water flux decreased somewhat, with the largest decrease occurring at low dopamine concentrations. Fig. 6 shows the pure water flux of unmodified membranes and of membranes modified at polydopamine deposition times of 30, 60, and 120 min; these studies were conducted using 2 mg/mL dopamine in Tris–HCl buffer at a pH of 8.8. Water flux decreased with increasing polydopamine deposition time. Several previous studies demonstrated that the polydopamine film thickness increases at higher dopamine concentration in the deposition solution [29,34,35] or with longer deposition time [25,28,29,33–35]. Also, the polydopamine coating growth rate [34] and dopamine reaction rate [48] increase with dopamine concentration. Our results corroborate McCloskey

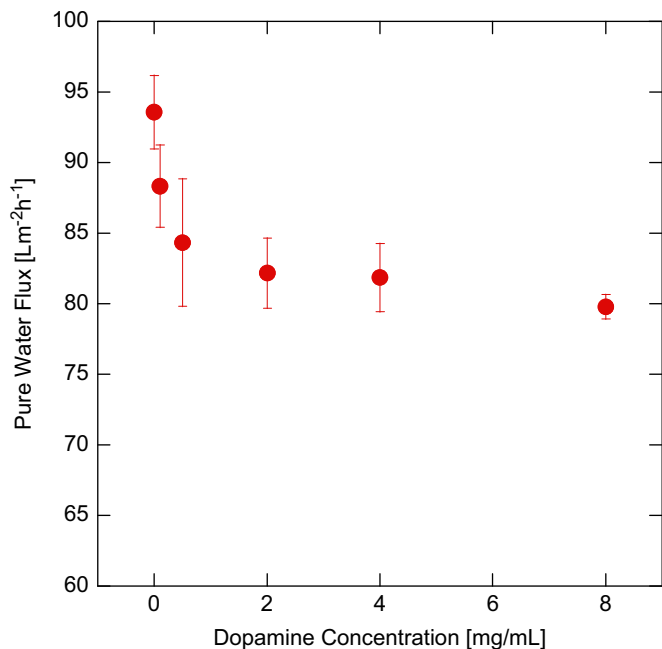


Fig. 5. Pure water flux as a function of dopamine concentration. The dopamine deposition time was 60 min, and the Tris–HCl buffer was at an initial pH of 8.8.

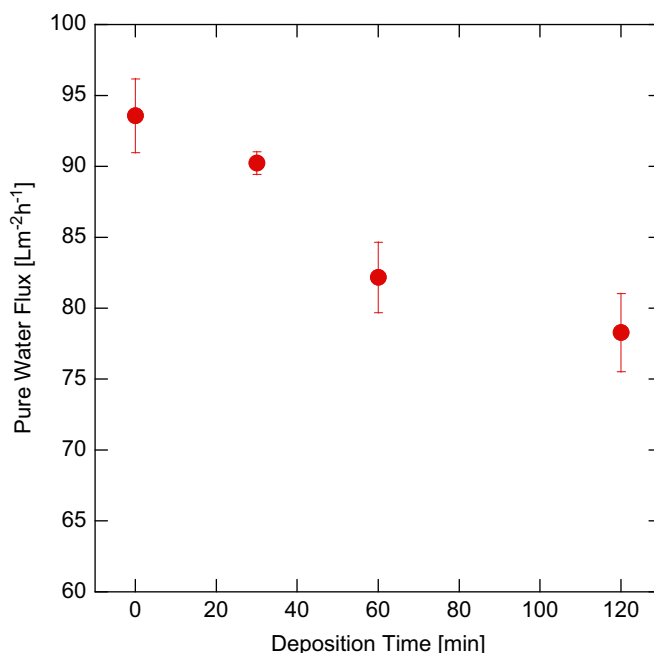


Fig. 6. Pure water flux as a function of polydopamine deposition time. The dopamine deposition solution concentration was 2 mg/mL, and the Tris–HCl buffer was at an initial pH of 8.8.

