Sacrificial polyelectrolyte multilayer coatings as an approach to membrane fouling control: Disassembly and regeneration mechanisms

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Abstract

This study evaluates polyelectrolyte multilayers (PEMs) as sacrificial separation layers on polysulfone ultrafiltration (UF) membranes. Exposure to surfactants and a swing in pH can disassemble PEMs by disrupting non-ionic and electrostatic bonds within the PEM and between the PEM and the support. Trends in frequency and dissipation in quartz crystal microbalance studies confirm layer-by-layer (LbL) adsorption of PEMs on the quartz crystal and subsequent PEM removal in response to acid/base treatment. After disassembly of PEMs on UF membranes, water permeability increases and methylene blue rejection decreases, in some cases reaching values close to those for pristine ultrafilters. PEM removal occurs even with fouled membranes. After fouling by aqueous solutions of bovine serum albumin and alginate, the PEM disassembly via exposure to acid, base and surfactant results in a 99% decrease in the hydraulic resistance of the PEM (compared to the unfouled PEM) and, on average, more than 80% recovery of pure water permeability (compared to an uncoated UF membrane). Repeated cycles of PEM disassembly and readsorption give stable water permeabilities and methylene blue rejections for the coated membranes.

Keywords: polyelectrolyte multilayers; fouling; sacrificial films; disassembly; regeneration
1. Introduction

Membrane-based separations have made remarkable inroads against competing technologies in applications such as water desalination and reuse, and gas separations [1, 2]. Significant advantages of membrane processes may include relatively low energy consumption and a small environmental footprint [3, 4]. Nevertheless, membrane fouling remains a major challenge that increases the energy costs for separations and limits membrane lifetime [5]. Managing membrane fouling requires substantial knowledge and experience, especially because fouling is often feed-specific. In most applications, periodic hydraulic cleaning limits short-term fouling, whereas more expensive chemical cleaning partly removes the hydraulically-irreversible fraction of the added resistance due to foulants [5-7]. With the increasing importance of water reuse and reliance on low-quality water sources of high fouling propensity, development of new cleaning approaches and anti-fouling membrane materials becomes even more important [8-12]. Unfortunately, the impact of surface morphology control and chemical modifications that improve fouling resistance will not endure after formation of the first fouling layer on the membrane surface. Ultimately, once chemically irreversible fouling exceeds a certain level, membrane replacement is required.

This work investigates the possible use of PEMs as sacrificial coatings that a membrane may shed along with foulants that cannot be removed by hydraulic cleaning. LbL assembly of PEMs is attractive for coating membranes due to its conceptual simplicity and control over film thickness, composition and surface charge [13, 14]. Thus, a
number of studies investigated PEMs as membrane skins for nanofiltration [15-21], reverse osmosis [22, 23], forward osmosis [24] and pervaporation [25]. As with other specially designed antifouling surfaces, however, PEMs may temporarily resist adhesion of feed components, but eventually a fouling layer will coat the surface and negate antifouling properties. Thus, we desire to develop conditions for removing PEMs from porous substrates prior to adsorption of a new PEM to create a fresh membrane surface. In this regard, previous studies employed surfactants [26-28] as well as changes in pH [21, 22], temperature [29] and ionic strength [30, 31] to disassemble PEMs. Hydrolysis [32], solvent exchange [33], electrochemical methods [34] and enzymes [35] may also alter PEMs, but such methods may be difficult to apply in membrane modules.

Previously, we studied the feasibility of regeneration of (PSS/PAH)$_4$ and (PSS/PAH)$_{4.5}$ PEMs fouled by SiO$_2$ colloids. To regenerate a PEM with a layer of colloids adsorbed on its surface, we employed a three-step procedure: (i) backflushing with deionized (DI) water, (ii) soaking in a buffer solution at pH 10, and (iii) PEM re-deposition by the LbL method [16]. Although the regenerated membranes showed permeabilities similar to those of the initial PEM-modified membranes, the rejection was 50% lower than that with the initial PEM. Apparently, residual polyelectrolytes or foulants decreased rejection, perhaps by creating film defects, but they did not add significant hydraulic resistance.
This study aims to develop PEM design and disassembly approaches that afford membrane regeneration for nearly complete recovery of flux and rejection after hydraulically-irreversible fouling. We assembled PEMs using poly(vinylsulfonic acid, sodium salt) (PVS), poly(sodium 4-styrenesulfonate) (PSS), deprotonated poly(acrylic acid) (PAA) and deprotonated poly(methacrylic acid) (PMAA) as polyanions; and poly(diallyldimethylammonium chloride) (PDADMAC), poly(allylamine hydrochloride) (PAH) and protonated chitosan (Chi) as polycations. Quartz crystal microbalance with dissipation monitoring (QCM-D) was employed to examine PEM assembly and disassembly kinetics on gold or silicon oxide surfaces, whereas reflectance FTIR spectroscopy demonstrated film removal from model spin-coated polyethersulfone substrates. Filtration studies confirmed that PEM-removal approaches restore membrane flux and rejection to values close to those of uncoated UF support membranes. Sequential acid/base and surfactant treatments effectively removed PEMs to give a membrane ready for adsorption of a new polyelectrolyte (PE) coating. Finally, we investigated whether removal methods are effective in disassembling PEMs fouled with bovine serum albumin (BSA) and alginate.
2. Materials and Methods

