Supplementary Content

for the manuscript

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

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Pejman Ahmadiannamini†, Merlin L. Bruening‡, Volodymyr V. Tarabara†*

† Department of Civil and Environmental Engineering, Michigan State University, East Lansing, MI 48824, USA
‡ Department of Chemistry, Michigan State University, East Lansing, MI 48824, USA

* Corresponding author:
tarabara@msu.edu; phone: (517) 432-1755; fax: (517) 355-0250
S1. Cleaning protocol for QCM-D sensors

Briefly, the sensor was exposed to a cleaning solution for 10 min, rinsed with DI water, dried with nitrogen and treated by a combination of ultraviolet and ozone (UVO) for 10 min. Aqueous solutions of ammonia and peroxide (5:1:1 H₂O:NH₄OH (25 wt%):H₂O₂ (30 wt%)) and 2 wt% sodium dodecyl sulfate (SDS) were employed as cleaning solutions for Au- and SiO₂-coated crystals, respectively.

S2. Dissipation

Complementary to changes in QCM frequency, dissipation measurements provide information about the structure of PEMs during their adsorption and disassembly. Most adsorbed films are not rigid and will not fully couple to the oscillation of the crystal. A soft film damps the amplitude of the crystal oscillation. Equation (S1) defines the energy dissipation $D$:

$$D = \frac{E_{\text{lost}}}{2\pi E_{\text{stored}}} \quad (S1)$$

where $E_{\text{lost}}$ is the energy dissipated during one oscillation cycle and $E_{\text{stored}}$ is the total energy stored in the oscillator. For a rigid film dissipation is negligible, and the Sauerbrey equation describes the relationship between frequency change and the absorbed mass. For a soft (viscoelastic) layer, changes in dissipation serve as a qualitative measure of stiffness or conformation. Furthermore, a viscoelastic model (e.g. the Voight model) of the adhering film can give estimates of film viscosity, elasticity, and corrected thickness.
Upon adsorption of PEMs, the dissipation often tracks changes in frequency. An increase in dissipation normally accompanies a decrease in frequency, indicating successful adsorption of the PE layer. A decrease in dissipation upon adsorption of a PE layer (e.g. PDADMAC/PVS films) indicates conformational changes in the PEM and formation of more rigid structures. In some cases, dissipation also decreased during rinsing (e.g. Chi/PAA films), suggesting the formation of more rigid films upon removal of loosely adsorbed PE chains.
Figure S-1: QCM-D data for adsorption and disassembly of a (Chi/PAA)$_4$ multilayer.
Figure S-2: QCM-D data for adsorption and disassembly of a (PAH/PAA)$_4$ multilayer.
Figure S-3: QCM-D data for adsorption and disassembly of a (PDADMAC/PAA)_4 multilayer.
Figure S-4: QCM-D data for adsorption and disassembly of a \((\text{Chi/PMAA})^4\) multilayer.
Figure S-5: QCM-D data for adsorption and disassembly of a (PAH/PMAA)$_4$ multilayer.
Figure S-6: QCM-D data for adsorption and disassembly of a (PAH/PAA)$_4$ multilayer.
Figure S-7: QCM-D data for adsorption and disassembly of a (Chi/PSS)$_4$ multilayer.
Figure S-8: QCM-D data for adsorption and disassembly of a (PAH/PSS)$_4$ multilayer.
Figure S-9: QCM-D data for adsorption and disassembly of a (PDADMAC/PSS)$_4$ multilayer.
Figure S-10: QCM-D data for adsorption and disassembly of a (Chi/PVS)$_4$ multilayer.
Figure S-11: QCM-D data for adsorption and disassembly of a (PAH/PVS)$_4$ multilayer.
Figure S-12: QCM-D data for adsorption and disassembly of a (PDADMAC/PVS)_4 multilayer.
Using OMNIC software, the FTIR spectrum of spin-coated PES on a Au-coated Si wafer (Figure S-13) was subtracted from spectra of PEMs on PES coated samples. In these subtractions, the spectrum of spin-coated PES was multiply by a factor that minimized the PES absorbance.
S3. Resistances-in-series model for estimating PEM removal

The resistances-in-series model assumes that pressure drops across specific membrane regions are proportional to flux and the hydraulic resistances of those regions. Thus, equations (S2-S4) describe the fluxes across a bare membrane ($J_1$), a PEM-coated membrane ($J_2$), and a membrane after PEM disassembly ($J_3$).

$$ J_1 = \frac{\Delta P}{\mu R_{PES}} \quad (S2) $$

$$ J_2 = \frac{\Delta P}{\mu (R_{PES} + R_{PEM})} \quad (S3) $$

$$ J_3 = \frac{\Delta P}{\mu (R_{PES} + R_{res})} \quad (S4) $$

In these equations, $\Delta P$ is the pressure drop across the entire membrane, $\mu$ is the dynamic viscosity, $R_{PES}$ is the hydraulic resistance of the bare PES UF membrane, $R_{PEM}$ is the hydraulic resistance of the PEM, and $R_{res}$ is the hydraulic resistance of the residual PEM after disassembly. Solving these equations for $R_{PES}$, $R_{PEM}$ and $R_{res}$ gives equation S5-S7.

$$ R_{PES} = \frac{\Delta P}{\mu J_1} \quad (S5) $$

$$ R_{PEM} = \frac{\Delta P}{\mu J_2} - \frac{\Delta P}{\mu J_1} \quad (S6) $$

$$ R_{res} = \frac{\Delta P}{\mu J_3} - \frac{\Delta P}{\mu J_1} \quad (S7) $$
We assume that the hydraulic resistance removal efficiency ($\varepsilon_R$) defined in equation (S8) is a reasonable measure of the extent of PEM removal (equation (S8) is equation (2) in the manuscript).