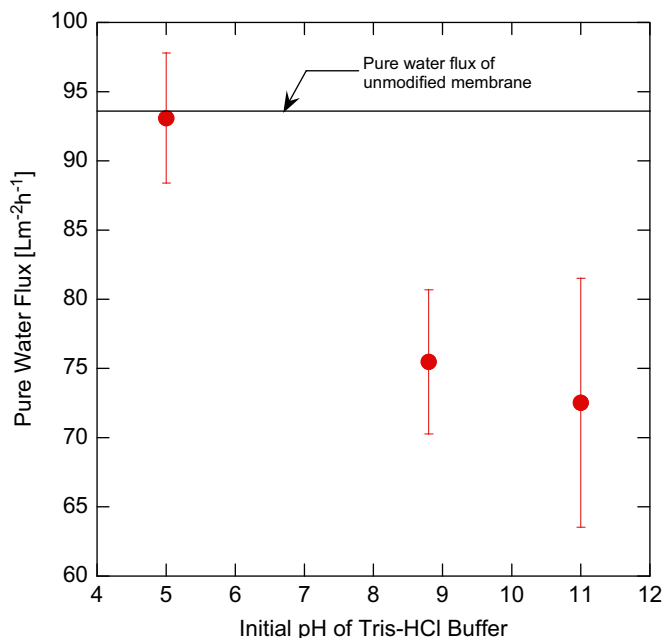


Fig. 7. Pure water flux as a function of Tris–HCl buffer initial pH. The dopamine deposition solution concentration was 2 mg/mL, and the dopamine deposition time was 60 min.

et al.'s findings in that the pure water flux of polydopamine-modified XLE RO membranes decreased relative to that of unmodified XLE RO membranes as deposition time increased [25]. Thicker polydopamine coatings, which result from high dopamine concentrations or long deposition times, were likely responsible for the reduced pure water flux observed in these experiments.

Fig. 7 presents pure water flux of membranes modified with Tris–HCl buffer at initial pH values of 5, 8.8, and 11. The concentration of dopamine was 2 mg/mL, and the deposition time was 60 min. The unmodified membrane pure water flux is

represented by the horizontal line. The pure water flux of membranes modified at a pH of 5 was nearly identical to that of unmodified membranes. The membranes modified under alkaline conditions (i.e., at initial pH values of 8.8 and 11) exhibited lower flux values than those modified at a pH of 5 or not modified at all. Interestingly, the pH of the coating solution (dopamine in Tris–HCl buffer) remained constant throughout the 60 min contact time of the solution with the membrane when the buffer initial pH was 5 or 8.8. When the initial pH of the buffer was 11, the pH of the coating solution decreased to 8.8 after the dopamine had been mixed in Tris–HCl buffer for about 15 s. The pure water flux of the membranes treated at a pH of 11 was, therefore, similar to the pure water flux of the membrane modified at a pH of 8.8. Previous studies suggest that dopamine polymerization begins with oxidation of the catechol moiety to a quinone [26,28,30,35,46,49,50]. A study on DOPA, the amino acid closely related to dopamine and largely responsible for the adhesive qualities of mussel byssus protein, suggested that oxidation of DOPA enhances its adhesion to organic surfaces (e.g., polymers) [51]. Alkaline pH enables rapid oxidation as the catechol/quinone equilibrium ( $pK_a=9.2$ ) favors the quinone [51]. Dopamine polymerization has been reported to proceed under acidic conditions only with the addition of oxidants (e.g., ammonium persulfate); under ambient atmosphere with oxygen present as the sole oxidant, dopamine polymerization does not proceed appreciably at acidic pH, which is consistent with the results shown in Fig. 7 [52].

