Constant flux crossflow filtration evaluation of surface-modified fouling-resistant membranes

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ABSTRACT

The surfaces of polysulfone ultrafiltration membranes were modified with polydopamine and polydopamine-g-poly(ethylene glycol) hydrophilic coatings. Unmodified and modified membranes were challenged with a soybean oil emulsion feed at six different permeate fluxes in constant flux crossflow filtration fouling studies. The threshold flux was determined for each membrane. Above the threshold flux, modified membranes generally exhibited lower transmembrane pressures than unmodified membranes. However, below the threshold flux, modified membranes had higher transmembrane pressures than unmodified membranes, likely due to a decrease in permeance resulting from the surface modification. To account for this difference in permeance, polydopamine-g-poly(ethylene glycol) modified membranes were compared to membranes with a thicker polydopamine coating and to an unmodified membrane with a smaller pore size than that used for the surface modified membranes; in this way, all three membranes had similar pure water permeances. In this case, the unmodified membrane exhibited a much higher transmembrane pressure during fouling than the modified membranes, so when membranes of the same permeance are compared, the surface modifications improved fouling resistance. Therefore, a potential strategy to achieve fouling resistance in a membrane of a desired flux and rejection is to modify the surface of a more permeable (and perhaps lower rejection) membrane, thereby making the resulting modified membrane fouling-resistant but leaving it with the desired flux and rejection characteristics.

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1. Introduction

Fouling is a significant challenge when using polymer membranes in water purification applications [1–3]. Many porous membranes are made of hydrophobic polymers by a phase inversion process [3], so hydrophobic solutes in feed water, such as emulsified oils, readily foul such membranes via strong hydrophobic interactions [4]. Such fouling typically decreases membrane productivity, requiring increased energy expenditure or cleaning frequency [5]. Surface modification is a common approach to control membrane fouling [6–8]. Because many polymeric membranes are hydrophobic, such surface modifications are frequently directed towards making the membrane surface more hydrophilic [7]. Hydrophilic surfaces are hypothesized to attract a strongly-bound layer of water molecules, which may act a buffer to the adhesion of hydrophobic foulants [9]. Historically, hydrophilic surface modifications may take the form of thin, highly-permeable dense films, such as crosslinked poly(ethylene glycol) (PEG)-based coatings [1,2,5,10], or grafted molecules, such as PEG brushes [11–13] or zwitterionic polymers [14,15]. Typically, such modifications reduce the membrane permeance, since the coating or grafted material contributes to the overall mass transfer resistance of the membrane [5,10,13,16–18].

Polydopamine (PDA) deposition has recently been used to hydrophilize a variety of materials [19], including many types of polymeric membranes [20–23]. PDA may be deposited under mild conditions from buffered, aqueous dopamine solution and forms a robust, thin layer on nearly any surface in contact with the solution [19,24]. The effects of polydopamine on the hydrophilicity, charge, and surface roughness of polymer films and polymeric membranes have been reported previously [19–21,23,25–32]. For example, we have previously reported a substantial increase in hydrophilicity when PDA films were deposited on polysulfone UF membranes [20]. PDA can also act as a surface primer, facilitating the grafting of other molecules to a PDA-modified surface [19,33]. Poly(ethylene glycol) (PEG) is of particular interest due to its widespread use as a fouling-resistant surface modification agent [11,34]; poly(ethylene glycol) monamine (PEG-NH₂) may be easily grafted to PDA-modified surfaces [19]. Many types of membranes, including microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), and reverse osmosis (RO), have shown improved resistance to fouling by emulsified oil...
after modification with PDA or PDA-g-PEG [21,29]. Furthermore, the non-specificity of PDA deposition allows for modification of entire membrane modules post-fabrication, as has been recently demonstrated in a report describing purification of flowback water from hydraulic fracturing [35]. In that study, commercial polyacrylonitrile UF modules and composite polyamide RO modules were modified with PDA \textit{in situ} by filling the feed side of the modules with buffered dopamine solution, permitting hydrophilization of the membrane surfaces, feed spacers, and other wetted parts. UF modules showed improved fouling resistance and enhanced recovery after typical chemical cleaning procedures [35].

Like most literature studies reporting the fouling performance of surface-modified membranes, studies on PDA and PDA-g-PEG-modified membranes have focused on constant transmembrane pressure experiments, where the transmembrane pressure (TMP) is fixed, and fouling is evaluated by monitoring permeate flux decline over time [21,29]. This technique is widely used in laboratory fouling studies [10,16,21]. However, many industrial membrane-based water purification systems operate at constant permeate flux to provide a steady rate of product water production with a given membrane area [36,37]. In this operational mode, the permeate flux is fixed, and the TMP increases over time, as the membrane fouls, to maintain the desired permeate flux [38]. Aside from the similarity to industrial practice, constant flux operation has several other benefits. As permeate flux declines in a constant TMP experiment, the rate of permeate flow through the membrane pores also decreases. Therefore, the rate at which foulants are brought to the membrane surface by permeate convection varies continuously during the experiment as the membrane fouls. Consequently, the observed fouling behavior is not only the result of interaction between foulants and the membrane surface (important when evaluating the effect of fouling-resistant surface modifications), but it is also influenced by the changing hydrodynamic environment and solute concentration near the membrane [39,40]. This variability may complicate comparison of membranes (such as modified membranes against their unmodified counterparts) and modeling of fouling phenomena [40]. An additional benefit of constant flux experiments is that the critical and threshold fluxes of a membrane may be determined by slowly increasing the flux through a series of constant flux steps [38]. The threshold flux contributes valuable information to the determination of sustainable fluxes for industrial operation [41]. However, there are very few reports describing the influence of surface modification of membranes on their fouling resistance at constant flux operation [17].

In this report, we describe constant flux fouling studies on PDA and PDA-g-PEG-modified polysulfone UF membranes. Fouling was compared among modified and unmodified membranes at six different fluxes. The threshold flux for each membrane was evaluated by three different parameters obtained from flux stepping experiments and analyzed in the context of constant flux fouling experiments. Additionally, due to the decrease in intrinsic membrane permeance caused by the application of the PDA and PDA-g-PEG coatings, modified membranes were compared to another polysulfone UF membrane with a smaller pore size, where this membrane had pure water permeance very similar to that of the modified membranes.

2. Materials and methods

2.1. Materials

Rolls of PS-10 and PS-20 polysulfone UF membranes were purchased from Sepro Membranes, Inc. (Oceanside, CA). The rolls were stored in a cardboard tube. PS-10 and PS-20 membranes were similar except that PS-10 had a nominal molecular weight cutoff of 10 kDa, and PS-20 had a nominal molecular weight cutoff of 20 kDa. Acrylic plastic plates (20 cm × 28 cm × 0.6 cm) were obtained from Interstate Plastics (Austin, TX). Frames were fabricated from these plates by cutting out a 15 cm × 23 cm rectangle from the center of some of the plates. Rubber gaskets with the same dimensions as the plastic frames were purchased from Advanced Gasket & Supply (Ft. Worth, TX).