2.1. Reagents

PVS (25 wt.% in H₂O); PSS (Mw~70,000); PAA (Mw~1,800); PMAA (Mw~9,500, sodium salt solution, 30 wt.% in H₂O); PDADMAC (Mw~100,000-200,000, 20 wt.% in H₂O), PAH (Mw~15,000), Chi (medium Mw), BSA, alginate, calcium chloride dihydrate (CaCl₂·2H₂O) and sodium chloride (NaCl) were purchased from Sigma-Aldrich. HCl solution (36.5% HCl in water, EMD, Millipore), NaOH (Macron) and Triton X-100 (Sigma-Aldrich) were used to prepare PEM disassembly solutions. Ethylenediaminetetraacetate (EDTA, Sigma-Aldrich) and sodium dodecyl sulfate (SDS, Roche) served as components of aqueous cleaning solutions for NF 270 membranes [36]. DI water used in all experiments was supplied by a commercial ultrapure water system (Lab Five, USFilter) equipped with a terminal 0.2 µm microfilter (PolyCap, Whatman Plc); the water resistivity was greater than 16 MΩ·cm.

2.2. Quartz crystal microbalance with dissipation (QCM-D) measurements

A four-channel quartz crystal microbalance with dissipation (QCM-D, Q-Sense E4) was employed for real-time studies of PEM adsorption and removal processes. Silicon oxide- or gold-coated quartz crystals with a resonance frequency of 4.95 MHz ± 50 kHz served as substrates for PEM deposition. Crystals were cleaned according to standard protocols provided by the manufacturer (see Supplementary Content (SC) file, section
S1). PEMs were prepared via the LbL technique by flowing alternating polyanion and polycation solutions through the QCM-D chamber using a peristaltic pump (Ismatec IPC-N 4). Four bilayers were deposited for each PE pair by pumping 1 g/L PE solutions in DI water through the QCM-D chamber and subsequently rinsing with DI water after each PE deposition step at a flow rate of 0.15 mL/min. PE deposition and rinsing steps were allowed to proceed until QCM frequency and dissipation reached constant values. PE solutions contained no added salt, and the pH of the PEM solutions and the pKₐ values (when known) of the corresponding PEs were as follows: PAA (pH=3.2, pKₐ=4.2-6.5 [37, 38]), PMAA (pH=9.2, pKₐ=5.5 [39]), PSS (pH=5.4, pKₐ≈1.0 [40]), PVS (pH=6.5), Chi (pH=6.0, pKₐ=6.5 [41]), PAH (pH=4.0, pKₐ=8.5-9.5 [38, 40]), PDADMAC (pH=4.7).

PEMs were then removed from the substrate by exposing them to HCl (1 M) or NaOH (1 M) solutions or both. The solutions were pumped through the chambers until the QCM frequency and dissipation reached constant values. All frequency shifts and dissipation factors are based on data recorded for the 5th overtone.

2.3 PEM adsorption on membranes and filtration tests

PEMs were adsorbed on PES UF membranes (Pall) with a molecular weight cutoff (MWCO) of 30 kDa. A small subset of tests was also done using PES membranes with a MWCO of 10 kDa. A PES membrane was placed in a stirred dead-end filtration cell (Sterlitech, membrane area of 14.6 cm²), and DI water was filtered through the membrane at 5 bar until a steady-state flux was achieved. A total of 15 mL of PE
solution (1 g/L) was then poured into the cell and stirred for 5 min. The solution was discarded and the membrane was rinsed thoroughly with DI water. The PE-adsorption and rinsing steps were repeated to form four PE bilayers on the PES substrate surface. PE solutions contained no added salt and the pH of the solutions was not adjusted.

In filtration experiments, membrane coupons were first compacted by filtering DI water at a transmembrane pressure of 5 bar until a steady permeate flux was attained. The permeate flux was calculated based on the time-derivative of the permeate mass, which was measured by collecting the filtered water on a digital balance (AV8101C, Ohaus) interfaced with a computer. Methylene blue (MB) served as a rejection probe. To evaluate rejection, the filtration cell was filled with 300 mL of 6 mg/L aqueous MB, and the feed solution was filtered under fast-stirring conditions (~1300 rpm) to minimize concentration polarization. In total, 30 mL of solution were filtered in each experiment and the first 20 mL was discarded to eliminate the effect of MB adsorption on rejection data. The MB concentration in the permeate was determined using UV-Vis spectrophotometry (MultiSpec 1501-Shimadzu). To account for an increase in the feed concentration during the filtration of the first 30 mL of solution, the rejection was calculated based on a simple differential equation (see SC, section S4).

The membrane in the cell was then exposed to 1 M HCl or 1 M NaOH or both sequentially, for 15 min each, to remove the PEM coating. Subsequent exposure to Triton X-100 solutions (2 wt% in water) for 15 min was also employed in some cases to disrupt non-ionic interactions. During the backflush treatment, the membrane was
flipped over in the filtration cell and a surfactant solution was directed from the permeate side of the membrane to PES-PEM interface at the transmembrane pressure of 5 psi. DI water flux and MB rejection measurements were repeated for the cleaned membranes. The efficiency of PEM removal was determined by comparing the DI water permeate flux and MB rejection values of the support PES membrane, the same membrane coated with a PEM film, and the same membrane after PEM removal.

