Designing a Biocidal Reverse Osmosis Membrane Coating: Synthesis and Biofouling Properties

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ABSTRACT

A biocidal coating was developed in order to reduce biofouling on a reverse osmosis (RO) membrane using a quaternary ammonium (QA) functionalized polymer. The synthesis of a series of polysulfone (PS) ionomers with QA groups is described, and a method for spraying these QA ionomers as an alcoholic solution, which dried into water insoluble coatings. Contact angle and streaming potential were used to analyze the coating's hydrophilicity and surface charge. Both PS-QA1 and the commercial RO membrane had an apparent contact angle of 68° that increased to 126° for PS-QA12 corresponding to alkyl chain length. A negatively charged particle-probe was used to measure coated and uncoated RO membrane interaction forces. Measured interaction forces correlated strongly with the length of alkyl chains or hydrophobicity of the coated surfaces. Uncoated RO membranes and ones coated with PS-QA were exposed to suspensions of *E. coli* cells. All four PS-QA coatings showed significant biotoxicity and killed 100 % of the *E. coli* cells, but uncoated RO membranes had metabolically active biofilms. However, coatings tested in a RO crossflow system showed a flux reduction that is attributed to mass transfer resistance due to excessively thick films.

Keywords

Reverse Osmosis membrane; Biofouling; Antibacterial activity; Polycation coating; Quaternary ammonium ionomer

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1. INTRODUCTION

Technical solutions are still needed to economically produce fresh water as populations and agricultural demands continue to grow due to increasing populations. If future water needs are not addressed with improved desalination and water remediation technologies, it is anticipated that water shortages may escalate globally. Membrane-based separation processes, such as reverse osmosis (RO), are commonly used in industrial applications for water desalination, and wastewater treatment. RO is generally considered the simplest and most efficient method to desalinate water [1]. Despite commercially available RO membranes successes, they are susceptible to a variety of types of fouling, which can reduce water flux through a membrane and lead to greater energy requirements to produce desalinated water. Among these types of fouling, biofouling is considered to be the most serious problem [2].

RO uses polymeric membranes comprised of a thin active layer supported on a porous substrate. This active layer is most commonly made of a cross-linked polyamide. Many attempts have been made to improve the performance of these membranes by modifying the active layer to minimize the interfacial energy at the polymer-water interface. Making a surface more hydrophilic has been shown to increase its resistance to the adsorption of foulants [3]. Hydrophilic membrane surface modification procedures have included the brush-like attachment of both PEG [4,5] and poly(acrylate) [6,7] oligomers, the use of hydrophilic block copolymers as coatings [8], and the incorporation of hydrophilic

macromolecules directly into the polyamide active layer [9]. Other approaches include creating polyamide nanocomposites based upon metal alkoxides (SiO_2 , TiO_2 , Al_2O_3 , Fe_3O_4 , ZrO_2), metals (Ag, Cu, Se), zeolites, clays, carbon nanotubes, organic materials (Chitosan, polyhedral oligomeric silsesquioxanes, polypyrrole), and biomaterials (Aquaporin, Lignin) [10, 11].

An alternative approach to reduce biofouling would be to modify the surface of the membrane or other system components in such a way that it would kill bacteria on contact. Various quaternary ammonium (QA) compounds have long been known to have excellent bactericidal properties. This is believed to be the result of two important structural features: (1) the positive charge on the nitrogen atom in the QA group creates an electrostatic attraction and strong interaction with the negatively charged surface of bacterial cells and (2) a lipophilic hydrocarbon chain (usually 12-18 carbon atoms long) can disrupt the cell membrane structure and interfere with the membrane function, which eventually causes the loss of cytoplasmic constituents leading to cell death [12]. Furthermore, it has been shown that polymers containing QA groups exhibit higher antibacterial activity against various types of bacteria than their monomeric analogues [13-15]. These QA ionomers were soluble in water making them unsuitable for coatings in aqueous environments.

A QA compound with trimethoxysilyl functionality was developed by Dow Corning (Dow Corning[®] 5700 Antimicrobial Agent) as a means of imparting antimicrobial activity to treated surfaces. The trimethoxysilyl groups can react with hydroxyl groups on surfaces such as glass and cotton to form covalent bonds that keep the compound from dissolving in water. The trimethoxysilyl groups can also react with each other such that a cross-linked silane network coats the treated surfaces. These coatings have been shown to impart biocidal activity to surfaces in many applications without the release of chemical agents into the surrounding environment [16-19]. Unfortunately, this approach cannot be used to treat RO membranes because they have no hydroxyl surface groups and the hydrophobic silane network may inhibit water flux through the membrane.

Other methods for activating a surface to attachment a QA species could be oxidative plasma treatment, which is cumbersome and would damage the thin polyamide layer if

used on a RO membrane [20, 21]. A series of polyurethane coatings with pendant QA groups have been reported that demonstrated excellent biocidal activity and durability in water, but it required curing conditions that could be damaging to a potential RO membrane substrate [22-28].

