



A bioinspired fouling-resistant surface modification for water purification membranes

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ABSTRACT

Surface deposition of polydopamine, PD, using facile aqueous-based chemistry at mild reaction conditions, was accomplished on reverse osmosis, nanofiltration, ultrafiltration, and microfiltration membranes. This surface treatment not only retained much of the membranes' intrinsic pure water permeability, but also improved the fouling resistance of polypropylene microfiltration (MF), poly(tetrafluoroethylene) MF, poly(vinylidene fluoride) MF, poly(arylene ether sulfone) ultrafiltration (UF), polysulfone UF, polyamide (PA) nanofiltration, and PA reverse osmosis membranes, as measured using oil/water emulsion filtration. To demonstrate scalability of this approach, PD was applied to, and improved the fouling resistance of, membrane modules. Following PD deposition, membranes could be further modified by grafting fouling-resistant macromolecules, such as poly(ethylene glycol), to further improve fouling resistance of MF membranes.

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1. Introduction

A pressing demand for compact, simple, energy-efficient water purification technologies has driven development of polymeric membranes that are widely used, for example, in applications such as desalination and to augment/intensify performance of traditional wastewater purification technologies, such as membrane bioreactors [1–3]. New opportunities, related to the purification of produced water, a byproduct of oil and gas exploration [4,5], may further extend the use of membranes for water purification [6,7].

Polymeric micro- and ultra-filtration (MF and UF, respectively) membranes are typically composed of robust hydrophobic polymers that are often highly prone to organic contaminant adsorption (e.g., proteins, natural organic matter, oily wastewater emulsions, and bacteria) due to favorable interactions between the membrane surface and the foulant [3]. Interfacially polymerized polyamide reverse osmosis (RO) and nanofiltration (NF) membranes are typ-

ically more hydrophilic than their MF and UF counterparts, but they are also prone to organic fouling [8–10]. As a result, strategies required to combat membrane fouling, such as pretreatment flocculation, aggressive and frequent chemical cleaning of membranes, and ultimately membrane replacement, increase product water cost [1,3]. Membrane surface modifications, therefore, have been identified as an attractive route to reduce favorable membrane surface-foulant interactions, thereby reducing fouling and enhancing membrane longevity and performance.

However, many surface modification techniques have limitations. For example, some polymeric membrane materials, such as poly(tetrafluoroethylene) (PTFE), are difficult to render fouling-resistant using typical surface modifications. Examples of surface modifications aimed at reducing fouling include thin-film coatings [10], self-assembled monolayers [11], and polymeric grafting by chemical treatment (e.g., UV or plasma treatment) [12–14]. The application of thin-film and self-assembled coatings usually decreases water permeability due to the presence of a thick, mass transfer resistant polymer layer. UV-grafting is membrane-specific, and plasma treatment may be difficult or expensive to apply in a manufacturing environment. Moreover, these techniques can typically only be applied prior to placing membranes into modules. Additionally, such membrane modifications do not address fouling of spacers or other wetted components in membrane modules, and fouling of these components can also decrease membrane module performance [15].

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This study describes a fouling-resistant modification of membranes, in both flat sheet and module form, using a dopamine-based biomimetic adhesive [16]. Previous research on biomimetic adhesives (i.e., “bioglue”) focused on 3,4-dihydroxy-L-phenylalanine, which can be deposited on a variety of substrates, including metals, ceramics and polymers [16–19]. This approach has been applied to prepare biofouling-resistant polymer coatings and to incorporate biofunctional groups in therapeutic and diagnostic nanoparticles [20]. A related compound, dopamine (4-(2-aminoethyl)benzene-1,2-diol), has been reported to deposit onto a wide variety of substrates when oxidized in the presence of oxygen in aqueous solution at basic pH (i.e., pH ~8.5) in the presence of Tris buffer [16,21–23]. The resulting surface modification layer, called polydopamine (PD) in the literature, is speculated to mimic foot protein 5 (Mefp-5) of *Mytilus edulis* by incorporating two chemical groups (catechols and amines) prevalent in Mefp-5, which is a key component of *M. edulis*’ adhesive plaque [16]. The detailed chemical structure of PD is still a subject of investigation, with recent studies suggesting it is a supramolecular aggregate rather than a covalently coupled polymer [24]. Nevertheless, deposition of PD can render even highly hydrophobic surfaces hydrophilic, which may be useful in improving the fouling resistance of, for example, membrane surfaces because increases in surface hydrophilicity have been linked to increases in membrane fouling resistance [25]. Furthermore, PD films were used as a versatile immobilization platform to covalently anchor poly(ethylene glycol) (PEG) on surfaces [16]. PEG is widely used to improve the hydrophilicity and biocompatibility of surfaces, including membrane surfaces [26]. PEG chains have a large excluded volume in water, with a Flory–Huggins interaction parameter ranging between 0.4 and 0.5 [27]. It is speculated that the coordinated water molecules around PEG chains create a hydration shell, allowing PEG grafts to render surfaces resistant to foulant adsorption [12].

PD surface deposition has found numerous uses in a broad range of fields. For example, it has been used to immobilize DNA onto surfaces [21], create patterned alternating superhydrophobic/hydrophilic surfaces [22], and improve biocompatibility of materials [23]. The use of PD in the membrane field has also been growing. For example, membranes made from PD have been proposed for both dehumidification [28] and pervaporation [29,30]. Additionally, deposition of PD onto membrane surfaces reportedly helps anchor atom transfer radical polymerization (ATRP) initiators to those surfaces, permitting facile growth of other polymers from the surfaces of such membranes [31]. Pure water flux and surface characterization of hydrophobic membranes modified with polydopamine were also reported [32]. Heparin has been conjugated to polyethylene porous membranes and the modified membranes were tested for hemocompatibility via platelet adhesion studies [33]. Recently, deposition of a related molecule, poly(3,4-dihydroxy-L-phenylalanine), or poly(L-DOPA), onto RO membranes has been reported to improve protein fouling resistance [34]. We have previously reported an overview of fouling resistant properties of PD [35] and the use of PD coatings on membrane support structures to enhance forward osmosis transport properties [36].