Dopamine hydrochloride, Trizma HCl, and ethanol were obtained from Sigma Aldrich (St. Louis, MO). Sodium hydroxide was purchased from Fisher Scientific (Pittsburgh, PA) and poly(ethylene glycol) monooamine (PEG-NH\textsubscript{2}) was purchased from JenKem Technology (Allen, TX). Soybean oil (Wesson) was purchased from a local supermarket. Xiameter OFX-0193 non-ionic, silicone-based surfactant was obtained from Dow Corning (Midland, MI). This surfactant is identical to the DC193 surfactant employed in previous studies [5,21,29]. All chemicals were used as received. Ultrapure water was produced by a Millipore Milli-Q Advantage A10 water purification system (18.2 MΩ-cm at 25 °C, 1.2 ppb TOC) (Billerica, MA). TRIS buffer (15 mM) was prepared by combining Trizma HCl (2.634 g) with ultrapure water (1 L) and adjusting the pH to 8.8 with sodium hydroxide.

2.2. Membrane pretreatment and modification

Membrane sheets approximately 20 cm × 28 cm were cut from the roll. Pretreatment to wet the porous structure was accomplished by immersing the membranes in ethanol overnight. The membrane sheets were carefully placed, selective side down, into a dish of ethanol so that they floated atop the ethanol, which wicked into the pores, allowing air to escape through the nonwoven backing. As the porous structure filled with ethanol, the membrane sheets sank to the bottom of the dish. After soaking in ethanol overnight, the membranes were transferred to a container of ultrapure water and soaked again overnight, changing the water at least once to promote exchange of ethanol for water in the pores.

Pretreated PS-20 membrane sheets were modified at ambient conditions with polydopamine. Some PS-20 sheets were reserved for use as unmodified control membranes, and no PS-10 membranes were modified. The polydopamine deposition procedure used to modify PS-20 membranes was similar to one previously reported [20,21]. Each membrane sheet to be modified with polydopamine was placed atop a plastic plate with its selective side facing up. A rubber gasket and matching plastic frame were placed on the membrane sample, and the stack was clamped together with large binder clips. A similar setup had previously been used to synthesize interfacial composite membranes [42]. TRIS buffer was prepared by dissolving Trizma HCl (2.634 g) (Sigma Aldrich, St. Louis, MO) in ultrapure water (1 L) to produce a 15 mM solution. The pH was adjusted to 8.8 using sodium hydroxide (Fisher Scientific, Pittsburgh, PA). Dopamine hydrochloride (200 mg) was dissolved in TRIS buffer (100 mL) and poured onto the membrane surface inside the gasket/frame. Typically, the membrane was placed on a rocking platform shaker (VWR International, Radnor, PA) for 60 min. (A few membranes, which will be discussed exclusively in Section 3.4, were modified with polydopamine for 75 min and will be referred to as “PDA75-modified.” Membranes referred to as “PDA-modified” were modified for 60 min, as described here.) As dopamine deposited on the membrane to form polydopamine, the membrane surface became brown. After the desired deposition time, the membrane sheet was removed from the plate/gasket/frame assembly and soaked in ethanol overnight to remove any weakly bound polydopamine from the membrane surface. Then, the membrane sheet was soaked in ultrapure water overnight, changing the water at least once, to exchange the ethanol for water.
Based on previous studies, deposition of polydopamine onto a dense, planar, spin-cast film of polysulfone under such conditions should give a polydopamine layer thickness of about 12 nm for a 60 min deposition time and 17 nm for a 75 min deposition time [20]. Poly(ethylene glycol) was grafted to the surface of some of the polydopamine-modified PS-20 membrane sheets. Only PS-20 membrane sheets modified with polydopamine for 60 min were used for PEG grafting; membranes modified with polydopamine for 75 min were not used for PEG grafting. The PDA-modified membrane sheet was reassembled with the plate/gasket/frame, carefully aligning the edges of the PDA-modified portion of the membrane with the inner edges of the rubber gasket. TRIS buffer (100 mL) was warmed to 60°C before use. PEG-NH$_2$ (100 mg) was dissolved in the warm TRIS buffer and poured onto the membrane surface. The assembly was placed in an oven at 60°C for 60 min. After 60 min, the membrane sheet was removed from the plate/gasket/frame assembly and soaked in ultrapure water overnight to remove any weakly bound PEG-NH$_2$. Based on previous studies, deposition of polydopamine onto a membrane under such conditions should give a PEG grafting density of about 17 μg/cm$^2$, where the surface area is the apparent surface area calculated from the macroscopic length and width of the membrane coupon [20].

2.3. Pure water permeance

Pure water flux measurements were made in dead end filtration cells from Advantec MFS (Dublin, CA). Circular membrane samples (4.3 cm diameter) were cut using a steel punch and rinsed in ultrapure water before measurement. Samples were clamped atop a porous plastic backing to provide mechanical support. The cell was filled with ultrapure water and pressurized to 2.1 barg (30 psig) with compressed air. Permeate exited at atmospheric pressure through a tube at the bottom of the cell into a beaker sitting on an electronic balance (Mettler Toledo, Columbus, OH). The balance was connected to a PC running LabVIEW, which automatically recorded the mass as a function of time. The flux ($J$) was calculated as follows:

$$J = \frac{\Delta V}{A \Delta t}$$

where $\Delta V$ was the volume of water collected between two mass measurements, $A$ was the membrane surface area, and $\Delta t$ was the time between two mass measurements. The permeance ($P$) was then calculated by normalizing the flux by the TMP ($\Delta p$):

$$P = \frac{J}{\Delta p}$$

Measurements were made on a minimum of 25 samples cut from across the width (i.e., transverse direction) of the membrane roll.

2.4. Constant flux fouling

The foulant employed in these studies was a 1500 ppm emulsion of soybean oil in water. Soybean oil (10.8 g) and OFX-0193 surfactant (1.2 g) were combined with ultrapure water (1 L) and added to 20,000 rpm for 180 s in a laboratory blender (Waring, Torrington, CT). The emulsion was diluted to 8 L with more ultrapure water, resulting in an overall concentration of 1500 ppm in a 9:1 ratio of oil: surfactant (1350 ppm oil, 150 ppm surfactant). Emulsified oil is a common component of industrial wastewater streams and has been widely studied in the ultrafiltration and microfiltration literature [4,43–48]. This soybean oil emulsion is a simple, model system where the oil represents a highly fouling, hydrophobic, oily component. Similar emulsions have been used previously in many other studies [5,16,21,49,50].

The apparatus used to perform constant flux crossflow filtration has been described in detail elsewhere [51]. A simplified diagram of the system is shown in Fig. 1. It had two temperature-controlled feed tanks, one filled with ultrapure water and one filled with the oil emulsion foulant. The feed temperature was 25°C for all fouling experiments. The selected feed was pumped through three crossflow cells in series. A membrane coupon (4 cm x 9 cm) was loaded into each cell with a porous plastic backing (for mechanical support) and sealed with a rubber O-ring, yielding a membrane filtration area of 19.4 cm$^2$. The feed flow rate was 0.8 L/min, corresponding to a crossflow velocity of 0.18 m/s and a Reynolds number of 1000 inside the cell flow paths (calculated by assuming that the flow path was two parallel plates of large aspect ratios, and the channel height was used as the characteristic dimension) [52]. The feed pressure was 2.1 barg (30 psig). The reject from the crossflow cells was recirculated to the feed tanks.