To study the effectiveness of the removal methods applied to fouled membranes, dead-end filtration was performed using a feed solution that contained BSA (0.3 g/L), alginate (0.3 g/L), NaCl (20 mM) and CaCl$_2$ (10 mM). Disassembly of fouled PEM-coated membranes was attempted as described above, and DI water flux was measured to quantify the efficiency of the disassembly methods.

2.4 Reflectance Fourier transform infrared (FTIR) spectroscopy

PES (17 mg) was dissolved in 10 mL of CH$_2$Cl$_2$ and 0.1 mL of this solution was placed onto Au-coated Si wafers (1.1 × 2.4 cm$^2$) for spin coating at 500 rpm [42]. Using the same PE solutions and conditions described above for membrane modification, PEMs were deposited by the LbL technique on the PES-coated wafers. Reflectance FTIR spectra of PEMs on PES were acquired using a Thermo Nicolet 6700 FTIR spectrometer equipped with a PIKE grazing angle (80°) attachment. A wafer cleaned with a combination of UV and ozone served as the IR background, and absorbance from PES (see SC, section S2) was subtracted from all spectra.
3. Results and Discussion

This study aims to exploit PEMs as sacrificial coatings and enable detachment of fouling layers that accumulate during filtration and cannot be fully removed by hydraulic cleaning. The subsections below describe our strategy for PEM removal, QCM-D studies that demonstrate PEM loss, MB nanofiltration before and after PEM disassembly to validate the PEM removal on membranes, and finally detachment of PEMs after filtration of protein and polysaccharide solutions to show that the strategy applies to fouled membranes.

3.1 Strategy for removal of PEMs

Layer-by-layer adsorption of polyelectrolytes typically occurs through multiple electrostatic interactions, although non-ionic interactions sometimes help stabilize PEMs [43-45]. However, when the first PE layer and the substrate possess charges of the same sign, the initial adsorption occurs only due to non-ionic bonding. Strategies for removal of PEMs from substrates must take into account the forces that stabilize films and bind them to the substrate (Fig. 1).

For PEMs containing a weak-base polycation or a weak-acid polyanion, exposure to high or low pH solutions promotes disassembly by decreasing the degree of PE ionization and limiting the extent of electrostatic cross-linking in the film [19, 46, 47]. Nevertheless, pH changes will not remove the initial layer from the substrate when
Figure 1: Mechanisms operative in the assembly of PEMs and their attachment to a supporting substrate in two cases: a) The first PE layer has the same charge as the substrate; and b) The first PE layer has a charge opposite to that of the substrate. For clarity, the diagram does not show the overlap that occurs over several layers or the release of charge-compensating counterions that helps to drive adsorption [48-50].

adsorption occurs primarily through non-ionic interactions. In this case desorption will require disruption of non-ionic bonds, for example through exposure of the PE-substrate interface to a surfactant. With membranes, this can occur during crossflow filtration of a surfactant solution through the PEM-coated membrane or, when the PEM is impermeable to the surfactant, by a backflush with the same solution. Figure 2 summarizes the disassembly strategy employed in this study when the first PE layer and support have charges of the same sign. Note that surfactant alone may be insufficient to remove a highly ionically cross-linked film from the surface without acid/base treatment.
3.2. Examination of film formation and disassembly on a quartz crystal microbalance

Figure 3 shows QCM-D data for the assembly and disassembly of (Chi/PAA)$_4$ on a QCM-D crystal coated with silicon oxide. After introduction of PE solutions into the QCM-D chamber, the crystal oscillation frequency decreased and then plateaued, indicating successful PE adsorption. Frequency drops after both Chi and PAA adsorption increased exponentially ($r^2 = 0.9973$) with the number of adsorbed layers (-28, -97, -284 and -765 Hz for 1, 2, 3 and 4 bilayers, respectively), consistent with prior studies that showed exponential growth for low charge-density PEs such as Chi [51].

Figure 2: Proposed PEM disassembly algorithm for the case when the first PE layer and support have charges of the same sign.
Figure 3: QCM-D data for adsorption and disassembly of a (Chi/PAA)$_4$ multilayer on a SiO$_2$-coated crystal. Chi, PAA, HCl, and NaOH labels denote times when solutions of the corresponding compounds were introduced into the QCM-D chamber. The rinse label points to times when the QCM-D chamber was rinsed with DI water.

Note: The data set presented in Fig. 3 shows a PEM removal of ~97%, which is lower than the 100% we observed in most other experiments. This specific data set was selected to facilitate graphical illustration of $\Delta \nu_2$. 
After depositing each PE layer, the QCM-D crystal was rinsed with DI water to remove loosely bound PEs from the surface. As expected, the oscillation frequency increased during rinsing, especially in the case of PEMs that included PAA.

