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Bacterial anti-adhesive properties of polysulfone membranes modified with polyelectrolyte multilayers

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ABSTRACT

The bacterial anti-adhesive properties of polysulfone (PSU) microfiltration membranes modified with poly(allylamine hydrochloride) (PAH)/poly(acrylic acid) (PAA) polyelectrolyte multilayers (PEMs) were investigated in this study. Using a direct microscopic observation membrane filtration system, the deposition kinetics of *Escherichia coli* cells on the membrane surfaces, as well as the reversibility of bacterial deposition, were examined in the absence and presence of calcium. The PEM-modified membranes exhibited significantly improved bacterial anti-adhesive properties compared to the PSU base membranes in both the tested solution chemistries. Specifically, the bacterial deposition kinetics on the modified membranes were slower than the deposition kinetics on the base membranes. Furthermore, the bacterial removal efficiency was significantly enhanced from $<10\%$ to as high as 99% after PEM modification. Interaction force measurements conducted through atomic force microscopy revealed strong, long-ranged repulsive interactions between a carboxylate modified latex colloid probe and PEM-modified membranes, while attractive interactions were detected between the colloid probe and PSU base membranes. The bacterial anti-adhesive properties exhibited by the PEM-modified membranes were attributed to the highly swollen and hydrated PEMs that inhibit the direct contact or close approach of bacteria to the underlying PSU membranes.

1. Introduction

Low pressure membranes (LPMs) are porous membranes that can be used at relatively low transmembrane pressures (less than 200 kPa). Microfiltration (MF) and ultrafiltration (UF) membranes are examples of LPMs, and MF and UF membranes have pore sizes of ca. 0.1–1.0 μm and 0.01–0.10 μm, respectively. LPM processes have gained popularity in drinking water treatment and wastewater reuse because of their small footprint, relatively low costs, and effectiveness in removing pathogenic microorganisms and particulate matter [1].

One of the key challenges of LPM processes is biofouling, or the formation of a biofilm on the membrane surface. As LPM filtration is continuously employed to filter water and wastewater effluents, planktonic bacteria in the bulk suspension may be transported to the membrane by the convective permeate flow, and some of the bacteria may deposit on the membrane surface. The deposited bacteria then produce extracellular polymeric substances (EPS) on the membrane surface and proliferate to form microcolonies which will grow and coalesce into a biofilm. The formation of a biofilm on a LPM surface will result in higher operating pressures, poorer product water quality, frequent chemical cleaning, and shortened membrane life [2].

Among the different types of membrane fouling for LPM processes (colloidal, organic, and biological), biofouling is arguably the most serious because even a small amount of biofilm growth results in a significant loss in clean water flux [3]. Moreover, biofilms tend to be very resistant to biocides because the microorganisms are protected by the matrix of EPS. Thus, it is extremely difficult to clean membranes that have been fouled by biofilms [4]. Currently, efforts to retard biofouling have centered on the use of disinfectants (e.g., chlorine). However, disinfectants are not always successful in controlling biofouling since it is impossible to inactivate all microorganisms in the influent waters and only a small number of microorganisms are required to form a biofilm [2,4]. Furthermore, the prolonged exposure of membranes to disinfectants can damage membrane structures which will result in the decline in the membranes' ability to reject contaminants [5,6]. The use of disinfectants can also lead to the generation of potentially carcinogenic disinfection byproducts [7].

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The initial bacterial deposition and adhesion play a critical role in the development of biofilms on membrane surfaces [8]. While the initial transport of planktonic bacteria to a membrane surface is mainly controlled by hydrodynamic factors (such as cross-flow velocity and permeate flow rate), the initial adhesion of bacteria on the membrane surface is governed by both hydrodynamic factors and interfacial interactions between the bacteria and membrane. It is generally understood that bacteria–membrane interfacial interactions can be comprised of electric double layer, van der Waals, steric (or electrosteric), and hydrophobic interactions. Past studies have demonstrated that membranes that are highly negatively charged or hydrophilic tend to exhibit strong bacterial anti-adhesive properties [2,9,10].

Several techniques have been explored, in recent years, to modify membrane surfaces with the goal of developing anti-biofouling membranes. One of the emerging techniques is the modification of membranes with polyelectrolyte multilayers (PEMs). PEMs can be assembled on a substratum through the layer-by-layer (LbL) adsorption technique [11–13]. This technique involves exposing the substratum, e.g., a membrane, to oppositely charged polyelectrolytes in a sequential manner, thus resulting in the electrostatic-driven adsorption of polyelectrolyte films on the substratum through the overcompensation of surface charge with the adsorption of each polyelectrolyte layer [14]. The main advantage of PEM modification is that it allows for the convenient construction of surface coatings with nanoscale control over the film thickness, composition, and surface chemistry [15]. In addition, PEM modification has been used to inhibit the attachment of cells on material surfaces [15,16]. For instance, Mendelsohn et al. [16] assembled highly hydrated PEM films comprised of poly(allylamine hydrochloride) (PAH) and poly(acrylic acid) (PAA) on polystyrene substrata that were remarkably resistant to the adhesion of an extremely adhesive murine fibroblast cell line.