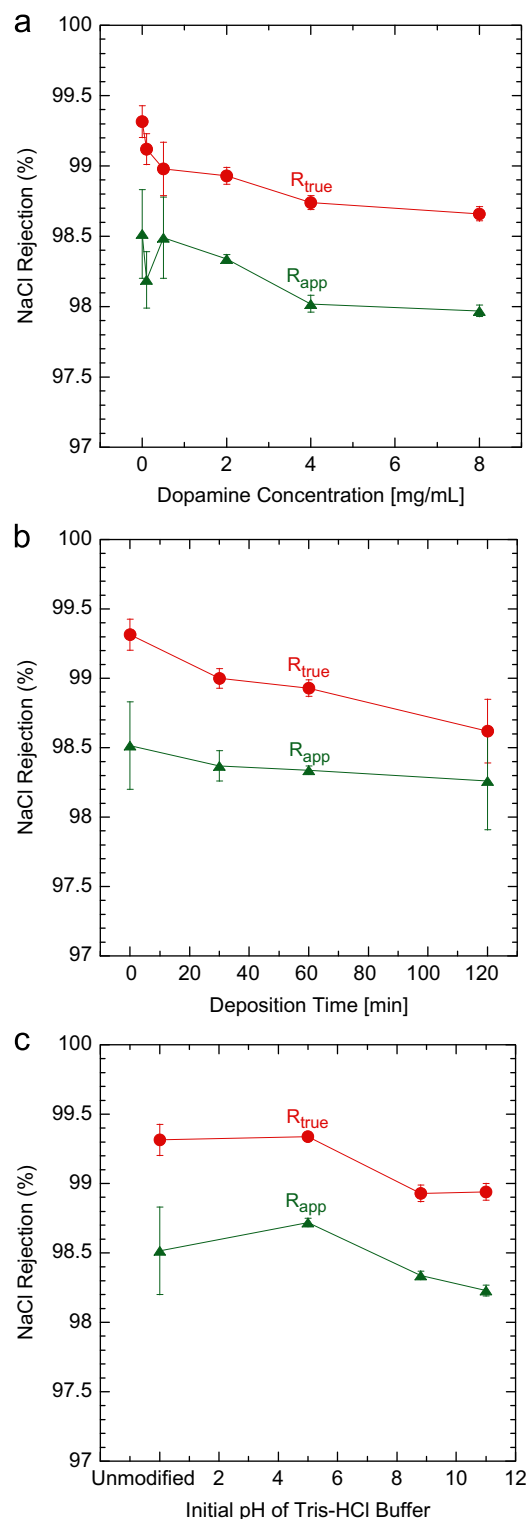
### 3.3. Effect of polydopamine modification conditions on NaCl rejection

Apparent,  $R_{app}$ , and true,  $R_{true}$ , NaCl rejection values during filtration of 2000 ppm NaCl feed are shown in Fig. 8. Fig. 8(a) and (b), which show results from membranes modified at various dopamine concentrations and deposition times, respectively, demonstrate that rejection generally decreased slightly with increasing dopamine solution concentration and polydopamine deposition time. Fig. 8(c) shows that true rejection was somewhat lower for membranes modified at alkaline conditions than for unmodified membranes and membranes modified at a pH of 5. Membranes modified at a pH of 5 exhibited essentially the same rejection as unmodified membranes.

Several possibilities may explain the observed results. First, a slight reduction in surface charge from polydopamine coatings, as reported by McCloskey et al. [31], may contribute to decreased salt rejection. Second, as described by Sagle et al. using a series-resistance model, coating a high salt rejection RO membrane with a lower rejection surface coating could reduce salt rejection [24]. Third, the polydopamine coating may penetrate the selective polyamide layer of the membranes, slightly altering the transport properties of the polyamide. Although a systematic decrease in true NaCl rejection with increasing dopamine concentration and deposition time was observed, the effect was small enough that all measured NaCl rejection values fall within the manufacturer's specified NaCl rejection range ( $> 98\%$ ) [53]. Therefore, while the polydopamine modification may result in some reduction in true NaCl rejection, the effect is small, so polydopamine modification had little effect on NaCl rejection of these reverse osmosis membranes.

### 3.4. Effect of polydopamine modification conditions on permeate flux during oil/water emulsion crossflow filtration

Table 2 shows organic rejection values of unmodified XLE RO membranes and polydopamine-modified XLE RO membranes (prepared by using 2 mg/mL dopamine concentration, 60 min



**Fig. 8.** Apparent NaCl rejections and true NaCl rejections of XLE RO membranes from 2000 ppm NaCl feed as a function of polydopamine modification conditions: (a) dopamine concentration, (b) polydopamine deposition time, and (c) initial pH of Tris–HCl buffer.

deposition time, and Tris–HCl buffer at a pH of 8.8). The rejection values were taken at the beginning and at the end (24 h) of oil/water emulsion crossflow filtration. In all cases, the organic rejection values were more than 99.9% which indicates that these membranes are suitable for oil/water separation.