We attempted to disassemble PEMs containing weak polyanions or weak polycations through treatments with dilute HCl and NaOH solutions, respectively. We did not employ surfactants in QCM-D tests because the interaction with the silica surface of the QCM-D crystal should be primarily electrostatic. Because Chi is a weak polybase and PAA is a weak polyacid, electrostatic interactions in (Chi/PAA)$_4$ should decline when the PEM is exposed to either HCl or NaOH. Figure 3 shows a dramatic increase in frequency for the (Chi/PAA)$_4$-modified QCM-D crystal after exposure to HCl, clearly demonstrating removal of most of the film from the substrate. Subsequent exposure to NaOH followed by rinsing decreases the frequency to nearly the same level as for a film with only a single PAA layer. We note that the SiO$_2$ coating on the crystal might be unstable in 1 M NaOH. However, the oscillation frequency returned to nearly its original value, suggesting minimal SiO$_2$ dissolution.

We carried out the same experiments with PEMs built from several different PE pairs (see the SC file for QCM-D frequency shifts for these PEMs (Figures S-1 – S-12) as well as dissipation data (section S2)). Table 1 summarizes QCM-D data on the efficiency of PEM removal, $\eta$:

$$\eta = \frac{\Delta \nu_1 - \Delta \nu_2}{\Delta \nu_1} \cdot 100\%,$$  

(1)
where $\Delta \nu_1$ and $\Delta \nu_2$ are QCM frequency shifts (relative to DI water prior to PEM deposition) before and after PEM disassembly, respectively (see Figure 3 for an example).

**Table 1:** Efficiency of PEM disassembly, $\eta$ (wt% removed) in response to sequential treatment by acid/base solutions as measured in QCM-D experiments with 4-bilayer PEMs.

<table>
<thead>
<tr>
<th>Polyanion</th>
<th>Polycation</th>
<th>Chi *</th>
<th>PAH *</th>
<th>PDADMAC **</th>
</tr>
</thead>
<tbody>
<tr>
<td>PAA *</td>
<td>99.4 ± 1.3</td>
<td>92.3 ± 3.0</td>
<td>94.3 ± 4.4</td>
<td></td>
</tr>
<tr>
<td>PMAA *</td>
<td>95.4 #↑</td>
<td>86.0 ± 4.9</td>
<td>82.4 ± 9.0</td>
<td></td>
</tr>
<tr>
<td>PSS **</td>
<td>84.3 ± 13.9 #</td>
<td>86.5 ± 5.9</td>
<td>7.5 ± 3.2</td>
<td></td>
</tr>
<tr>
<td>PVS **</td>
<td>94.5 ± 7.8</td>
<td>72.1 ± 6.1</td>
<td>17.8 ± 11.3</td>
<td></td>
</tr>
</tbody>
</table>

Among the PEMs, removal was highest for (PAA/Chi)$_4$, which contains two weak PEs. The high water solubilities of Chi and PAA and the very low $M_W$ of PAA may also lead to the essentially 100% disassembly of films containing these polymers. Moreover, all the films that contained at least one weak PE had removal efficiencies higher than 72%. As expected, disassembly was least effective with PEMs composed of two strong PEs:
(PSS/PDADMAC)$_4$ and (PVS/PDADMAC)$_4$. In these cases, a change in pH had little effect on ionization and removed on average 20% or less of the mass of the PEMs.

We note that, ideally, the surface for QCM-D tests should be the same as the surface of the UF supports for PEM adsorption. Unfortunately, such an ideal model is not feasible. Spin-coating a QCM-D crystal with polysulfone would produce a non-porous polymer layer that would interact with the 1st PE layer differently than a porous layer of the UF support’s skin. In principle, one can attempt to replicate the phase inversion process to prepare a UF polysulfone membrane on the surface of a QCM-D crystal. While the desired surface morphology might form, the membrane would be too thick (300 μm) and, therefore, too heavy to serve as a coating for a QCM-D crystal. In addition, the small size of the crystal would lead to boundary effects, and insufficient post-processing (i.e. no possibility to pre-compact the membrane or to flow water through the membrane to flush out the porogen) would make true replication impossible.

3.3. Filtration before and after PEM disassembly

To initially assess disassembly of a range of PEMs on membranes, we measured DI water flux and MB rejection before and after PEM disassembly by the acid/base treatment. Figure 4 shows results of these tests with the data plotted in the order of decreasing DI water permeate flux values for membranes with as-assembled PEMs. Adsorption of PEMs on the UF substrates decreased permeability to DI water and increased MB rejection.
Figure 4: DI water flux (top) and MB rejection (bottom) of PEM-coated 30 kDa PES membranes before (dark gray) and after (light gray) PEM removal. For comparison the figure shows data for pristine PES membranes at the far left (hashed gray). All PEMs were disassembled by sequential treatment with acid and base solutions.
Upon PEM disassembly, flux and rejection did not return to the levels typical of the unmodified UF support suggesting incomplete removal of the PEM. In the few cases where disassembly conditions decreased flux, e.g. (PAH/PMAA)_4, or increased rejection, e.g. (PDADMAC/PMAA)_4, the acid and base likely induce conformational changes in the film without removing sufficient PE to enhance permeability [52].