This report describes the modification of membranes, in both flat sheet and module form, using PD deposition and PD deposition followed by PEG-NH₂ grafting to improve fouling resistance of the membranes when filtering oil/water emulsions [37]. The modifications were performed under mild aqueous conditions, were not membrane material-specific, and could be applied to membranes either prior to or following assembly into modules. When applied to membrane modules, this surface treatment has the potential to modify all wetted parts of the module (e.g., spacer and tubing), not just the membrane surface itself. PD deposition was used to modify polypropylene (PP) microfiltration (MF), PTFE MF, poly(vinylidene fluoride) (PVDF) MF, poly(arylene ether sulfone) (PES)

Table 1
Membranes used in this study.

Membrane polymer	Manufacturer (product designation)	Pore size	Study ID
Polyamide	Dow (XLE RO)	N/A	XLE RO
Polyamide	Dow (NF-90)	N/A	NF-90
Polysulfone	GE (A1 support)	~100 kDa MWCO	PSf A1 UF
Polysulfone	Sepro (PS-20)	~20 kDa MWCO	PS-20 UF
Polyethersulfone	Sepro (PES-30)	~20 kDa MWCO	PES UF
Poly(vinylidene fluoride)	Millipore (GVHP)	0.22 μm	PVDF MF
Poly(tetrafluoroethylene)	GE (F02LP)	0.22 μm	PTFE MF
Polypropylene	GE (M01WP)	0.1 μm	PP MF

ultrafiltration (UF), polysulfone (PSf) UF, polyamide (PA) nanofiltration, and PA RO membranes. Compared to their unmodified counterparts, fouling resistance, as measured using a dynamic oil-in-water emulsion filtration, of modified membranes was improved for nearly all membranes studied.

2. Experimental

2.1. Materials

Dopamine hydrochloride, Trizma hydrochloride, sodium hydroxide, and sodium chloride were purchased from Sigma Aldrich (St. Louis, MO, USA) and used as received. Dow Water Solutions (Edina, MN, USA) kindly provided flat-sheet XLE reverse osmosis (XLE RO) and NF-90 nanofiltration (NF-90) membranes. GE Water and Process Technologies (Minnetonka, MN, USA) kindly provided ultrafiltration polysulfone membranes (PSf A1 UF) with a nominal molecular weight cutoff of 92.5 kDa [25]. Polypropylene (PP MF, Cat. #M01WP, average pore diameter of 0.1 μm) and PTFE (PTFE MF, Cat. #F02LP, average pore diameter of 0.22 μm) microfiltration membranes were purchased from GE Water and Process Technologies. Poly(vinylidene fluoride) (PVDF MF, average pore diameter of 0.22 μm) microfiltration membranes were purchased from Millipore Corp. (Cat. #GVHP, Billerica, MA, USA). Polysulfone ultrafiltration membranes (PS-20 UF) were purchased from Sepro Membranes (Cat. #PS-20 UF, Oceanside, CA, USA). Detailed information regarding membrane specifications are provided in Table 1. Methyl-terminated poly(ethylene glycol) amine (mPEG-NH₂, M_w = 5 kDa) was purchased from JenKem, USA, Inc. (Allen, TX, USA). Jeffamine M-1000 was kindly provided by Huntsman Corp. (The Woodlands, TX, USA) and was used as a cost-effective alternative to PEG-NH₂ for the module modifications. Soybean oil (Wesson) was purchased from a local supermarket, and DC193 non-ionic surfactant was purchased from Dow Corning (Midland, MI, USA).

2.2. PD and PD-g-PEG modification

Fig. 1 presents a schematic outlining the general PD modification procedure. PD deposition on all membranes was performed as described previously [35]. Briefly, membranes were initially immersed in isopropyl alcohol for at least 10 min to wet the membrane pores, then in ultrapure water (18.2 MΩ cm, produced from an in-house Millipore Advantage A10/RiOs water purification unit) for at least 30 min to exchange the alcohol in the membrane pores with water. The membrane was then taped to a glass plate and a glass ring was secured to the membrane surface. A 2 mg/mL dopamine solution (15 mM Tris-HCl, pH = 8.8 buffer) was placed in the glass ring (in contact with the membrane surface) and constantly stirred at ambient conditions. The oxidation of dopamine to form PD requires oxygen [16], so the solution was left open to air. After the desired contact time of the membrane with the dopamine