The permeate flux was controlled by a peristaltic pump on the permeate line leaving each crossflow cell. The permeate flow rates were measured by Coriolis-type flow meters positioned on the permeate lines immediately after each peristaltic pump. The peristaltic pumps, by occluding the permeate line tubing, isolated the pressure on the permeate side of the membrane from the atmosphere. The TMP could, therefore, be measured by a differential pressure transducer connected to the feed and permeate lines of each cell. (The pressure difference between the feed inlet and reject outlet of a cell was small relative to the transmembrane pressures measured during fouling experiments [51].) As the membrane fouled, the pressure on the permeate side of the membrane decreased. Because the feed pressure was fixed throughout each experiment, the TMP increased. In cases of extreme fouling (at the highest fluxes considered), the permeate pressure decreased to atmospheric pressure, resulting in a TMP equal to the gauge feed pressure. In such cases, the experiment was terminated, since a permeate line pressure less than atmospheric pressure could lead to the formation of bubbles in the permeate line, resulting in instabilities in the permeate flow rate. For experiments where severe fouling was expected, differential pressure transducers with 3.5 bar (50 psi) spans were used. For less severe fouling at lower fluxes, differential pressure transducers with smaller spans, such as 1 bar (15 psi) or 0.17 bar (2.5 psi) were used to improve accuracy.

Results of the crossflow fouling studies will be presented as a function of permeate volume per unit filtration area ($V/A$). For a constant flux experiment, $V/A$ is proportional to the experiment...
time. The mass transfer resistance, \( R \), of a porous membrane is often defined as the ratio of the TMP \( (\Delta p) \) to the permeate flux \( (J) \) and permeate viscosity \( (\mu) \) as follows [53]:

\[
R = \frac{\Delta p}{\mu J}
\]

(3)

The resistance at any \( V/A \) value in a constant flux experiment can, therefore, be calculated by dividing the TMP by the flux and viscosity. By combining Eqs. (2) and (3), the resistance can be written as the reciprocal of the membrane permeance \( (P) \) multiplied by the viscosity \( (\mu) \):

\[
R = \frac{1}{\mu P}
\]

(4)

As will be demonstrated, the application of surface coatings affects the membrane permeance. To gain an improved understanding of the effect of the surface modifications on membrane fouling, the resistances during fouling (calculated using Eq. (4)) were normalized by the initial membrane resistance [54-56]:

\[
R_N = \frac{R}{R_0}
\]

(5)

where \( R_N \) is the normalized resistance and \( R_0 \) is the initial resistance. The initial resistance was measured during pure water filtration immediately prior to fouling and calculated using Eq. (4). The initial resistance can also be calculated using Eq. (4) from the pure water permeance measured in dead end filtration (cf., Table 1).

Membrane rejection was determined by the total organic carbon (TOC) content of the permeate and feed solutions. Permeate and feed samples were analyzed using a Total Organic Carbon Analyzer from Shimadzu Scientific (Japan). Permeate samples were collected at the end of each constant flux fouling experiment. The rejection was calculated as follows:

\[
\mathbf{R} = \left(1 - \frac{C_p}{C_f}\right) \times 100\%
\]

(6)

where \( \mathbf{R} \) is the rejection, \( C_p \) is the organic carbon concentration in the permeate, and \( C_f \) is the organic carbon concentration in the feed.

### 3. Results and discussion

#### 3.1. Pure water permeance and membrane pore size characterization

The pure water permeances of unmodified, PDA-modified, and PDA-g-PEG-modified PS-20 membranes were measured by dead end filtration. Results are shown in Table 1. The average permeance of unmodified PS-20 membrane was about 900 L m\(^{-2}\) h\(^{-1}\) bar\(^{-1}\) (LMH/bar), matching the manufacturer’s specification [57]. The application of PDA and PDA-g-PEG surface modifications, while increasing the hydrophilicity of the membrane surface [20,21], reduced the membrane permeance. Similar reductions in membrane permeance following the application of various surface coatings, such as adsorbed polymers [58], adsorbed surfactants [59], crosslinked hydrogels [5], grafted polymers [60], and polydopamine [21], have been reported elsewhere. The PDA modification resulted in a 22% reduction in permeance, and the PDA-g-PEG modification resulted in a 36% reduction in permeance relative to that of the unmodified membrane. Although a clear decrease in average permeance was observed with the application of the coatings, the standard deviations of these measurements were relatively large (± 22% for the unmodified membrane, ± 14% for the PDA-modified membrane, and ± 12% for the PDA-g-PEG-modified membrane), reflecting the inherent variability of the small samples cut from a large membrane roll. Interestingly, the standard deviation decreased as the membrane was increasingly modified. Larger pores may have been more readily modified than smaller pores, as their larger diameter may have allowed improved access by dopamine and oxygen (both of which are required for the formation of polydopamine [23]), or bulky PEG chains to the pore walls, thereby reducing their sizes and making the modified membrane more uniform than its unmodified analog. In the following constant flux fouling experiments, these average permeance values were used to guide the selection of membrane samples for testing; if a sample’s pure water permeance was not within 10% of the specified average, it was discarded, and a new sample loaded in its place.

The unmodified PS-20 membrane had a molecular weight cutoff of 20 kDa (95% PEG rejection) [57]. To provide a crude, order-of-magnitude approximation of the average effective pore size of such a membrane, one might use the size of a 20 kDa PEG chain. The Stokes radius of a PEG chain may be calculated from its molecular weight [61]:

\[
a = 16.73 \times 10^{-3} M^{0.557}
\]

(7)

where \( a \) is the Stokes radius (in nm) and \( M \) is the molecular weight. The Stokes radius of a 20 kDa PEG chain is 4.2 nm. Thus, PEG molecules significantly larger than this radius are effectively excluded from the membrane, presumably because they are too large to pass though the pores of the membrane.