Flux recovery after PEM disassembly (flux after disassembly divided by the flux through the pristine membrane) does not correlate directly with the extent of polyelectrolyte removal because both the PEM and the underlying PES membrane provide resistance to flow. Thus, we employed a resistance-in-series model to determine the resistances of the UF substrate, the PEM and residual material left on the membrane after PEM removal. These data allow definition of the resistance removal efficiency ($\varepsilon_R$), defined as follows:

$$\varepsilon_R = 1 - \frac{R_{res}}{R_{PEM}}$$

(2)

where $R_{PEM}$ and $R_{res}$ are hydraulic resistances of the PEM and residual film left after PEM removal, respectively. The resistance removal efficiency is indicative of the extent of PEM removal, so we also term it the PEM removal efficiency.

Table 2 provides values for both flux recovery after PEM removal and $\varepsilon_R$. Note that for (Chi/PAA)_4 (top entry in the table), even though flux recovery is only 54%, the PEM removal efficiency (i.e. resistance removal efficiency) is 98%.
Table 2: Recovery and regeneration of PEM properties (DI water permeate flux and rejection) in response to four methods of PEM disassembly.

<table>
<thead>
<tr>
<th>PEM</th>
<th>MWC of PES support, kDa</th>
<th>PEM removal method</th>
<th>Flux recovery, %</th>
<th>PEM removal efficiency $\varepsilon_R$, %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>M1</td>
<td>M2</td>
<td>M3</td>
<td>M4</td>
</tr>
<tr>
<td>1. (Chi/PAA)$_4$</td>
<td>x</td>
<td>x</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2. (Chi/PMAA)$_4$</td>
<td>x</td>
<td>x</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3. (Chi/PSS)$_4$</td>
<td>x</td>
<td>x</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4. (Chi/PVS)$_4$</td>
<td>x</td>
<td>x</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5. (PAH/PAA)$_4$</td>
<td>x</td>
<td>x</td>
<td></td>
<td></td>
</tr>
<tr>
<td>6. (PAH/PMAA)$_4$</td>
<td>x</td>
<td>x</td>
<td></td>
<td></td>
</tr>
<tr>
<td>7. (PAH/PSS)$_4$</td>
<td>x</td>
<td>x</td>
<td></td>
<td></td>
</tr>
<tr>
<td>8. (PAH/PVS)$_4$</td>
<td>x</td>
<td>x</td>
<td></td>
<td></td>
</tr>
<tr>
<td>9. (PDADMAC/PAA)$_4$</td>
<td>x</td>
<td>x</td>
<td></td>
<td></td>
</tr>
<tr>
<td>10. (PDADMAC/PMAA)$_4$</td>
<td>x</td>
<td>x</td>
<td></td>
<td></td>
</tr>
<tr>
<td>11. (PAA/Chi)$_4$</td>
<td>30</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>12. (PAA/Chi)$_4$</td>
<td>x</td>
<td>x</td>
<td></td>
<td></td>
</tr>
<tr>
<td>13. (PSS/Chi)$_4$</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td></td>
</tr>
<tr>
<td>14. (PSS/Chi)$_4$</td>
<td>x</td>
<td>x</td>
<td></td>
<td></td>
</tr>
<tr>
<td>15. (PSS/PDADMAC)$_4$</td>
<td>x</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>16. (PAA/Chi)$_4$/fouled†</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td></td>
</tr>
<tr>
<td>17. (PSS/Chi)$_4$/fouled†</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td></td>
</tr>
<tr>
<td>18. (PSS/Chi)$_4$/fouled†</td>
<td>x</td>
<td>x</td>
<td></td>
<td></td>
</tr>
<tr>
<td>19. (PSS/PDADMAC)$_4$/fouled†</td>
<td></td>
<td></td>
<td>x</td>
<td></td>
</tr>
</tbody>
</table>

Notes: M1 = exposure to high pH; M2 = exposure to low pH; M3 = exposure to Triton X-100; M4 = backflush with Triton X-100.

* Uncertainties represents standard deviations based on sets of 3 replicate measurements performed with different membranes. Other data in the table were obtained in experiments with only one membrane for each PE pair.
† Prior to PEM removal, these membranes were fouled by filtering solutions containing BSA, alginate, and Ca\(^{2+}\).
‡ Note that in the calculations of \(\varepsilon_R^{(i)}\) for fouled membranes, \(R_{PEM}\) represents the hydraulic resistance of fouled PEM membranes.

This occurs because \(R_{PEM}\) is very high compared to the resistance of the untreated membrane (see the SC, section S3, for a discussion of the series resistance model).

Similarly, for (PAH/PAA)\(_4\), the flux recovery is only 82%, but the resistance recovery rounds to 100%. All other PE pairs show lower removal efficiencies. Thus, of all the PE pairs, (Chi/PAA)\(_4\) and (PAH/PAA)\(_4\) are the best choices for disassembly by acid/base treatment and regeneration. However, the DI water flux through membranes coated with (PAH/PAA)\(_4\) is very low, so the work that follows focuses on membranes coated with (Chi/PAA)\(_4\). The (Chi/PAA)\(_4\) system also showed the highest removal efficiency in QCM-D studies (Table 1), and these films on membranes show relatively high MB rejections. We note that zero or negative \(\varepsilon_R\) values in Table 1 represent membranes whose flux does not increase after a disassembly treatment. A pH swing or exposure to surfactant may induce PEM conformational changes that are not accompanied by sufficient removal of PEs to decrease PEM resistance, so \(\varepsilon_R\) is not positive.