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

(S8)

Substituting equations (S6) and (S7) into (S8) gives equation (S9).

$$\varepsilon_R = 1 - \frac{\frac{1}{J_3} - \frac{1}{J_1}}{\frac{1}{J_2} - \frac{1}{J_1}}$$

(S9)

Rearrangement gives equation (S10).

$$\varepsilon_R = 1 - \frac{J_2(J_1 - J_3)}{J_3(J_1 - J_2)}$$

(S10)

Note that when PEM removal restores the flux to that of the bare membrane, $J_1 = J_3$ and $\varepsilon_R = 1$. However, even if flux recovery is not 100% after PEM disassembly, the value of $\varepsilon_R$ will approach unity if $J_2$ is small compared to $J_3$ and $J_1$. As an example if $J_2$ is 1% of $J_1$ and $J_3$ is 80% of $J_1$, $\frac{R_{res}}{R_{PEM}} = 0.0025$, and $\varepsilon_R = 99.75$. 
S4. Calculating rejection in a dead-end filtration test based on a single measurement of solute concentration in the permeate at time \( t^* \) into the filtration.

The mass of solute, \( dM_p \), in the increment of permeate volume \( dV_p \) is given by

\[
dM_p = C_p dV_p, \tag{S11}
\]

where \( C_p \) is a function of time. Using the definition of observed rejection \( R = 1 - C_p/C_f \):

\[
dM_p = C_f (1 - R) dV_p \tag{S12}
\]

where \( C_f \) is a function of time.

Substituting eq. (S13) for the feed concentration

\[
C_f = \frac{M_f}{V_f} = \frac{M_f^{t=0} - M_p}{V_f^{t=0} - V_p} \tag{S13}
\]

into eq. (S12) gives

\[
dM_p = \frac{M_f^{t=0} - M_p}{V_f^{t=0} - V_p} (1 - R) dV_p \tag{S14}
\]

and, after separation of variables:

\[
\frac{dM_p}{M_f^{t=0} - M_p} = (1 - R) \frac{dV_p}{V_f^{t=0} - V_p} \tag{S15}
\]

In our study the permeate sample analyzed for MB concentration was the 10 mL volume collected after the first 20 mL of the permeate were discarded. To determined rejection based on this measurement, we solved eq. (S15) numerically using forward finite difference scheme and calculated \( C_p \) in the 10 mL collected between 20\(^{th}\) and 30\(^{th}\) mL of the permeate. We then used rejection as a fitting parameter to match measured and calculated value of \( C_p \).

Eq. (S15) can be integrated analytically as well:

\[
\int_0^{M_p} \frac{dM_p}{M_f^{t=0} - M_p} = (1 - R) \int_0^{V_p^{t=0}} \frac{dV_p}{V_f^{t=0} - V_p} \tag{S16}
\]
where we assume that rejection is not changing with time.

Here, $M_p^* = C_p^* V_p^*$, where $C_p^*$ is the measured concentration of the solute in the permeate after $V_p^*$ of the permeate are collected.

Integration gives:

$$\ln \frac{M_f^{t=0}}{M_f^{t=0} - M_p^*} = (1 - R) \ln \frac{V_f^{t=0}}{V_f^{t=0} - V_p^*}$$

(S17)

and the final expression for rejection is

$$R = 1 - \frac{\ln \frac{M_f^{t=0}}{M_f^{t=0} - M_p^*}}{\ln \frac{V_f^{t=0}}{V_f^{t=0} - V_p^*}}$$

(S18)

In our case, the initial mass of the solute (MB) in the feed is $M_f^{t=0} = 6 \text{ (mg/L)} \times 0.3 \text{ (L)} = 1.8 \text{ (mg)}$ and the initial volume of the feed is $V_f^{t=0} = 0.3 \text{ (L)}$. We used this analytical expression to confirm the correctness of the numerical solution.

This procedure assumes a constant rejection and no adsorption. If adsorption in the membrane occurred in the initial stage of filtration, the procedure would overestimate rejection because the value of $C_f$ would be smaller than calculated using equation S13. In the procedure employed in this work, we sampled the permeate only after an initial 20 mL of filtration. In the worst-case scenario if 100% adsorption occurred during this 20 mL of filtration, the feed concentration would remain unchanged. In contrast, the feed concentration would increase 7% if 100% rejection occurred without adsorption (the rejected solute remained in the feed). Smaller increases in feed concentration would occur for <100% rejection without adsorption. Such small changes will have a minimal effect on calculated rejections, and no effect on the conclusions in this work.