The permeance \( (P) \) is defined as the average membrane hydraulic permeability \( (L_p) \) divided by the permeate viscosity \( (\mu) \):

\[
P = \frac{L_p}{\mu}
\]

(8)

The permeate viscosity is assumed to be equal to that of water, since the organic rejection of these membranes was very high (typically > 98%), as will be described later. The average membrane hydraulic permeability is defined as follows [62]:

\[
L_p = \frac{\epsilon \mu \nu}{\Delta p}
\]

(9)

where \( \epsilon \) is the membrane porosity, \( \nu \) is the average permeate fluid velocity, and \( \Delta p \) is the TMP. Poiseuille’s law may be used to relate the fluid velocity through a pore to the pore radius [62]:

\[
\nu = \frac{r^2 \Delta p}{8 \mu \delta}
\]

(10)

where \( r \) is the average, effective pore radius, and \( \delta \) is the membrane thickness. The pores are assumed to be straight cylinders through the membrane, and the membrane thickness was measured to be 190 \( \mu \)m, which is the average thickness of the samples used for dead end filtration. By combining Eqs. (8)–(10), an expression for the permeance of a membrane consisting of pores of radius \( r \) may be obtained:

\[
P = \frac{\epsilon r^2}{8 \mu \delta}
\]

(11)
If the Stokes radius of a 20 kDa PEG chain is used as the pore radius of the unmodified membrane, the average, effective radius of a modified membrane may be calculated from the ratio of the permeances as expressed in Eq. (11):

$$\frac{P_M}{P_{UM}} = \left( \frac{\varepsilon_M}{\varepsilon_{UM}} \right)^{1/2} \left( \frac{r_M}{r_{UM}} \right)^{1/2}$$

(12)

where \(r_M\) and \(r_{UM}\) are the average, effective pore radii of the modified (PDA or PDA-g-PEG) and unmodified membranes, \(P_M\) and \(P_{UM}\) are the permeances of the modified and unmodified membranes, and \(\varepsilon_M\) and \(\varepsilon_{UM}\) are the porosities of the modified and unmodified membranes, respectively. If the porosities of the modified and unmodified membranes are similar, the ratio of radii may be directly related to the ratio of permeances:

$$\frac{P_M}{P_{UM}} = \left( \frac{r_M}{r_{UM}} \right)^{1/2}$$

(13)

Based upon this calculation methodology, Table 1 shows the average, effective pore radii of the unmodified and modified membranes. The average, effective pore radius of the unmodified membrane was calculated using Eq. (7) (where the pore radius was assumed equal to the Stokes radius of a PEG chain with a molecular weight of 20 kDa), and the average, effective pore radii of the PDA- and PDA-g-PEG-modified membranes were calculated using Eq. (13).

The values given in Table 1 are likely the smallest average pore sizes that would be expected for the modified membranes. The PDA and PDA-g-PEG modifications may occlude some of the smallest pores, which would cause the membrane porosity to decrease. If the modified membranes had porosities less than those of the unmodified membranes, the effective pore radii would have been larger than those shown in Table 1 (see Eq. (12)).

Ellipsometry has been used to measure the thickness of polydopamine deposited on the surface of spin-cast polysulfone films [20]. At the conditions used here (2 mg/mL dopamine, 15 mM TRIS buffer, pH=8.8, 60 min, RT), the reported polydopamine thickness was approximately 12 nm. Increasing the deposition time to 75 min resulted in a polydopamine thickness of approximately 17 nm [20]. Based on the estimated effective radii shown in Table 1, such polydopamine thicknesses could not develop within the pores of the membrane. Limited diffusion of oxygen into the porous structure may have resulted in thinner coatings within the porous structure than predicted by deposition on top of a dense polysulfone surface with extensive access to oxygen. Dissolved oxygen has recently been shown to be critical in the oxidative polymerization of dopamine from aqueous solution [23]. Thus, most of the polydopamine was likely deposited on the surface of the membrane. Given that the average size of the oil droplets used in this study was about 1.4 μm, with nearly all droplets in the range of 0.8–3.0 μm [63,64], which is far larger than the average pore size of the membranes considered, having the polydopamine largely on top of the membrane surface puts it in the region where it can most directly interact with the foulant and potentially have the most beneficial effect on fouling.

The graft density of PEG on PDA-modified PS-20 membrane has been previously reported [20]. For PEG grafted to a PDA-modified membrane (2 mg/mL dopamine, 15 mM TRIS buffer, pH=8.8, 60 min, RT) under the same grafting conditions used here (1 mg/mL PEG-NH₂, 15 mM TRIS buffer, pH=8.8, 60 min, 60 °C), a PEG density of approximately 17 μg/cm² was achieved [20].

3.2. Constant flux crossflow fouling

Constant flux crossflow filtration was performed on unmodified, PDA-modified, and PDA-g-PEG-modified PS-20 membranes at 25, 40, 55, 70, 85, and 100 L m⁻² h⁻¹ (LMH). Fig. 2 presents the TMP evolution as a function of the permeate volume divided by the filtration area (V/A) at 55, 70, and 85 LMH when the membranes were challenged with a soybean oil emulsion feed. Results at 25, 40, and 100 LMH are shown in Fig. S1 of the Supporting information. For results at 55 LMH, data are only shown to a maximum V/A value of 4 cm, because any changes in TMP occurring beyond this point were insubstantial relative to those occurring at smaller V/A values. For fluxes of 70 and 85 LMH, at least one of the three membranes exhibited severe fouling, causing the TMP to reach a value equal to the gauge feed pressure, requiring that the experiment be terminated. In these cases, TMP results are not shown to the same final V/A value for all membranes. The initial TMP (i.e., that reported at V/A=0 in these graphs) is the TMP observed during pure water filtration just before fouling was initiated. That is, a V/A value of zero marks the point when the oily water emulsion began to be fed to the membranes. The time for the oily water emulsion to transit from the feed tank to the last membrane in the train of sample cells was approximately three seconds, which corresponds to V/A values of 0.002 cm at 25 LMH and 0.008 at 100 LMH, so all of the fouling experiments started, to good approximation, essentially instantaneously at a V/A value of zero. Because the unmodified membrane had the highest pure water permeance (cf., Table 1), it exhibited the lowest initial TMP relative to the modified membranes.

At 55 LMH (Fig. 2a), the TMP of all three membranes increased most at V/A values less than 1 cm, then approached a plateau. Qualitatively similar behavior has been reported elsewhere [65,66]. Ghosh et al. suggested that the initial rapid TMP increase is due to a combination of concentration polarization and fouling effects, while a subsequent linear TMP increase was ascribed to fouling alone [65]. At all three fluxes, the unmodified membrane had the lowest TMP. The PDA-modified membrane had a higher TMP than the unmodified membrane, and the PDA-g-PEG-modified membrane had a TMP substantially higher than that of either the unmodified or PDA-modified membranes. The higher TMP in the modified membranes is indicative of increased mass transfer resistance resulting from the application of the PDA and PDA-g-PEG modifications to the membrane surface. Similar results have been reported in other studies, where membranes exhibited a decrease in permeance following surface modification [5,10,13,16–18].