3.4. Effects of substrate MWCO on PEM disassembly and regeneration

To understand how the pore size of the substrate affects PEM removal, we examined assembly and disassembly of (Chi/PAA)\(_4\) films on PES substrates with MWCOs of 10 kDa and 30 kDa. Further, to study the durability of membranes under chemical treatments and whether the PEM slowly builds up on the membrane, we repeated the
assembly-disassembly cycle three times (Fig. 5). Flux and rejection data show similar trends for filtration through PEMs prepared on both 10 kDa and 30 kDa PES supports, although flux is lower and rejection higher with the 10 kDa support. However, disassembly does not lead to complete flux recovery with either membrane, suggesting partial blocking of pores by residual PEs. The incomplete PEM removal even on the 10 kDa membrane suggests that a mechanism other than physical entrapment retains some PE on the membrane. In particular, non-ionic interactions may prevent detachment of the first PE layer from the PES substrate. Nevertheless, the $\varepsilon_R$ values in Table 2 (see entries 11 and 12) suggest that a higher membrane MWCO may result in greater polyelectrolyte entrapment and lower removal efficiency. Most importantly, fluxes and rejections with the PEM-coated membranes are similar for the initial film and films formed after one or more regeneration cycles (i.e. disassembly-buildup), although both flux and rejection decline after the second disassembly and third film-formation step.
Figure 5: DI water permeate flux and MB rejection data during filtration of a 17.5 μM MB solution through (Chi/PAA)$_4$ films on the surface of (a) 30 kDa PES membranes and (b) 10 kDa PES membranes. (Each error bar represents
a standard deviation for a set of 3 replicate measurements with different membranes.)

3.5. Disassembly with surfactants

Surfactants may disrupt non-ionic interactions between the PES substrate and PEs to enable more complete PEM removal [26-28]. However, if both electrostatic and non-ionic interactions immobilize the initial PE, removal of this layer may require simultaneous treatment with base/acid and surfactant rather than sequential treatments. Thus, to prevent electrostatic interactions between the PES membrane, which carries a negative surface charge, and the first PE layer, we employed a polyanion as the initial layer in PEM-coated membranes on a PES substrate with a 10 kDa MWCO. After treating the (PAA/Chi)₄-modified membrane with low and high pH solutions, we filtered a surfactant solution through the membrane for 15 min and reexamined its filtration properties. Although the pH treatment results in only 59 ± 9% recovery of the DI water permeate flux through the bare membrane (Table 2, entry 12), subsequent treatment with surfactant leads to 94% flux recovery (Table 2, entry 13). The MB rejection decreased from 99% to 55% after PEM removal by pH swing and to 36% after PEM removal by pH swing and surfactant. Note that MB rejection by the PEM-free UF membrane (10 kDa MWCO) is 31%, or nearly the same as by the membrane after PEM disassembly.

We also examined the effectiveness of surfactant treatment for the disassembly of (PSS/Chi)₄, a PEM that contains one strong PE. For these films, pH affects only the
ionization of the weakly basic Chi, so the disassembly procedure included sequential
treatment with NaOH (no HCl) and surfactant to break electrostatic and non-ionic
bonds, respectively. DI water filtration through (PSS/Chi)$_4$-coated PES membranes
showed flux recoveries (relative to the bare PES membrane) of 28% after treatment with
NaOH and 86% after subsequent treatment with surfactant (Table 2, entry 14). MB
rejection decreased from 73% for (PSS/Chi)$_4$-coated membranes, to 54% after
treatment with NaOH and 34% after subsequent surfactant filtration. Clearly, surfactant
treatment enhanced the PEM removal.

Finally, we studied surfactant-induced disassembly of membranes composed of two
strong PEs (PSS and PDADMAC). Because pH does not affect the charge density of
strong PEs, the disassembly procedure only included exposure to the surfactant.
Remarkably, after surfactant treatment, flux recovery was 96% (Table 2, entry 16) while
MB rejection decreased from 48% to 18%, a rejection slightly lower than that of even
the pristine membrane. We speculate that in this case, the PEM film remains integral
and is “peeled off” the substrate.

3.4. Investigation of PEM disassembly on PES-coated wafers using FTIR spectroscopy
(PAA/Chi)$_4$, (PSS/Chi)$_4$ and (PSS/PDADMAC)$_4$ films were also prepared on PES-
coated wafers to enable corroborating FTIR spectroscopy studies of PEM removal from
a surface similar to that of PES membranes (although without pores). Figures 6 (a-c)
present reflectance FTIR spectra for the three PEMs before and after different
disassembly treatment steps. In the spectrum of (PAA/Chi)$_4$ (Fig. 6a), peaks at ~1550 and ~1400 cm$^{-1}$ most likely stem from the PAA asymmetrical and symmetrical $\text{--COO}^-$ stretches, respectively.
Figure 6: FTIR spectra of PEMs prepared on Au-coated silicon wafers modified with spin-coated PES and treated with various steps in the PEM buildup/disassembly sequence: after PEM adsorption, after pH treatment, and after surfactant treatment. The PEMs were a) (Chi/PAA)\textsuperscript{4}; b) (PSS/PAA)\textsuperscript{4}; c) (PSS/PDADMAC)\textsuperscript{4}.