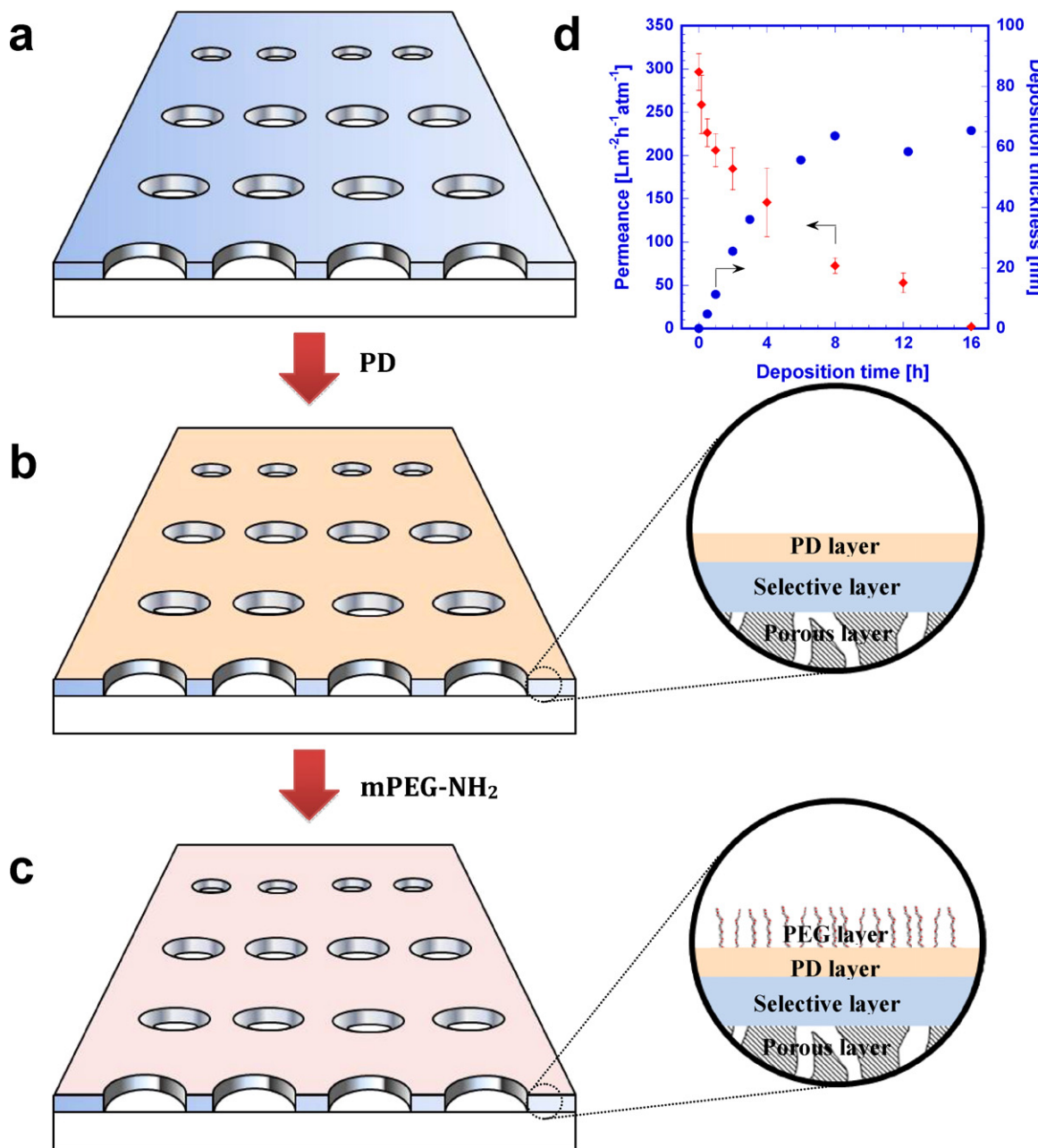


Fig. 1. Hydrophilization of microporous membranes via polydopamine (PD) deposition and grafting of poly(ethylene glycol) (PEG). (a) A hydrophobic microporous membrane, (b) a hydrophilic PD-modified microporous membrane. (c) PEG macromolecules grafted to a PD-modified microporous membrane and (d) polysulfone UF (PSf A1 UF) membrane permeance as a function of PD deposition time (♦), and PD deposition thickness on dense, nonporous polysulfone films (●), as measured using ellipsometry. (d) is adapted from a previous study [35,37]. Standard deviation (not shown) of deposition thicknesses is approximately 5% of each measured value, based on replicate trials of various samples.

solution, the modified membrane was removed from the glass plate and thoroughly rinsed under running ultrapure water. Membranes were stored in ultrapure water.

The effect of various PD deposition parameters on membrane hydraulic permeability and resistance to static protein adhesion on PVDF MF, PSf UF, and XLE RO membranes was reported by us previously [35]. Additionally, this previous study reported the grafting density of PEG-NH₂ as a function of PEG-NH₂ grafting time and PEG-NH₂ grafting solution concentration to the surface of membranes that had been coated with PD. Results from this previous study were used to guide the selection of PD deposition and PEG grafting parameters, such as dopamine/PEG-NH₂ concentrations in the modifying solution and modification duration, in this study. A

1 h PD deposition time (i.e., contact time) was used for MF membranes modified in this study; UF membranes were modified using a contact time of 45 min, and the NF and RO membranes were modified using a contact time of 30 min. These deposition times ensured that: (1) all modified membranes retained at least 80% of their respective unmodified membrane pure water flux, and (2) significant increases in membrane surface hydrophilicity (as measured by contact angle) were observed. The membranes were allowed to rinse in ultrapure water for several hours before testing or PEG conjugation.

PEG conjugation was accomplished by contacting a PD-treated membrane in a 1 mg/mL 5 kDa mPEG-NH₂ solution (15 mM Tris-HCl, pH = 8.8 buffer) at 60 °C for 1 h. The primary amine groups

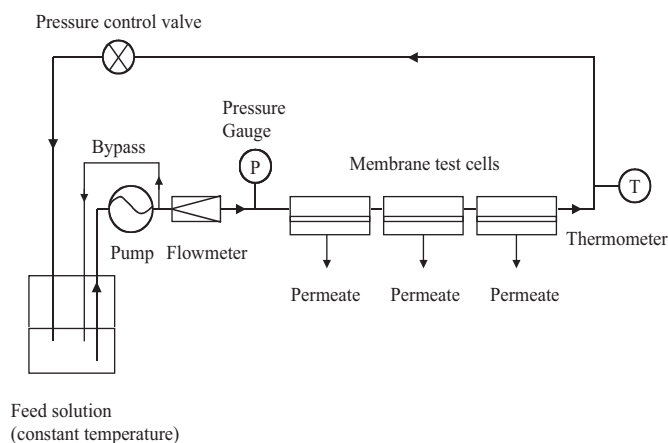


Fig. 2. NF and RO crossflow filtration system schematic. The MF and UF filtration system used a similar flow diagram; however, only one membrane test cell was used, and a peristaltic pump was used instead of a diaphragm pump.

at the termini of these PEG chains are known to react and form covalent linkages with PD; that is, PEG-NH₂ covalently grafts to the PD layer [16]. In our previous study, various PEG-NH₂ grafting parameters, and the resultant grafting densities (as measured using a highly sensitive gravimetric procedure), were reported for MF, UF, and RO membranes [35]. In contrast, if a PD-coated membrane was contacted with PEG that did not have a primary amine group, no measurable adsorption of PEG occurred [35]. Following grafting, the membrane was removed from the solution and thoroughly rinsed under running ultrapure water and stored in ultrapure water until use.

2.3. Contact angle measurements

Contact angle measurements were performed using captive *n*-decane bubbles in water, as described previously [25]. In these measurements, lower values of contact angle represent more hydrophilic surfaces. The values reported are the average and standard deviation of at least five measurements.