As shown in Fig. 2b, at 70 LMH, the unmodified membrane exhibited qualitatively different behavior than at lower fluxes (i.e., Figs. 2a, S1a, and S1b). The TMP increased nonlinearly very early in the experiment (i.e., at V/A < 1.0 cm), then increased approximately linearly between 1.0 cm and 3.0 cm, similar to the results observed at 25, 40, and 55 LMH. However, unlike the results at lower flux, the TMP of the unmodified membrane at 70 LMH did not approach a plateau but, rather, began to increase rapidly at V/A > 3.0 cm, indicating a substantial increase in the fouling rate. Several other authors have reported similar results, where a dramatic upturn in TMP occurs after a relatively slow, linear increase [54,55,67–70]. Ho and Zydney developed a model based on pore blockage and cake formation laws that was capable of describing similar behavior in constant flux protein microfiltration [68]. They suggested that, during the relatively slow, linear increase, pore blockage is the dominant fouling mechanism. Once pores are blocked, a cake layer is able to form [68]. Ognier et al. also observed similar behavior during constant flux microfiltration of bioreactor effluent [70]. They proposed that fouling occurs (and the TMP rises) due to sequential pore closure, which occurs in two stages. During the first stage, pores gradually become closed due to the accumulation of foulant on the membrane. To maintain the same flux globally over the entire filtration area, the flux through open pores must increase as other pores gradually become closed. This increase in local flux accelerates fouling, causing open pores to more quickly close. Once a pore is closed, the local flux around it is reduced, which blocks a consecutive pore, and the cycle continues.
become closed. If the local flux becomes sufficiently high, the second stage of fouling begins, during which a cake begins forming on the membrane surface. The formation of this cake dramatically increases the hydraulic resistance, and the TMP rises rapidly to maintain constant flux [70].

After the upturn at $V/A = 3.0 \text{ cm}$, the TMP continued rising until it reached a value approximately equal to the gauge feed pressure (2.1 barg), at which point the experiment was terminated. In contrast, the PDA-modified membrane, although exhibiting a higher initial TMP than the unmodified membrane, experienced a relatively slow and stable rate of fouling after the brief rise in TMP at the beginning of the experiment. This result may suggest that foulant did not form a cake on the PDA-modified membrane [68]; perhaps the hydrophilic coating mitigated pore blockage sufficiently to prevent cake formation atop blocked pores. The PDA-g-PEG-modified membrane exhibited behavior between that of the unmodified and PDA-modified membranes at 70 LMH. Like the unmodified membrane, the PDA-g-PEG-modified membrane exhibited a period between $V/A = 2.0 \text{ cm}$ and $V/A = 6.0 \text{ cm}$ where the TMP rise was slightly concave up. However, the TMP did not rapidly increase to the maximum TMP possible for the experiment during the course of these measurements. Rather, the rate of fouling appears to have decreased around $V/A = 6.0 \text{ cm}$, and the TMP profile began to plateau near the end of the experiment.

Unlike the case of 55 LMH, at 70 LMH, the surface-modified membranes, despite their higher initial TMP, ultimately yielded a reduced TMP relative to the unmodified membrane at the highest $V/A$ values considered. The PDA-modified membrane exhibited much less fouling, based on TMP, than the unmodified membrane, particularly after a $V/A$ of around 4 cm, so the PDA-modified membrane could be operated stably at these conditions whereas the unmodified membrane could not. The PDA-g-PEG-modified membrane had a higher TMP at all $V/A$ values than the PDA-modified membrane, but it also did not exhibit the sharp runaway in TMP exhibited by the unmodified membrane. The long PEG chains, which extend away from the membrane, have high mobility and a large excluded volume, and they sterically hinder the approach of foulants to the surface [12]. Foulant particles also cannot easily approach the surface by compressing the PEG brushes, as doing so incurs a significant free energy penalty [71]. The increased hydrophilicity of the modified membranes relative to the unmodified membrane, which may have reduced foulant adhesion, likely helped to overcome the higher membrane resistance resulting from the application of the PDA and PDA-g-PEG modifications at 70 LMH.

At 85 LMH (Fig. 2c), the TMP of all three membranes increased to levels requiring the experiment to be terminated. That is, all three membranes experienced an upturn in TMP leading to a rapid
rise until the TMP reached the gauge feed pressure. The unmodified membrane, while starting at the lowest TMP, reached the maximum TMP first, at a $V/A$ value of approximately 2.0 cm. In comparison, the unmodified membrane reached the maximum TMP at a $V/A$ of about 7.0 cm when operated at 70 LMH. Presumably, the higher flux of 85 LMH brought foulants to the membrane surface more quickly than at 70 LMH, resulting in the more rapid TMP increase. This finding is consistent with other reports in the literature, where TMP increases more rapidly as the imposed flux increases [65,68,69].

The TMP of the unmodified membrane eclipsed that of the PDA-modified membrane at a $V/A$ value of approximately 1.1 cm and that of the PDA-g-PEG-modified membrane at around 1.3 cm. The PDA-modified membrane reached the maximum TMP at a $V/A$ value of 3.2 cm. The PDA-g-PEG-modified membrane reached the maximum TMP at a $V/A$ value of 4.2 cm, so it had a lower TMP than the PDA-modified membrane at $V/A$ values greater than about 2.3 cm. The large excluded volume of the PEG chains, which help create a substantial buffer to foulant adsorption [12], may have helped retard the rapid formation of a cake layer on the membrane surface observed with the unmodified and PDA-modified membranes. The PDA modification is conformal [28], so the PDA-modified membrane, while substantially more hydrophilic than the unmodified membrane [20], still may permit the close approach of foulants to the surface, facilitating rapid cake buildup. A similar result was reported by Chan et al., where a minimum in rejection was observed at fluxes just below the critical flux of a UF membrane challenged with a protein mixture [72].

The organic rejection was similar for all three membranes at each of the fluxes tested. The soybean oil emulsion foulant had an average droplet size of approximately 1.4 $\mu$m [63,64], so the oil droplets were much larger than the estimated pore sizes (Table 1), which was reflected in the generally high rejection values. The PDA-modified membrane showed a minimum in rejection at 70 LMH. As will be described later, this flux is slightly below the membrane’s threshold flux of 72 LMH. Therefore, at 70 LMH, concentration polarization is severe, which would cause the rejection to decrease [3,72], but foulant has not accumulated substantially on the membrane surface, which would cause the rejection to increase due to blockage of pores by cake layer formation [72].

Fig. 3 presents the normalized resistance as a function of $V/A$ for unmodified, PDA-modified, and PDA-g-PEG-modified membranes at 55, 70, and 85 LMH. Normalized resistance profiles at 25, 40, and 100 LMH are shown in Fig. S2 of the Supporting information. At 55 LMH (Fig. 3a), the unmodified membrane reached a normalized resistance of about 2.75 at $V/A=4.0$ cm. The PDA-modified membrane had a normalized resistance of 2.25 at $V/A=4.0$ cm at 55 LMH. Thus, the PDA modification, while mitigated foulant accumulation despite their higher initial TMP than the unmodified membrane.

Fig. 3. Normalized resistance evolution during constant flux fouling of unmodified, PDA-modified, and PDA-g-PEG-modified PS-20 UF membranes with 1500 ppm soybean oil emulsion feed. Normalized resistances calculated using Eqs. (3) and (5) from data shown in Fig. 2. (a) 55, (b) 70, and (c) 85 LMH.
increasing the overall resistance, mitigated fouling, because the unmodified membrane exhibited a greater increase in resistance during fouling than the PDA-modified membrane.