The peak at 1720 cm\textsuperscript{-1} results from the acid carbonyl stretch, and the absorbance at 1457 cm\textsuperscript{-1} is a -CH\textsubscript{2} band. Most importantly, these peaks disappear after either HCl or NaOH treatment, and the spectrum is featureless after the NaOH treatment, implying complete film removal.

The spectra of PEMs containing PSS show absorbance peaks at 1127, 1036 and 1009 cm\textsuperscript{-1}, which correspond to sulfonic acid group (SO\textsubscript{3})\textsuperscript{−} stretches (Fig. 6b and Fig. 6c). With PSS/Chi films, these peaks disappear after treatment with NaOH. (We did not treat PSS/Chi films with HCl because they do not contain a weak acid.) However, the surfactant treatment alone did not appear to completely remove the films from PES-coated wafers. In contrast to filtration results, the spectra of (PSS/PDADMAC)\textsuperscript{4} coatings suggest no removal after surfactant treatment. This could be due to the high density of the (PSS/PDADMAC)\textsuperscript{4} films, which does not allow the surfactant molecules to diffuse through the PEM and reach the substrate-PEM interface to break the non-ionic bonds between substrate and first PE layer. Note that surfactant treatment for the (PSS/PDADMAC)\textsuperscript{4} membrane was performed via back flushing or filtration to bring the surfactant to the PEM-substrate interface.
Figure 7: DI water flux through (1) 10 kDa PES membranes, (2) NF 270 or PEM-modified PES membranes, (3) NF270 or PEM-coated membranes fouled by a solution of BSA and alginate, (4) hydraulically cleaned NF270 or PEM-coated membranes, (5) PES membranes after PEM removal, (6) PES membranes with re-deposited PEMs or chemically cleaned NF 270. (a)
(Chi/PAA)₄, (b) (PSS/PAA)₄, (c) (PSS/PDADMAC)₄, and (d) NF 270. PEM removal protocols are described in Table 2, entries 17-19.

Notes:
1) Each error bar represents a standard deviation for a set of 3 replicate measurements with different membranes.
2) DI water fluxes for PAA/Chi, PSS/Chi, PSS/PDADMAC and NF 270 membranes are $1.67 \times 10^{-11}$, $4.44 \times 10^{-11}$, $4.67 \times 10^{-11}$, and $3.17 \times 10^{-11}$ m/s/Pa (6.0, 16.0, 26.8 and 11.4 LMH/bar), respectively.

3.5. Removal of fouled PEMs

We also examined removal of fouled PEMs and whether a second PEM deposition gives the same separation properties as the originally deposited coating. These experiments included filtering mixtures of BSA and alginate through (PAA/Chi)₄-, (PSS/Chi)₄-, and (PSS/PDADMAC)₄-coated PES membranes, application of PEM removal protocols, coating the cleaned substrate with a new PEM, and reexamining filtration performance. Figure 7 shows that in all cases, removal of the fouled PEM (chemical treatment column) led to DI water fluxes within ±10% of those through the bare membrane. Adsorption of a fresh PEM gave fluxes within ±20% of those through the initial PEM-coated membrane. However, we should note that fouling is partly hydraulically reversible as indicated by the significant (73 ± 19 %) flux recovery observed for the NF 270 membrane. Treatment of fouled NF 270 with a cleaning solution containing 1 mM EDTA and 10 mM SDS at pH 10 resulted in complete flux recovery (115 ± 15%).
3.6. Limitations and possible applications of the proposed approach

The proposed PEM removal procedures may not be compatible with some membrane materials. For example, cellulose acetate and, to a lesser extent, its di- and tri-acetate derivatives hydrolyze at high and low pH. However, PEMs can adsorb to almost any material and serve as sacrificial coatings on polymeric or ceramic membranes that are stable over a wide range of pH. This work focused on surface fouling, but for membranes with very large pores PEMs may serve as sacrificial coating to mitigate intrapore fouling. When pores are too large to be bridged by PEs, their internal pore surface can be coated. Perhaps the biggest limitation of PEMs is the multistep removal and film formation process. Simplification of the deposition procedure will likely be necessary to make the regeneration process economical. Although polyelectrolyte redeposition may require more than one hour, replacement of only the top layers of a film [27, 28] could shorten the process.