While the modification of membranes with PEMs has been found to enhance the selectivity of ion rejection [17–21], only a few studies, to date, have reported the application of PEM modification to enhance membranes' resistance to fouling. Shan et al. [22] reported the reduction in fouling by silica colloids when polyethersulfone (PES) membranes were modified with PEMs comprised of PAH and poly(styrene sulfonate) (PSS). Wang et al. [20] demonstrated in their study that the modification of polyacrylonitrile (PAN) membranes with PEMs comprising fewer than 5 bilayers of sulfonated poly(ether ether ketone) and branched polyethyleneimine can retard organic fouling by bovine serum albumin, sodium alginate, and humic acid due to the hydrophilic nature of the PEMs. Diagne et al. [23] assembled 1.5 bilayers of PSS and poly(diallyldimethylammonium chloride) (PDADMA) on PES membranes, and they observed that the PSS/PDADMA multilayer-modified membranes were more resistant to fouling by humic acid, as well as the adhesion of *Escherichia coli* cells, compared to unmodified membranes. The authors attributed the anti-fouling properties of the PEM-modified membranes to the enhancement of surface charge and hydrophilicity of the modified membranes. Qi et al. [24] showed that the assembly of 3 PAH/PSS bilayers on the feed-solution side of a PAN forward osmosis membrane can enhance its resistance to fouling by dextran and alginate. In addition, PEMs have been used to incorporate biocidal agents, e.g., silver nanoparticles, on the membrane surfaces to inactivate deposited bacteria [23,25].

The objective of this research is to examine the bacterial anti-adhesive properties of polysulfone (PSU) MF membranes that are modified with PEMs comprised of PAH and PAA. In this study, PSU base membranes are modified with PAH/PAA PEMs using the LbL adsorption technique with the employment of a flow cell. A direct microscopic observation membrane filtration system is used to observe the deposition of fluorescent *E. coli* cells on PEM-modified membranes under a constant permeate flux and a constant cross-flow velocity in the absence and presence of calcium cations (10 mM NaCl and 1 mM $CaCl_2$+7 mM NaCl, respectively). After the deposition stage of each filtration experiment, the reversibility of bacterial deposition on the PEM-modified membrane is evaluated by first rinsing the membrane with the same solution that is used for bacterial deposition, followed by a low-ionic strength solution (1 mM NaCl), in the absence of permeate flux. The deposition kinetics and reversibility of bacterial deposition for the PEM-modified membranes are then compared to the values for the PSU base membranes in order to assess the anti-adhesive properties of the modified membranes. Our results show that the modification of PSU membranes with PAH/PAA PEMs can reduce the bacterial deposition kinetics and significantly enhance the reversibility of bacterial deposition both in the absence and presence of calcium. Interaction forces between a carboxylate modified latex (CML) colloid probe and the membrane surfaces are measured through atomic force microscopy (AFM) to elucidate the mechanisms for the bacterial anti-adhesive properties of the PEM-modified membranes.

2. Materials and methods

2.1. Base membranes

In this study, PSU membranes (Pall Corporation, Ann Arbor, MI) were used as the base membranes on which PEMs were assembled. The MF membranes are asymmetric in structure and have a nominal pore size of 0.2 μm on the active side. Through attenuated total reflection infrared spectroscopy (ATR-IR) analysis, the composition of the membranes was verified to be PSU. Details about the ATR-IR analysis are provided in the Supporting Information (SI) and the ATR spectrum is presented in Fig. S1 of the SI. The membranes were received as flat sheets and cut into smaller coupons. The membrane coupons were then rinsed and soaked in deionized (DI) water (Millipore, Billerica, MA) for at least three days at 4 °C before use.

2.2. Polyelectrolytes

PAH (M_w=15,000) and PAA (M_w=50,000) were purchased from Sigma-Aldrich (St. Louis, MO) and Polysciences, Inc. (Warrington, PA), respectively. Both polyelectrolytes were used as received without any further purification. The PAH and PAA solutions that were used to modify the membrane surfaces were prepared by dissolving the polyelectrolytes in DI water and were used within eight days after preparation. The concentration of both polyelectrolyte solutions was 20 mM (based on the repeat unit molecular weight). The ionic strength of both polyelectrolyte solutions were adjusted to 150 mM with NaCl, and the pH was adjusted to 3.0 with either 1 M HCl or 1 M NaOH.

2.3. Membrane modification by layer-by-layer adsorption technique

PSU membranes were modified with PAH/PAA multilayers through the LbL adsorption technique using an approach similar to that of Mendelsohn et al. [16]. A custom-made flow cell was used for membrane modification. The flow cell comprised two polycarbonate plates, and the cross-flow channel was 89.0 mm in length, 45.0 mm in width, and 2.5 mm in height. The PSU membrane to be modified was held tightly between the top and bottom plates with double O-rings, with the active side facing the top plate, to provide a leak-proof seal. To assemble a single bilayer of PAH and PAA on the PSU membrane surface, the active side of the PSU membrane was first rinsed with a PAH solution for 12 min