**Table 2**

Organic rejection values of unmodified and polydopamine-modified XLE RO membranes at the beginning and end (24 h) of oil/water emulsion crossflow filtration.

Membrane modification	Organic rejection	
	Beginning	End
Unmodified	99.91 ± 0.01	99.95 ± 0.02
Polydopamine-modified	99.91 ± 0.05	99.9 ± 0.1

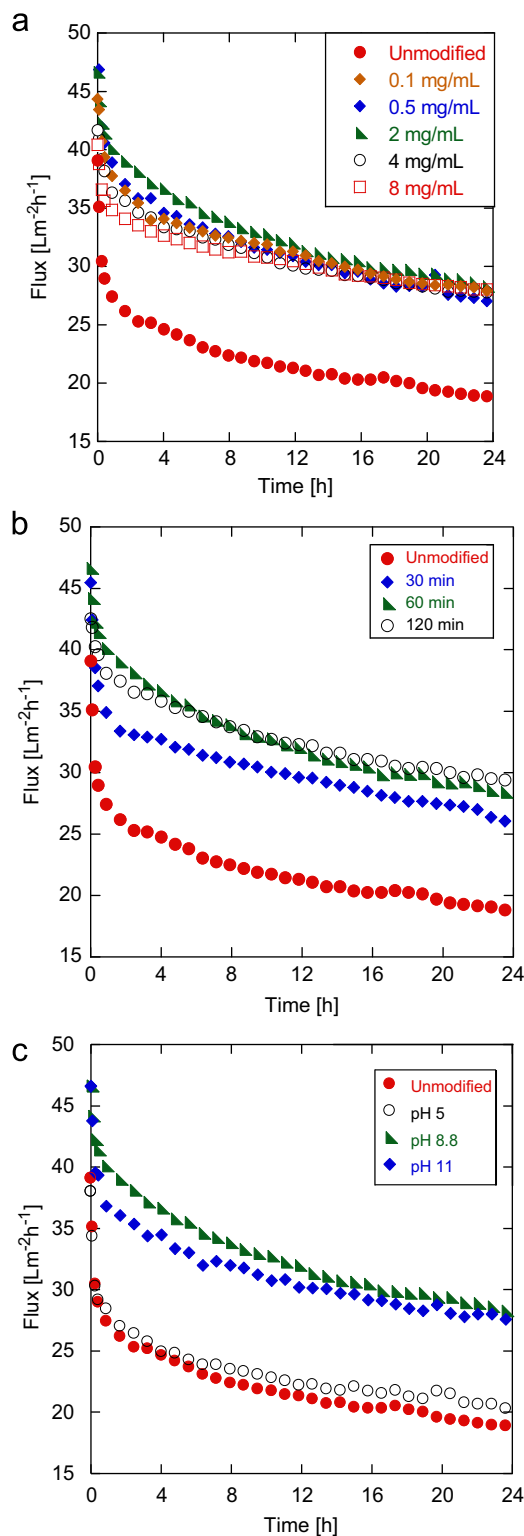
Note: Polydopamine-modified membranes were prepared using deposition solutions at 2 mg/mL dopamine concentration, an initial pH of 8.8, and a deposition time of 60 min.

Fig. 9 presents the permeate flux during oil/water emulsion crossflow filtration with XLE RO membranes modified at various: (a) dopamine coating solution concentrations (0.1, 0.5, 2, 4, and 8 mg/mL in Tris-HCl buffer at a pH of 8.8 for 60 min), (b) deposition times (30, 60, and 120 min with 2 mg/mL of dopamine in Tris-HCl buffer at a pH of 8.8), and (c) initial pH values of Tris-HCl buffer (5, 8.8, and 11 with 2 mg/mL of dopamine solution for 60 min). These figures also include results on unmodified membranes for comparison.

Fig. 9(a) presents the fouling behavior of membranes modified with various dopamine solution concentrations. All modified membranes exhibited higher flux than unmodified membranes, but increasing the dopamine concentration did not further increase flux, particularly at longer filtration times. Although a decrease in pure water flux was observed with increasing dopamine concentration (as shown in Fig. 5), this did not result in lower flux during filtration of oily water. Thus, a large contribution to mass transfer resistance during fouling was likely to be foulant accumulation on the membrane surface; the changes in mass transfer resistance observed in the pure water flux test due to the polydopamine coating are masked by the mass transfer resistance of adsorbed foulants. For this reason, variations in the dopamine concentration did not produce systematic changes in the permeate flux during fouling.