This work describes the preparation of a series of QA-containing polymers that can be applied to a variety of surfaces by spraying alcohol-ionomer solutions. These coatings were created in order to kill bacteria at the membrane surface in order to prevent their attachment. The objective is to determine whether these coatings result in a reduction in surface biofouling for a RO membrane.

2. EXPERIMENTAL

2.1. Materials

4,4'-Isopropylidenebis(2,6-dimethylphenol) (tetramethyl bisphenol A or TMBPA) was recrystallized from toluene and dried under vacuum, and 4-fluorophenyl sulfone was recrystallized from ethanol and dried under vacuum. All other reagents and solvents were purchased from commercial vendors and used without further purification.

2.1.1. Tetramethyl polysulfone synthesis (TMPS)

A 3-necked flask equipped with a mechanical stirrer used a nitrogen atmosphere that flowed through the flask and a distillation head. A typical polymerization reaction involved charging the reaction vessel with TMBPA (8.53 g, 30 mmol), 4-fluorophenyl sulfone (7.63 g, 30 mmol), K₂CO₃ (8.29 g, 60 mmol), anhydrous N-methylpyrrolidinone (NMP, 98 mL), and toluene (49 mL). The polymerization reaction was heated at 150 °C for 4 h while toluene and water were removed as an azeotrope by distillation. The temperature was raised to 160 °C and held there for 19 h. After cooling to room temperature, the reaction was poured into 0.1 M HCl (0.5L) and mixed in a Waring blender. The precipitate was Soxhlet extracted with water for 24 hours and then dried under vacuum to yield a tan solid (14.66 g, 98%). The tetramethyl polysulfone (TMPS) weight average molecular weight was 132,000 with a polydispersity of 2.1.

2.1.2. Brominated tetramethyl polysulfone synthesis (Br-TMPS)

The brominated TMPS (Br-TMPS) was prepared by dissolving TMPS (32.0 g) with 1,1,2,2-tetrachloroethane (470 mL) in a flask equipped with a magnetic stir bar and a condenser. The solution was heated to 85 °C and N-bromosuccinimide (20.0 g, 112 mmol) and benzoyl peroxide (1.36 g, 5.62 mmol) were added. After 3 h, the reaction was cooled and poured into excess ethanol. The precipitate was mixed with ethanol in a Waring blender, and the solid was rinsed with water and then ethanol before drying under vacuum at room temperature to yield an orange-tan solid (37.01 g, 91%). The overall synthesis and conversion method is based upon Hibbs and Cornelius [29].

2.1.3. Polysulfone synthesis with Benzytrimethyl Ammonium (PS-QA1)

Br-TMPS (1.70 g) was dissolved in 42 mL dimethylacetamide (DMAc). A 45 wt. % aqueous solution of trimethylamine (1.0 mL, 6.5 mmol) was added and the solution was stirred at room temperature for 48 h. The solution was poured into 1 M HCl (200 mL), mixed, and filtered. The precipitate was mixed with water in a Waring blender and then triturated with more water before drying under vacuum at room temperature to yield a white solid (1.61 g, 92%). The dry polymer was mixed with a solution of lauric acid in methanol (1 wt. %) to form a solution with a polymer concentration of 2 wt%.

2.1.3. Polysulfone synthesis with Benzydimethyl-n-octyl Ammonium (PS-QA8)

This synthesis was the same as described for PS-QA1 except that dimethyl-n-octylamine was used instead of trimethylamine. The dry polymer was mixed with a solution of lauric acid (1 wt%) in methanol to form a solution with a polymer concentration of 3 wt%.

2.1.4. Polysulfone synthesis with Benzydimethyl-n-decyl Ammonium (PS-QA10)

This synthesis was the same as described for PS-QA1 except that dimethyl-n-decylamine was used instead of trimethylamine. The dry polymer was mixed with a solution of lauric acid (1 wt%) in a mixture of methanol and ethanol (1:1 v/v) to form a solution with a polymer concentration of 2.5 wt%.

2.1.5. Polysulfone synthesis with Benzydimethyl-n-dodecyl Ammonium (PS-QA12)

This synthesis was the same as described for PS-QA1 except that dimethyl-n-dodecylamine was used instead of trimethylamine. The dry polymer was mixed with a

solution of lauric acid (1 wt%) in ethanol to form a solution with a polymer concentration of 1.7 wt%.

2.1.6. QA Coating on RO Membrane

An airbrush was used to spray known polymer mass solutions onto substrates such that the mass coverage was 10 mg/in^2 m_c , and the average density ρ of PS-QA series is 1.72 g/cm^3 . The ratio of m_c/ρ is the thickness of the film, which was set at $9 \text{ }\mu\text{m}$ for this set of experiments. This coating process led to very producible coatings in terms of thickness and uniform coverage. The substrates were either poly(sulfone) EW ultrafiltration membranes or GE Sepa™ polyamide RO membranes both purchased from GE Osmonics. The RO membrane nominal active layer thickness was $0.2 \text{ }\mu\text{m}$.

2.2. