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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.

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 not removable 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

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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 H_2O); PSS (Mw ~ 70,000); PAA (Mw ~ 1800); PMAA (Mw ~ 9500, sodium salt solution, 30 wt% in H_2O); PDADMAC (Mw ~ 100,000–200,000, 20 wt% in H_2O), PAH (Mw ~ 15,000), Chi (medium Mw), BSA, alginate, calcium chloride dihydrate ($CaCl_2 \cdot 2H_2O$) 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 materials, 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 pK_a values (when known) of the corresponding PEs were as follows: PAA (pH = 3.2, pK_a = 4.2–6.5 [37,38]), PMAA (pH = 9.2, pK_a = 5.5 [39]), PSS (pH = 5.4, p$K_a \approx 1.0$ [40]), PVS (pH = 6.5), Chi (pH = 6.0, pK_a = 6.5 [41]), PAH (pH = 4.0, pK_a = 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 cm^2), 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 spectrophotomery (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 Supplementary materials, 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 the PES–PEM interface at a 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.