2.4. Emulsified oil fouling analysis

The crossflow filtration unit used to test oil fouling in NF and RO membranes was purchased from Separations Systems Technologies (San Diego, CA, USA) and was similar to those used in other studies [10,25,38,39]. A schematic of this system is shown in Fig. 2. The crossflow unit was equipped with three filtration cells, each with an effective filtration area of 7.8 cm × 2.5 cm (19.4 cm²). The system used in the NF and RO fouling employed a diaphragm pump (Wanner Hydra Cell, Minneapolis, MN, USA). To test UF and MF membranes at lower pressures, a similar system was built using a peristaltic pump (Cole Parmer, USA). The same cell used in the RO system was used in these experiments; however, the UF and MF systems were equipped with only one test cell. To test the UF membranes, a diaphragm pump head was used on the peristaltic pump motor drive to achieve higher pressures with stable flow rates. The RO and NF membranes were tested at a crossflow rate of 3.8 L/min (*Re* ~ 4900) and 10.2 atm (150 psig) transmembrane pressure difference, the MF membranes were tested at a crossflow rate of 2.0 L/min (*Re* ~ 2600) and 0.3 atm (5 psig) transmembrane pressure difference, and the UF membranes were tested at 2.1 atm (30 psig) transmembrane pressure difference and 0.8 L/min crossflow rate (*Re* ~ 1000).

The permeate of each membrane was collected in a beaker placed on an electronic balance. The balances were connected to a

computer and weight measurements were collected every 10–60 s by a Labview (National Instruments, Austin, TX) program. Membrane flux, *J*, was calculated using Eq. (1):

$$J = \frac{\Delta V}{a \cdot \Delta t} \quad (1)$$

where ΔV is the volume of permeate collected between two weight measurements, *a* is the membrane surface area, and Δt is the time between two weight measurements.

Organic rejection was calculated using the following equation:

$$R = \left(1 - \frac{C_p}{C_f}\right) \times 100\% \quad (2)$$

where *R* is rejection, *C_p* is the organic concentration in the permeate, and *C_f* is the organic concentration in the feed. *C_p* and *C_f* were measured using a Total Organic Carbon Analyzer (TOC5050, Shimadzu Corp., Japan). Salt rejection was also calculated using Eq. (2) with *C_p* and *C_f* being the salt concentrations of the permeate and the feed solutions, respectively (NaCl was added to the feed prior to RO and NF fouling studies to make the total NaCl feed concentration equal to 2000 ppm). The salt concentrations were measured using a conductivity meter (Oakton, Vernon Hills, IL, USA).

The oil/water emulsion was prepared by blending 4.5 g DC193 surfactant and 40.5 g soybean oil in 3 L of water using an industrial-sized blender (Waring LBC15, Torrington, CT) for 3 min at the blender's highest speed (~20,000 rpm) [25,39]. This mixture was then diluted to a total volume of 30 L using ultrapure water (the final organic concentration was 1500 ppm). The same emulsified oil mixture used for RO membranes was also used for UF and MF membranes, although the feed tank for the UF/MF apparatus contained 8 L of fluid, rather than 30 L.

2.5. Irreversible fouling determination

Irreversible fouling was characterized by comparing the pure water permeance of a membrane before and after a fouling experiment. Before a fouling experiment, the pure water flux of a membrane was determined at the same pressure and crossflow rate at which the fouling experiment took place (for example, at 2.1 atm and 0.8 L/min for a UF membrane). For NF and RO membranes, saltwater flux and rejection (with no organics present) were determined immediately after the pure water flux (concentrated salt water was added to the feed until the total salt concentration in the feed solution was 2000 ppm). A fouling experiment was then performed on the membranes (for the NF and RO membranes, the fouling experiment time was 24 h, for the UF and MF membranes, fouling experiments were conducted for 1 h). With the membranes remaining in the crossflow system membrane cells, after the fouling experiment, the crossflow system was flushed with ultrapure water at least three times, after which water was allowed to circulate through the system for 10 min (the rinsing cycle took a total of 1 h to complete for the NF and RO membranes and 20 min for the UF and MF membranes). The post-fouling pure water flux was recorded immediately after the rinsing cycle.

2.6. Membrane module modification and fouling

To demonstrate the feasibility of modifying a membrane module, rather than simply modifying flat sheet membrane samples, TW30-1812-36 Dow Filmtec membrane modules (along with their polypropylene module housings) were purchased from waterfilters.net. Ultrapure water was circulated through the module using a peristaltic pump for approximately 10 min before modification. Fig. 3 presents a schematic of the flow system used to modify these membrane cartridges. 400 mL of 2 mg/mL dopamine in Tris buffer (15 mM, pH = 8.8) was charged to a beaker that was

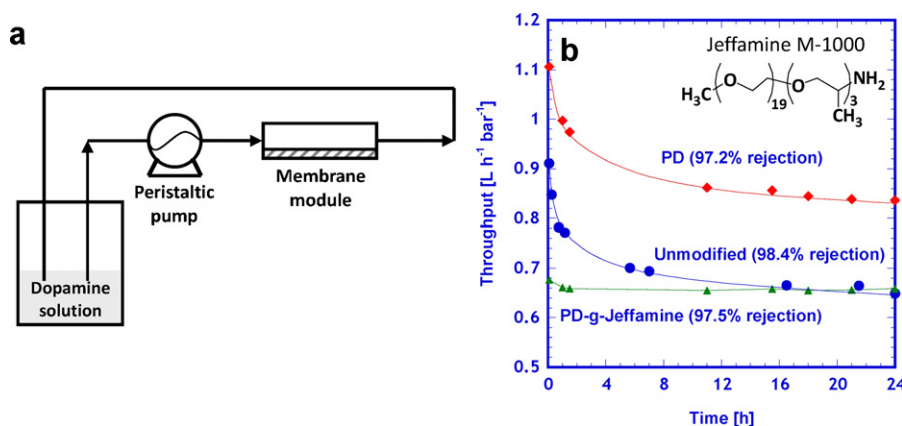


Fig. 3. PD modification and oily water fouling of membrane modules. (a) Schematic of the module modification apparatus. The module's feed and retentate ports (NPT 1/8 in.) were connected to flexible tubing which led to the beaker containing the PD solution. PD deposition was visibly present on the tubing and the membrane module after ~30 min deposition time. (b) Effect of filtration time on permeate water flow rate, normalized by the transmembrane pressure difference, for an unmodified TW30 membrane module, a PD-modified module, and a PD-g-Jeffamine-modified module filtering an oil/water emulsion. NaCl rejection values were taken at the end of the fouling experiments ($t = 24$ h).

open to the atmosphere, and this solution circulated through the module, using a peristaltic pump, at approximately 1 L/min at ambient conditions. After 30 min, the module was rinsed by circulating ultrapure water at the same flow conditions for approximately 1 h. To further modify the membrane, a 0.25 wt% Jeffamine solution in water was circulated through the module for 30 min at 50 °C, after which the module was rinsed using room temperature ultrapure water at the same flow conditions for approximately 1 h. Jeffamine is a block copolymer consisting of PEG and poly(propylene glycol), with PEG being the dominant component (see structure in Fig. 3b). Like PEG-NH₂, Jeffamine has a primary amine on one end of its chain and therefore covalently grafts to a PD-treated membrane surface. Compared to PEG-NH₂, Jeffamine is much more cost-effective, which may be important in using such modifications for large scale applications.