As shown in Fig. 9(b), membranes modified for 30, 60, and 120 min all exhibited higher flux than unmodified membranes. The membranes modified for 30 min showed a slightly lower permeate flux throughout the fouling experiment than those prepared at deposition times of 60 and 120 min. Previous studies reported that polydopamine deposition thickness decreases with shorter deposition times [25,28,29,33–35], and at short coating times, less polydopamine may be present on the coated substrate surface relative to that obtained following longer coating times [32]. Therefore, the membranes modified for 30 min showed less fouling resistance than those prepared using deposition times of 60 and 120 min. Increasing the deposition time from 60 min to 120 min did not significantly improve the fouling resistance of the modified membranes, leading to the same permeate flux at extended filtration time.

From Fig. 9(c), membranes modified at alkaline conditions (i.e., at initial pH values of 8.8 and 11) had higher fluxes than unmodified membranes. Membranes modified at a pH of 5 showed no enhancement in flux over that of unmodified membranes. As noted previously, dopamine oxidation, an initial step in dopamine polymerization, proceeds very slowly under acidic conditions at ambient conditions [52]. Membranes modified at a pH of 5, therefore, were likely not successfully coated with polydopamine, and they showed no improvement in flux during fouling tests relative to that of unmodified membranes. Polydopamine formation occurs readily at alkaline pH [33,48,51,52]; membranes modified with dopamine coating solution by using Tris-HCl buffer at initial pH values of 8.8 and 11 exhibited improved flux values during oily



**Fig. 9.** Permeate flux as a function of time during oil/water emulsion crossflow filtration of XLE RO membranes modified with varied (a) dopamine concentrations, (b) polydopamine deposition times, and (c) initial pH values of Tris-HCl buffer.

water filtration. Modification at both alkaline coating conditions (i.e., initial pH values of 8.8 and 11) appeared to lead to similar polydopamine coatings on the membranes, as judged by their similar flux values in the fouling experiment. This result is consistent with pure water flux data reported in Fig. 7, since pure water

flux values for membranes modified at initial pH values of 8.8 and 11 are essentially indistinguishable from each other.

Membrane surface modification to decrease roughness has been associated with reduced membrane fouling in many studies [22,23]. McCloskey et al. [31] reported a slight decrease in the surface roughness of polydopamine-modified XLE RO membranes relative to unmodified membranes. A decrease in surface roughness from polydopamine coatings may contribute to improvement of modified membrane fouling resistance. Additionally, an increase in surface hydrophilicity has been suggested to reduce organic fouling, such as that from oil emulsions [19–21]. Although we did not see increased hydrophilicity of the modified membranes over that of unmodified membranes via our contact angle experiments, perhaps the technique we used was not sensitive to small or subtle changes in hydrophilicity which may also help alleviate membrane fouling. However, a complete understanding of the cause for the observed increase in fouling performance is not yet available, and further studies are needed to more completely understand this phenomenon.

#### 4. Conclusions

XLE RO membranes were modified with polydopamine using various dopamine concentrations, polydopamine deposition times, and Tris–HCl buffer initial pH. The pure water flux of coated membranes decreased with increasing dopamine concentration and deposition time, presumably because the polydopamine coating layer thickness increased. Membranes modified at a pH of 5 exhibited no change in pure water flux or fouling resistance relative to unmodified membranes, suggesting that polydopamine was not successfully deposited onto the membranes under acidic conditions. Membranes modified with polydopamine at all dopamine concentrations, deposition times, and alkaline pH values were significantly more resistant to fouling in oil/water emulsion fouling tests than uncoated membranes, as judged by higher permeate flux values when filtering oil/water emulsions. Additionally, they maintained salt rejection values within the manufacturer's specification. Variations in dopamine concentration, deposition times of at least 60 min, and alkaline pH values had little effect on the fouling resistance of coated membranes, suggesting that the mass transfer resistance of the polydopamine coating was insignificant relative to that of the foulant layer.

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