The normalized resistance profiles at 70 LMH (Fig. 3b) were qualitatively similar to the TMP profiles (Fig. 2b). The unmodified membrane reached a normalized resistance of about 24, corresponding to the maximum allowable TMP of 2.1 bar. The PDA-modified membrane and the PDA-g-PEG-modified membrane exhibited much lower normalized resistances. At 85 LMH (Fig. 3c), the unmodified membrane had a maximum normalized resistance of 23, while the PDA-modified membrane had a maximum of 18, and the PDA-g-PEG-modified membrane had a maximum of 13. This effect is due to the increased initial resistance of the PDA- and PDA-g-PEG-modified membranes relative to the unmodified membrane. Furthermore, the PDA- and PDA-g-PEG-modified membranes showed lower normalized resistances than the unmodified membrane at V/A values greater than about 1.1 cm. The PDA- and PDA-g-PEG-modified membranes exhibited similar normalized resistances up to V/A = 1.8 cm. Afterwards, the PDA-g-PEG-modified membrane had a lower normalized resistance than the PDA-modified membrane.

3.3. Threshold flux determination

All three membranes showed qualitatively similar behavior during constant flux fouling at 55 LMH (Fig. 2a). However, as the flux increased to 70 LMH (Fig. 2b) or 85 LMH (Fig. 2c), each membrane exhibited a more dramatic, and qualitatively different, increase in TMP than at lower fluxes. Such a change in the fouling behavior indicated a substantial increase in the rate of fouling at high fluxes. Recently, Field et al. have described the threshold flux as the flux below which a constant rate of fouling occurs. Above the threshold flux, the rate of fouling substantially increases [41].

The threshold flux for each membrane was evaluated by flux stepping. This well-known technique is commonly used to determine critical and threshold fluxes [73–77]. In a flux stepping experiment, the membrane was operated at a low, constant flux for 20 min. After 20 min, the flux was increased and maintained at a higher value for another 20 min. In this study, the initial flux was 10 LMH, and the flux was increased by 10 LMH during each step until a flux of 100 LMH was reached. Previously, the effects of beginning at a different initial flux (e.g., 30 LMH), changing the step length (e.g., 10 min), and using a different step protocol (e.g., a step up/down method) were investigated, but only minor changes in the resulting threshold flux were observed [51]. During each flux step, the increase in TMP was recorded.

Fig. 4 shows an example of data obtained during flux stepping experiments and three parameters that may be used to determine the threshold flux from those data. These parameters were described by Beier and Jonsson [74] and Le Clech et al. [76]. The flux increase, accomplished by changing the permeate flow set point and allowing LabVIEW to automatically adjust the permeate pump speed to achieve that flux, typically required less than 30 s. In response to this flux increase, (from Jn to Jn+1), the TMP rose quickly. After a few minutes (depending upon how quickly the flux was able to reach its new setpoint), the TMP entered a period of slow, linear rise over the remainder of the 20-min interval. Regressions were made through the linear portion of the TMP vs. time data at each flux. The slope of this regression over each interval, d(TMP)/dt, was used as one parameter to determine the threshold flux. In this study, d(TMP)/dt was always greater than zero, even at the lowest flux (i.e., 10 LMH). Therefore, a critical flux could not be determined for any of the membranes, as the critical flux is strictly defined as the flux below which no rise in membrane resistance is observed with time [39,41]. Instead, the flux stepping experiments revealed threshold fluxes.

Another parameter used to estimate the threshold flux was the average transmembrane pressure during a flux step (TMPavg). TMPavg was calculated as the arithmetic mean over all transmembrane pressures recorded during the slow, linear TMP rise after the initial, abrupt increase following an increase in flux. The use of TMPavg was proposed by Choi and Dempsey to determine the critical flux when a membrane was challenged with complex, highly fouling natural waters [73]. Their aim was to develop a critical flux definition that was operationally relevant, since d(TMP)/dt = 0 may be rarely observed in practice. In light of relatively recent clarifications of the definition of critical and threshold fluxes [41], it seems likely that Choi and Dempsey were calculating what is now known as the threshold flux, rather than the critical flux. The third parameter used for threshold flux definition is ΔTMP, which is the TMP difference between the linear regressions of TMP data recorded over two adjacent flux steps at the time of flux increase. Others, such as Le Clech et al., have chosen an arbitrary time after increasing the flux to measure the TMP at the increased flux, from which ΔTMP may be calculated using the last TMP recorded at the previous flux [76]. In this work, the time required for the TMP to reach the linear regime at a new flux varied with flux (i.e., the time became longer as fouling became more severe at higher fluxes), so the present technique was adopted to standardize measurements at all fluxes. Each of the three threshold flux determination parameters, d(TMP)/dt, TMPavg, and ΔTMP, were plotted as a function of flux.

Fig. 5 presents the threshold flux determination for the unmodified membrane. Results of the flux stepping experiment are shown in Fig. 5a. TMPavg values at each flux, calculated from the data in Fig. 5a, are presented as a function of flux in Fig. 5b. All TMPavg values for fluxes less than 60 LMH lie on a single linear regression, indicating that the resistance was constant at these fluxes. Above 60 LMH, the slope of the TMPavg vs. flux relationship increases, indicating that the resistance is increasing. The flux at which the slope changes, 65 LMH
(indicated by the vertical dotted arrow) is identified as the threshold flux based on this method [73].

Fig. 5c presents ΔTMP as a function of flux. The ΔTMP values shown are those observed when the flux was increased to the corresponding value on the horizontal axis (e.g., ΔTMP = 0.02 bar was observed when the flux was increased from 10 LMH to 20 LMH). No ΔTMP value is shown at 10 LMH because 10 LMH was the lowest flux at which the membrane was challenged with the soybean oil emulsion foulant. The threshold flux is the flux above which the relationship between ΔTMP and flux becomes convex to the flux axis [76]. At 40, 50, and 60 LMH, ΔTMP varied approximately linearly with flux. Above 60 LMH, ΔTMP began to increase nonlinearly with increasing flux. A horizontal dotted line was drawn to denote the ΔTMP corresponding to the beginning of this nonlinear increase. The threshold flux based on this method, 65 LMH, is identified by the vertical dashed arrow [76].

Fig. 5d presents the rate of fouling, d(TMP)/dt, as a function of flux. At flux values below the threshold flux, d(TMP)/dt is low and constant. In this case, d(TMP)/dt is close to, but slightly greater than, zero up to a flux of 60 LMH. Some rise in d(TMP)/dt is seen from 50 LMH to 60 LMH, but the value at 60 LMH is very near the value recorded at 20 LMH (denoted with a horizontal dashed line). Therefore, further increases in d(TMP)/dt beyond the value observed at 60 LMH suggest that the flux has exceeded the threshold flux. Therefore, the threshold flux (denoted by a vertical dashed arrow) was 65 LMH according to this method [76].

In Fig. 5b, the linear regressions of TMP_avg at fluxes below the threshold flux do not pass through the origin. This result may be explained by considering a comparison with the pure water TMP_avg/flux relationship, which would pass through the origin and exhibit lower TMP_avg values than those exhibited during fouling. Even at the lowest fluxes explored, fouling rates were non-zero. The non-zero rate of fouling would have caused the TMP_avg/flux relationship during fouling to increasingly deviate from the pure water relationship as flux increased. The slope of the TMP_avg/flux relationship during fouling would, therefore, have been greater than that in pure water, causing the fouling regression to intersect the flux axis at a value greater than zero. Similar observations have been reported elsewhere [78,79].