The removal strategy has several potential advantages. First, regenerating a membrane’s selective layer in situ can allow for on-demand assembly of a membrane with desired surface and separation properties. Second, regeneration of the selective layer is an alternative method of managing irreversible fouling; this method may remove hydraulically-irreversible fouling as a substitute for or in addition to chemical cleaning. Third, the membrane can be “replaced” without changing the support layer (UF membrane) or the membrane module, potentially leading to cost savings.
4. Conclusions

This work examined controlled disassembly of PEMs on several substrates and explored the use of sacrificial PEMs as an approach to managing membrane fouling. On the surface of QCM crystals, exposure to 1 M HCl or 1 M NaOH or both effectively removed most (70-100%) of the mass of PEMs composed of weak PEs. In contrast, PEMs made of only strong PEs were stable under these conditions. For the same PEMs assembled on the surface of PES UF membranes (MWCO 10 kDa and 30 kDa), exposure to 1 M NaOH and 1 M HCl did not completely restore permeate flux to the value of a PEM-free support. A subsequent treatment with a surfactant successfully removed PEMs consisting of weak/weak, weak/strong and strong/strong PE pair combinations and restored >86% of the flux, presumably by disrupting non-ionic interactions between the PES support and PEs that remain adsorbed after exposure to low or high pH or both. If a PEM contains strong PEs only, the PEM can be removed from the substrate by disrupting non-ionic bonding between the substrate and the first PE layer by a surfactant treatment. The proposed method is also efficient in removing PEMs that have been fouled by a mixture of BSA and alginate.
Acknowledgements

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Figure 1: Mechanisms operative in the assembly of PEMs and their attachment to a supporting substrate in two cases: a) The first PE layer has the same charge as the substrate; and b) The first PE layer has a charge opposite to that of the substrate. For clarity, the diagram does not show the overlap that occurs over several layers or the release of charge-compensating counterions that helps to drive adsorption [48-50].

Figure 2: Proposed PEM disassembly algorithm for the case when the first PE layer and support have charges of the same sign.

Figure 3: QCM-D data for adsorption and disassembly of a (Chi/PAA)₄ multilayer on SiO₂-coated crystal. Chi, PAA, HCl, and NaOH labels denote times where solutions of the corresponding compounds were introduced into the QCM-D chamber. The rinse label points to times when the QCM-D chamber was rinsed with DI water.
Note: The data set presented in Fig. 3 shows a PEM removal of ~97%, which is lower than the 100% we observed in most other experiments. This specific data set was selected to facilitate graphical illustration of $\Delta \nu_2$.

Figure 4: DI water flux (top) and MB rejection (bottom) of PEM-coated 30 kDa PES membranes before (dark gray) and after (light gray) PEM removal. For comparison the Figure shows data for pristine PES membranes at the far left (hashed gray). All PEMs were disassembled by the sequential treatment with acid/base solutions.

Figure 5: DI water permeability and MB rejection data during filtration of a 17.5 μM MB solution through (Chi/PAA)₄ films on the surface of (a) 30 kDa PES membranes and (b) 10 kDa PES membranes. (Each error bar represents a standard deviation for a set of 3 replicate measurements with different membranes.)

Figure 6: FTIR spectra of PEMs prepared on Au-coated silicon wafers modified with spin-coated PES and treated with various steps in the PEM buildup/disassembly sequence: after PEM adsorption, after pH treatment, and after surfactant treatment. The PEMs were a) (Chi/PAA)₄; b) (PSS/PAA)₄; c) (PSS/PDADMAC)₄.
**Figure 7:**  DI water permeate flux through (1) 10 kDa PES membrane, (2) NF 270 or PEM-modified PES membrane, (3) NF270 or PEM-coated membranes fouled by a solution of BSA and alginate, (4) hydraulically cleaned NF270 or PEM-coated membranes, (5) PES membranes after PEM removal, (6) PES membranes with re-deposited PEMs or chemically cleaned NF 270. a) (Chi/PAA)₄, b) (PSS/PAA)₄, c) (PSS/PDADMAC)₄ and NF 270. PEM removal protocols are described in Table 2.

Notes:

1) Each error bar represents a standard deviation for a set of 3 replicate measurements with different membranes.

2) DI water fluxes for PAA/Chi, PSS/Chi, PSS/PDADMAC and NF 270 membranes are 1.67·10⁻¹¹, 4.44·10⁻¹¹, 4.67·10⁻¹¹, 3.17·10⁻¹¹ m/s/Pa (6.0, 16.0, 26.8 and 11.4 LMH/bar), respectively.
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Table 1: Efficiency of PEM disassembly, \( \eta \) (wt% removed) in response to sequential treatment by acid/base solutions as measured in, based on QCM-D experiments with measurements for films 4-bilayer PEMs composed of 4 bilayers.

Notes:

* weak PE

** strong PE

# PEMs assembled on Au-coated QCM-D crystals; all other PEMs were assembled on SiO\(_2\)-coated crystals

† Based on one QCM-D test

Table 2: Recovery and regeneration of PEM properties (DI water permeate flux and rejection) in response to the four methods of PEM disassembly.

Notes:

M1 = exposure to high pH; M2 = exposure to low pH; M3 = exposure to Triton X-100; M4 = backflush with Triton X-100.

* Uncertainties represents standard deviations based on sets of 3 replicate measurements performed with different membranes. Other data in the table were obtained in experiments with only one membrane for each PE pair.

† Prior to PEM removal, these membranes were fouled by filtering solutions containing BSA, alginate, and Ca\(^{2+}\).

‡ Note that in the calculations of \( \varepsilon_R^{(i)} \) for fouled membranes, \( R_{PEM} \) represents the hydraulic resistance of fouled PEM membranes.
References