Both PD- and PD/Jeffamine-modified modules were tested in a fashion similar to that of the flat-sheet membranes. The flat sheet cells were removed from the crossflow system and replaced with two modules, connected in series. The feed and retentate pressures were monitored to account for any pressure loss through the modules. Before a fouling experiment, the pure water flux of the modules was determined at a transmembrane pressure difference of 3.4 atm and 3.8 L/min feed flowrate. Salt water flux and rejection (with no organics present) were determined immediately after the pure water flux (concentrated salt water was added to the feed until the total feed concentration of salt was 250 ppm). A fouling experiment was then performed using the 1500 ppm emulsified oil mixture described earlier with a total NaCl concentration of 250 ppm. After the fouling experiment, the crossflow system was flushed with ultrapure water at least three times, after which water was allowed to circulate through the system for 1 h. The post-fouling pure water flux was recorded after the rinsing cycle.

3. Results and discussion

Water transport through PD-modified PSf UF membranes (original pore size: ~11 nm) [25] depends on the deposition thickness, which was measured and previously reported for thin, non-porous polysulfone films using ellipsometry (Fig. 1d) [35]. Although large decreases in flux are observed at very long dopamine contact times, because long deposition times lead to a thick PD deposition layer on the membrane surface and, presumably, in the pores, flux decreases only modestly at short deposition times because PD forms very thin coatings (at most a few nm) at low solution contact

time (e.g., 30 min). Additionally, the hydrophilicity of the initially hydrophobic PSf membrane increased substantially after only short (<1 h) PD deposition times [35]. Thus, even short deposition times enhance the hydrophilicity of these membranes due, presumably, to the deposition of conformal, nanometer-thick layers of PD on the membrane surface and in the membrane pore structure. Consequently, the results reported here have focused on short (i.e., 1 h or less) deposition times, since such short deposition times are long enough to deposit enough PD to enhance fouling resistance but short enough to avoid a highly deleterious effect on membrane flux. Table 2 presents pure water permeance values for all modified and unmodified membranes studied. For PD-modified MF membranes, which have larger pores than UF membranes, modified via 60 min immersion in PD solution, the pressure-normalized water fluxes of PD-modified and unmodified membranes are essentially equal, presumably because the addition of the PD layer decreases the overall pore size by a negligible amount. However, the hydrophilicity of the membranes is being altered due to PD deposition, so even if there were some modest decrease in pore size, it may have been effectively offset by making the membrane pore structure more hydrophilic, which would have tended to promote flow through channels that might have been inaccessible to water with the membrane in its native hydrophobic form. Indeed, such effects have recently been reported by Arena et al., where modification of an RO polysulfone support membrane was found to markedly increase the flux of the membrane in forward osmosis experiments [36]. Interestingly, highly hydrophobic MF membranes (i.e., PP and PTFE) exhibited higher pure water flux (by ~5–30%) following PD modification [35,37]. This PD-enhancement in water transport may be linked to the membranes' increased wettabil-

Table 2

Pure water (non-fouled) permeance for unmodified, PD modified, and PD-g-PEG modified membranes. Membranes were modified using a 60 min PD deposition and a 60 min PEG-NH₂ grafting time unless otherwise noted.

	Unmodified (L m ⁻² h ⁻¹ atm ⁻¹)	PD modified (L m ⁻² h ⁻¹ atm ⁻¹)	PD-g-PEG modified (L m ⁻² h ⁻¹ atm ⁻¹)
PTFE MF	6500	8300	7500
PP MF	2400	2900	2900
PVDF MF	5300	4900	4800
PS-20 UF	1300	690	430
PES UF	300	270	150
NF-90	10.5	8.0 ^a	2.7 ^a
XLE RO	8.6	7.0 ^a	3.0 ^a

^a 30 min PD deposition time used.

Table 3

Captive *n*-decane-in-water bubble contact angles. A 30 min PD deposition time was used for all modified membranes.

Sample	Contact angle (°)	
	Unmodified	PD modified
XLE RO	45 ± 3	36 ± 4
NF-90	49 ± 2	40 ± 3
PP MF ^a	81 ± 2	33 ± 5
PTFE MF ^a	120 ± 6	50 ± 3
PVDF MF ^a	31 ± 1	31 ± 4

Note: PSf A1 UF was measured in a previous study and had unmodified and PD modified contact angles of 109° and 49°, respectively.

^a Air-in-water bubbles were used (*n*-decane would readily absorb into the porous membrane structure of the unmodified membranes). Values are the average of at least five replicate trials, and the standard deviation of these trials is also reported.

ity, which increases the accessibility of small pores, which may have been too hydrophobic to wet (and transport water) otherwise. A more complete study of the influence of PD deposition and PD/PEG grafting on pore size in MF membranes will be reported in the future.

The small loss of pure water flux at low deposition times suggests that PD deposited conformally on the membrane surface and pore structure rather than bridging and blocking pores. As indicated previously, surface hydrophilicity was enhanced at even very short modification times [35]. The wettability of a membrane surface is reported to play a significant role in governing fouling resistance to, for example, emulsified oil droplets, proteins, bacteria, activated sludge in bioreactors, and other solutes [40]. In this regard, all polymer membranes considered, except for PVDF MF membranes, exhibited an increase in surface wettability following PD modification (cf. Table 3). PVDF MF membranes were highly hydrophilic before PD deposition, probably due to the presence of hydrophilic additives in the PVDF.

Oil emulsion fouling is a key challenge in membrane-based purifications of a variety of wastewaters, including bilgewater aboard naval vessels, metalworking wastewater, and produced water from oil and gas recovery [25,41]. Based on our oil emulsion fouling experiments, which employed a synthetic vegetable oil/non-ionic surfactant emulsion, regardless of membrane type, PD-modified and most PD-g-PEG membranes exhibited higher flux during fouling experiments than their unmodified counterparts. For example, after 1 h of crossflow filtration of an oily water emulsion, the water flux of a PD-modified PTFE MF membrane is 20% higher (103 L m⁻² h⁻¹) than that of an unmodified membrane (85 L m⁻² h⁻¹) and exhibited higher organic rejection (Fig. 4a). Further improvements in membrane flux are achieved when a PEG ad-layer is present. In this case, the water flux through a PD-g-PEG PTFE MF membrane is 56% higher (120 L m⁻² h⁻¹) than that of an unmodified membrane after 1 h of filtration. Relative to their unmodified analogs, PES UF, PS-20 UF, PVDF MF, and PP MF all showed improved water flux and higher organic rejection following surface modifications (Fig. 4b–e). Additionally, all modified MF and UF membranes generally had higher organic rejection than their unmodified analogs.

The flux of a PD-modified PS-20 UF membrane is 125% higher than that of an unmodified membrane after 1 h of oil emulsion filtration and exhibited similar organic rejection (Fig. 4b). A small additional improvement in membrane flux, relative to the PD-modified membrane, is observed when PEG is added to the polydopamine layer. For example, after 1 h of filtration of an oily water emulsion, the PD-g-PEG-modified PSf UF flux is 145% higher than that of an unmodified membrane. Behavior similar to this, although modest when compared to PS-20 UF membranes, was also seen in the modified PES UF membranes, where PD-modified and PD-g-PEG PES UF membranes improved oil emulsion filtration flux

approximately 35% compared to their unmodified counterpart after 1 h of filtration (cf. Fig. 4c).

For both the PES and PS-20 UF membranes, the PD and PD-g-PEG membranes show very similar fluxes; this result is somewhat surprising given the oil emulsion filtration flux improvement measured between PD and PD-g-PEG MF membranes (Fig. 4a, d and e). This result is likely due to the high added mass transfer resistance of the PEG ad-layer, whose hydrodynamic diameter is a significant fraction of the nominal UF membrane pore diameters used in this study (the UF MWCO values are approximately 20 kDa, whereas the PEG-NH₂ M_w is 5 kDa). Therefore, the PEG molecules may constrict the pores of the PES and PS-20 to a much larger degree than the larger MF pores, which led to a larger effective PEG ad-layer mass transfer resistance in the UF membranes. For example, the pure water flux ratio of a non-fouled PD-g-PEG modified to a PD-modified PES UF membrane is 0.6, whereas the same ratio between a PD-g-PEG modified and a PD-modified PP MF membrane is 1.0. Optimization of PEG attachment conditions to reduce its mass transfer resistance while maintaining good anti-fouling characteristics was reported previously.

The PD-modified PVDF MF membrane exhibited a similar flux to the unmodified PVDF MF membrane (Fig. 4d). However, the PD-modification increased the organic rejection. A 50% improvement in flux, coupled with a further increase in organic rejection, was observed in the PD-g-PEG modified PVDF MF membrane. For MF membranes in general, unlike in the UF, RO, and NF membranes, the PEG ad-layer did not lead to a strong increase in mass transfer resistance, because the pure water flux of PD-modified and PD-g-PEG PVDF membranes were approximately the same and ~90% of the unmodified PVDF MF membrane's flux (Table 2). The PEG did not increase the mass transfer resistance presumably because its Stokes radius (~1.9 nm) is very small compared to the membrane's average pore size (220 nm), leading to very little pore constriction. PP MF membranes (Fig. 4e) yielded similar results to the PVDF MF membranes, with PD-modified membranes having slightly higher organic rejection and flux than an unmodified PP MF membrane after 1 h of oil emulsion filtration and PD-g-PEG having ~100% higher flux than the unmodified PP membranes. Higher organic rejection is also observed in the PD-g-PEG membrane.

Highly hydrophobic MF membranes (PP MF and PTFE MF) actually exhibited a non-fouled pure water flux increase when modified by PD and PD-g-PEG (see Table 2). For example, the pure water flux ratio of a non-fouled PD-modified to an unmodified PP MF membrane was 1.15, with PD-modified and PD-g-PEG PP MF membranes having similar fluxes. For PTFE MF membranes, the PD-modified to unmodified flux ratio was 1.3 and the PD-g-PEG to unmodified membrane flux ratio was 1.15. PD deposition would not be expected to lead to a flux increase through damage to the membrane or its porous structure. Therefore, the most likely explanation of increased flux in these MF membranes is that PD increased the wettability of the membrane porous structure which, when coupled with a negligible reduction in pore size associated with the deposition, allowed more pores to wet and contribute to the overall membrane flux.

PD-modified XLE RO and NF-90 membranes also achieved 30–50% higher flux than an unmodified membrane after 1 h of oil emulsion filtration (Fig. 4f and g), and the PD-g-PEG RO and NF membranes exhibited no flux decline, and therefore no fouling, during filtration. Furthermore, all modified membranes exhibited an increase in irreversible fouling resistance (Fig. 5), which enhances cleaning cycle efficiency and lowers overall operating costs. For example, PD-g-PEG RO membranes recovered 100% of their original water flux after simply rinsing in water following the fouling experiment.

For the RO and NF membranes considered, surface modification with PD led to enhanced flux, relative to that of the native

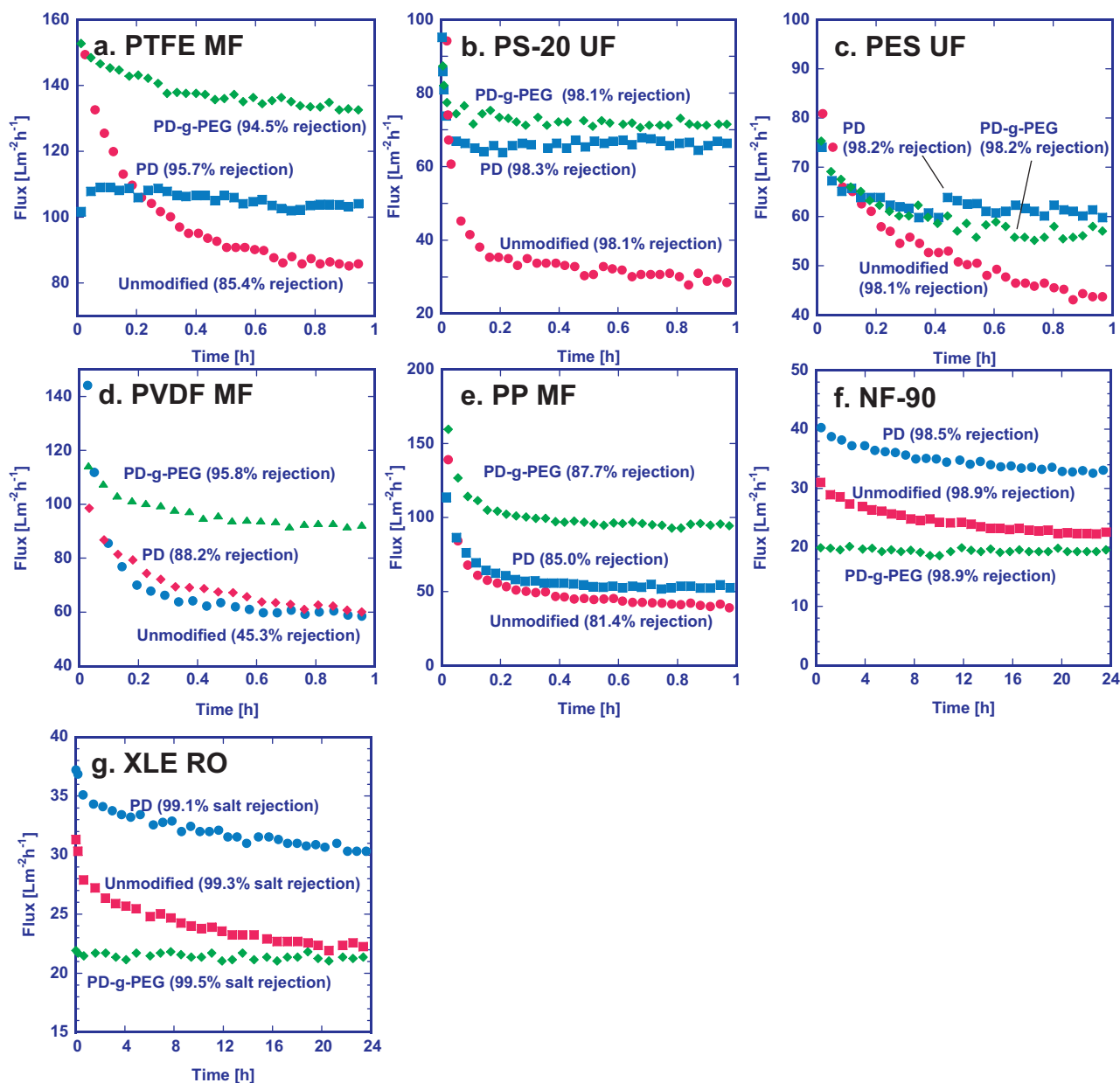


Fig. 4. Oily water fouling behavior of flat-sheet membranes. Oil emulsion filtration membrane flux versus time using unmodified, PD-modified, and PD-g-PEG-modified (a) PTFE MF, (b) PS-20 UF, (c) PES UF, (d) PVDF MF, (e) PP MF, (f) NF-90, and (g) XLE RO membranes. Organic rejection values reported for (a)–(e), NaCl rejection values reported for (f) and (g). Rejection values were taken at the end of fouling experiments (i.e., $t = 1$ h for (a)–(e), and $t = 24$ h for (f) and (g)).

membrane, during the fouling experiments. However, when PEG was attached to these membranes (i.e., PD-g-PEG samples), the additional PEG layer provided sufficient mass transfer resistance that it lowered the flux so that it was below that of the native membranes, even during fouling experiments (see Fig. 4f and g). The pure water flux of PD-g-PEG NF and RO membranes was also considerably reduced, relative to that of the native unmodified membranes and the PD-modified membranes (see Table 2).

During oil/water emulsion filtration, the flux of the PD-g-PEG membranes did not change in time (see Fig. 4f and g), suggesting good fouling resistance, but the flux was low from the very beginning of the experiment due to the large mass transfer resistance imposed by the PEG grafting. For the NF and RO membranes, therefore, the fouling results are improved by PD modification. Following PD-g-PEG modification, the membranes do not exhibit fouling, but the flux is low, so this modification is not as useful as it is on, for

example, the MF membranes, where the PD-g-PEG samples have higher flux during fouling experiments and exhibit less fouling than the unmodified or PD-modified membranes.

When filtering a 2000 ppm NaCl solution (without any organic foulants), the PD-modified NF and RO membranes exhibited slightly higher salt rejection than their unmodified analogs. For example, an unmodified NF-90 membrane had a NaCl rejection of 95.4% and a 30 min PD-modified NF-90 membrane had a rejection of 96.7% (Fig. 6a). A slight increase in rejection was also observed in the PD-modified XLE RO membranes (Fig. 6b). PD-g-PEG modified membranes had even higher initial rejections (98.7% for NF membranes, 98.9% for RO membranes). However, when an oil/water emulsion was added to the feed, the NaCl rejection of both modified and unmodified membranes increased, with the unmodified membranes exhibiting higher rejection than the PD-modified membranes. This phenomenon is most likely caused by

Table 4
Initial salt rejection and irreversible fouling data for TW30 unmodified and modified modules.

Module type (TW30)	250 ppm NaCl rejection (%)	Water throughput (L h ⁻¹ bar ⁻¹)		P_{AF}/P_{BF}
		Before oil/water filtration, P_{BF}	After oil/water filtration, P_{AF}	
Unmodified	96.5	1.65	0.73	0.44
PD	96.1	1.42	0.96	0.68
PD-g-Jeffamine	96.9	0.78	0.77	0.99

Note: The salt rejection was measured with no organics in the feed solution.

the higher amount of oil fouling of the unmodified membranes. More extensive fouling leads to higher mass transfer resistance, which, in turn, leads to higher membrane rejection. Oily water fouling was shown to increase NaCl rejection in RO membranes in a previous study [10]. Furthermore, NF membranes exhibited increases in rejection when PEG molecules were grafted to their surface [42,43]. As expected, organic rejection was high (>99.9%; the permeate organic concentration was lower than the detection limit of our total organic carbon analyzer).

A significant benefit of this approach is its ease of application to entire membrane modules, not only flat membrane sheets. Spiral wound RO modules with housings were modified by circulating a PD solution on the feed side of the module (Fig. 3a). Further modification using Jeffamine M-1000 polyetheramine was performed to PEGylate the membrane surface and all wetted components. Fig. 3b presents emulsified oil fouling of unmodified, PD-modified, and PD-g-Jeffamine modified TW30 membrane modules. In a similar fashion to flat sheet RO membranes, the throughput of the PD-modified module is approximately 30% higher than that of an unmodified membrane module after 1 day of operation. The PD-g-Jeffamine modified module had a lower starting flux than the other two membrane modules, but exhibited persistent fouling resistance (Table 4), similar to the results observed in the flat sheet NF and RO membrane tests (see Fig. 4f and g). Moreover, PD-g-Jeffamine modified modules showed higher salt rejection (without organics present in the feed) than unmodified modules, but the unmodified modules exhibited slightly higher rejection after one day of emulsified oil filtration as a result of fouling increasing the membrane's mass transfer resistance.

No PD delamination or leaching was detected, as measured by UV spectroscopy, after approximately 4 days of rinsing a PD mod-

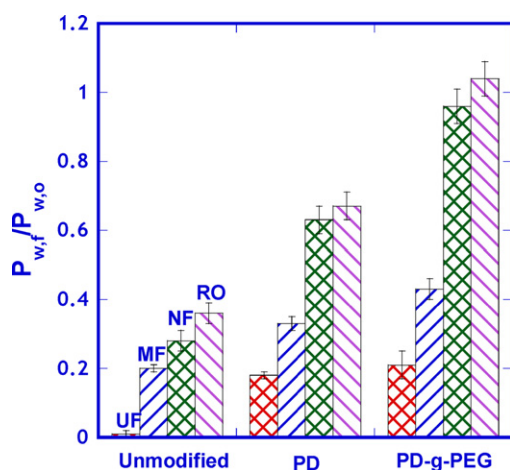


Fig. 5. Irreversible fouling of selected membranes. Irreversible fouling resistance of flat-sheet PS-20 UF, PTFE MF, NF-90, and XLE RO membranes. P_{wf} is the pure water permeance following the filtration experiments in Fig. 4, and $P_{w,o}$ is pure water permeance before the filtration experiments. After the fouling experiments, all membranes were rinsed by circulating ultrapure water through the crossflow system before measuring P_{wf} . $P_{wf}/P_{w,o} = 1$ is indicative of completely reversible fouling (i.e., the membrane's initial pure water flux is completely recovered after a pure water rinse). Error bars are the standard deviation of replicate trials.

ified TW30 RO membrane module in water, although the coating layer was still visibly present on wetted parts of the membrane module (see Fig. S1c in Supporting information). This negligible leaching has led to the modified modules being certified for drinking water use by the National Sanitation Foundation (NSF standard 61). Furthermore, no significant surface discoloration or change in wettability occurred even after sonicating a PD-modified PSF UF membrane for 10 min in 3 M HCl solution. PD's excellent adhesion may be due, at least in part, to the extraordinary strength reported for the catechol-substrate physical bond [44].

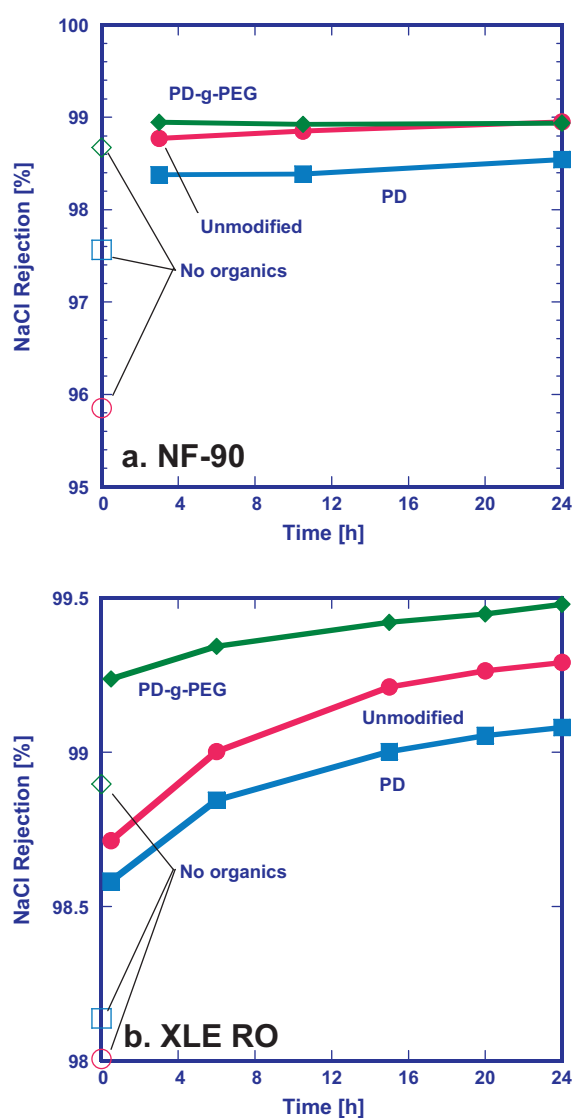


Fig. 6. NF and RO salt rejection. NaCl rejection before oil emulsion filtration (open symbols) and during an oil emulsion filtration (filled symbols) for: (a) NF-90 and (b) XLE RO membranes.

4. Conclusions

PD was deposited on MF, UF, NF, and RO membranes using an aqueous-based surface modification strategy. PD deposition was found to improve the oil/water fouling resistance of all membranes studied. PD-modified membranes were further functionalized using poly(ethylene glycol) to promote further fouling resistance, particularly in MF membranes. PD-based membrane modifications were also readily scalable, as membrane modules could be modified by circulating a dopamine solution through the module. As a result, PD-based membrane modifications offer a promising platform to improve the fouling resistance of membranes operating in large-scale water purification facilities.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.memsci.2012.04.021>.

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