Flux stepping experiments were also performed on PDA- and PDA-g-PEG-modified membranes, and values for the three parameters described above were determined for the two modified membranes. Plots analogous to those shown in Fig. 5 are shown in Figs. S3 (for the PDA-modified membrane) and S4 (for the PDA-g-PEG-modified membrane) in the Supporting information. A summary of threshold flux values for the three membranes as determined by the three determination parameters is shown in Table 2. As pointed out by Beier and Jonsson, threshold flux determinations should be validated with constant flux fouling studies [74]. For the unmodified membrane, all threshold flux parameters yielded a value of 65 LMH. This value is in qualitative agreement with the constant flux fouling experiments shown in
particularly sensitive to the foulant ingress. The small effective pore diameter of the PDA-modified membrane monitored the fouling behavior after the step increase in TMP. The other two parameters increased, the high local threshold of the foulant as the buildup of foulant increased the pressure. Therefore, even though an increase in fouling rate was observed between 50 and 60 LMH (Figs. 1b and 2b), the PDA-PEG modification may have acted to assuage rapid fouling, preventing the increase in TMP (or normalized resistance) to extremely high values at fluxes near the threshold flux. The TMP and resistance profiles began to flatten again at 70 LMH, operation of the PDA-PEG-modified membrane at 70 LMH may represent an unusual scenario where sustained operation may be possible at a flux greater than the threshold flux identified via these methods. The PEG chains may facilitate this behavior, since such operation was not observed with either the unmodified or PDA-modified membranes. The long PEG chains extending from the membrane surface may disrupt the accumulation of a thick, dense layer of foulant on the surface, frustrate adsorption, or facilitate removal of the foulant. Therefore, several parameters have been used to determine the threshold flux for unmodified and surface-modified membranes. In unmodified membranes, each parameter produced the same threshold flux value. The three parameters yield less-reproducible threshold flux values for membranes modified with hydrophilic PDA and PDA-PEG coatings. As interactions between the membrane surface and foulants become less favorable as the surface becomes more hydrophilic (relative to the hydrophobic unmodified membrane), the phenomena measured by each of the three parameters may become less severe and, therefore, more difficult to observe. Flux stepping experiments provide a rapid means of screening a membrane/foulant pair for fuel regimes of likely sustainable operation. However, as pointed out by Beier and Jonsson [74], flux stepping techniques should only be used to estimate the critical or threshold flux, and estimated values may be used to plan longer-term constant flux fouling studies to verify regimes of sustainable operation. From the results presented here, flux stepping experiments alone should likely not be used to determine operational parameters for long-term operation.

3.4. Constant flux crossflow fouling with membranes of similar initial permeances

Sections 3.1 and 3.2 clearly demonstrated that membrane surface modification decreased the membrane permeance, resulting in higher transmembrane pressures during pure water filtration and during fouling at fluxes below the threshold flux of the unmodified membrane (25, 40, and 55 LMH, Figs. S1a-b and 1a). It is of interest, therefore, to assess the fouling performance of unmodified and modified membranes with similar initial (pure water) permeances. PS-10 is a polysulfone UF membrane similar to PS-20, but PS-10 has a lower molecular weight cutoff (10 kDa for PS-10 rather than 20 kDa for PS-20) and, consequently, a lower permeance than PS-20. The pure water permeance of PS-10, as measured by dead end filtration, was 570 LMH/bar, similar to the permeance of a PS-20 membrane after PDA-PEG modification (cf., Table 1). Furthermore, McCloskey et al. have previously demonstrated that increasing the time that a polysulfone UF membrane is in contact with dopamine solution results in a decreased permeance, likely due to thicker polydopamine accumulation on the membrane surface and within

Table 2
Threshold fluxes (LMH) of unmodified, PDA-modified, and PDA-PEG-modified PS-20 UF membranes determined by three different parameters, as shown in Fig. 4, 53, and 54.

<table>
<thead>
<tr>
<th>Determination parameter</th>
<th>Unmodified</th>
<th>PDA-modified</th>
<th>PDA-PEG-modified</th>
</tr>
</thead>
<tbody>
<tr>
<td>TMPavg</td>
<td>65</td>
<td>33</td>
<td>58</td>
</tr>
<tr>
<td>ΔTMP</td>
<td>65</td>
<td>72</td>
<td>52</td>
</tr>
<tr>
<td>d(TMP)/dt</td>
<td>65</td>
<td>&gt; 100</td>
<td>62</td>
</tr>
<tr>
<td>Estimated threshold flux</td>
<td>65</td>
<td>72</td>
<td>60</td>
</tr>
</tbody>
</table>

Figs. 1 and 2. At all fluxes tested below 65 LMH, the TMP (and normalized resistance) remained at a relatively low value, so the membrane fouled slowly. At fluxes greater than 65 LMH, the TMP and, consequently, resistance, rose to their maximum values, so the apparent threshold flux of 65 LMH deduced from the three methods described previously is coherent with the fouling data.

The three threshold flux determination parameters yielded different values in the case of the PDA-modified membrane. For example, the TMPavg parameter gave a threshold flux value of 33 LMH. This value is unreasonably low relative to the results of the constant flux fouling studies (cf., Fig. 2), because fouling studies conducted at 55 and 70 LMH resulted in low TMP and resistance values, indicative of fouling behavior below the threshold flux. A threshold flux of 72 LMH was estimated by plotting ΔTMP as a function of flux. This value is coherent with the results from the fouling studies, since fouling at fluxes higher than 72 LMH (e.g., 85 LMH) resulted in a rapid rise in TMP. A threshold flux value could not be determined from d(TMP)/dt, suggesting that the threshold flux was higher than the highest tested flux in the flux stepping experiment (i.e., 100 LMH). Since severe fouling was observed at 85 LMH, the actual threshold flux must be lower than 85 LMH, meaning that d(TMP)/dt was not sensitive to the threshold flux of the PDA-modified membrane. This scenario, in which different threshold flux determination parameters yield different threshold flux values, reinforces the conclusions drawn by Beier and Jonsson, who stated that critical flux value (or, in this case, threshold flux value) determined by flux stepping experiments must be validated against the results of constant flux experiments [74]. Additional discussion of the threshold flux values estimated by the three evaluation parameters is provided in the Supporting information.

In the PDA-PEG-modified membrane, the three parameters yielded three threshold flux values much closer to each other than those determined for the PDA-modified membrane. Only the threshold flux value determined by ΔTMP (52 LMH) was not coherent with the fouling data, because constant flux fouling at 55 LMH with the PDA-PEG-modified membrane resulted in relatively low TMP and normalized resistance values (cf., Figs. 1a and 2a). As described above, the ΔTMP parameter likely measures the instantaneous response of the membrane to a sharp increase in foulant ingress. The small effective pore diameter of the PDA-PEG-modified membrane (cf., Table 1) and, consequently, its high local flux relative to the unmodified and PDA-modified membranes at the same overall flux, may have made this membrane particularly sensitive to the ΔTMP parameter. When the flux was increased, the high local flux of the PDA-PEG-modified membrane resulted in a rapid ingress of foulant, causing a large, nearly instantaneous increase in the TMP. The other two parameters monitored the fouling behavior after the step increase in flux, where the PEG chains may have been more effective in mitigating the buildup of foulant as the flux is maintained over the constant flux interval. The ΔTMP parameter, therefore, produced a lower threshold flux value than the other two parameters. At 70 LMH, the TMP and resistance did not reach their maximum values, but an increase in the rate of fouling was observed as a slight, concave upwards shape in the TMP and resistance profiles between V/A values of 2 and 6 cm (cf., Figs. 1b and 2b). The flux stepping experiment and parameters subsequently used to determine the threshold flux appear sensitive to this behavior, since all three threshold flux determination parameters yielded threshold flux values less than 70 LMH. Because the TMP and resistance profiles began to flatten again at V/A values greater than 6 cm, operation of the PDA-PEG-modified membrane at 70 LMH may represent an unusual scenario where sustained operation may be possible at a flux greater than the threshold flux identified via these methods. The PEG chains may facilitate this behavior, since such operation was not observed with either the unmodified or PDA-modified membranes. The long PEG chains extending from the membrane surface may disrupt the accumulation of a thick, dense layer of foulant on the surface, frustrate adsorption, or facilitate removal of the foulant. Therefore, several parameters have been used to determine the threshold flux for unmodified and surface-modified membranes. In unmodified membranes, each parameter produced the same threshold flux value. The three parameters yield less-reproducible threshold flux values for membranes modified with hydrophilic PDA and PDA-PEG coatings. As interactions between the membrane surface and foulants become less favorable as the surface becomes more hydrophilic (relative to the hydrophobic unmodified membrane), the phenomena measured by each of the three parameters may become less severe and, therefore, more difficult to observe. Flux stepping experiments provide a rapid means of screening a membrane/foulant pair for flux regimes of likely sustainable operation. However, as pointed out by Beier and Jonsson [74], flux stepping techniques should only be used to estimate the critical or threshold flux, and estimated values may be used to plan longer-term constant flux fouling studies to verify regimes of sustainable operation. From the results presented here, flux stepping experiments alone should likely not be used to determine operational parameters for long-term operation.
its pores [20]. Increasing the polydopamine deposition time from 60 min to 75 min decreased the pure water permeance of the PDA-modified PS-20 membrane from 700 LMH/bar (cf., Table 1) to 570 LMH/bar. PDA-modified membranes subjected to polydopamine deposition for 75 min are labeled “PDA75-modified.”

Constant flux fouling at 55 LMH was performed on unmodified PS-10, PDA75-modified PS-20, and PDA-g-PEG-modified PS-20 membranes, and the results are shown in Fig. 6. Because the PS-10, PDA-75-modified PS-20, and PDA-g-PEG-modified PS-20 all had similar initial permeances, they all had the same initial TMP at each flux. The TMP profiles of the PDA75- and PDA-g-PEG-modified PS-20 were lower than that of the unmodified PS-10 membrane. This result demonstrates the fouling mitigation offered by the hydrophilic coating. By applying these surface treatments to a membrane with relatively large pores, a hydrophilic membrane may be prepared with a similar permeance to that of a hydrophobic membrane having somewhat smaller pores. This methodology avoids the resistance increase penalty of modifying a membrane and comparing its performance with the unmodified version, as exhibited in Fig. 2, thereby helping to isolate the influence of changing the surface characteristics per se on fouling. Thus, when modifying the surface of membranes to improve fouling resistance, one potentially interesting strategy would be to begin with a membrane having a nominal pore size larger than that required for a given application and applying the surface modification, thereby simultaneously increasing its fouling resistance and bringing its permeance (and rejection) to desired values. Notably, the two surface-modified PS-20 membranes, both of which had a permeance of 570 LMH/bar, showed similar or nearly identical TMP increases during fouling at all three fluxes. Furthermore, the two modified PS-20 membranes had statistically identical organic rejections to those of the unmodified PS-10 membranes. Thus, a hydrophilic membrane with the same permeance and rejection as an unmodified, hydrophobic membrane has been fabricated using a simple, aqueous-based surface modification with polydopamine. Therefore, this methodology could be useful for the modification of membranes that will be operated in constant flux crossflow mode (as are many industrial membranes [36,37]) to separate feeds containing hydrophobic solutes (like many industrial wastewater streams [43,46,48]). Membranes modified using this methodology should also be tested for performance in other ultrafiltration processes of interest, such as food processing, pharmaceutical, or bioprocessing applications [3].

4. Conclusions

PS-20 polysulfone UF membranes were modified with PDA and PDA-g-PEG hydrophilic coatings. Fouling behavior of the modified membranes was compared to that of an unmodified membrane when challenged with a soybean oil emulsion under constant flux filtration at six different fluxes. The threshold flux was estimated for the unmodified and modified membranes using a flux stepping procedure. At fluxes below the threshold flux, membranes showed a brief increase in TMP at the start of fouling, but thereafter, a very slow TMP increase at large permeated volumes. Above the threshold flux, membranes generally showed a characteristic concave up increase in TMP, indicating rapid fouling. At fluxes below the threshold flux, unmodified membranes showed the lowest TMP during fouling. PDA- and PDA-g-PEG-modified membranes exhibited transmembrane pressures higher than that of the unmodified membrane, likely due to the decreased permeance resulting from the application of the surface modifications on the membrane surface and within its porous structure. At fluxes higher than the threshold flux, the modified membranes initially exhibited transmembrane pressures greater than that of the unmodified membrane, but rapid fouling of the unmodified membrane typically resulted in the modified membranes having lower transmembrane pressures than the unmodified membrane as fouling progressed.

Modified membranes were also compared to an unmodified membrane with a similar permeance. PS-10, a polysulfone UF membrane with a smaller pore size than PS-20, was used. The polydopamine modification time of the PS-20 membrane was increased so that the permeance of the PDA- and PDA-g-PEG-modified PS-20 membranes were similar. In this scenario, where all three membranes had similar initial (pure water) permeances, the TMP of the unmodified PS-10 membrane during fouling was significantly higher than that of the PDA-modified and PDA-g-PEG-modified PS-20 membranes, which exhibited very similar behavior. When the membranes had the same initial permeance and, therefore, the same local flux through the pores at the start of fouling, the hydrophilic surface modification helped reduce fouling. Therefore, a useful strategy for developing fouling-resistant membranes may be to apply a surface modification to a membrane with larger pores than desired. The surface modification will effectively decrease the membrane pore size; furthermore, the modification may be tailored such that the post-modification membrane has a permeance that matches the desired permeance for an unmodified membrane.

Acknowledgments

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at http://dx.doi.org/10.1016/j.memsci.2013.10.037.


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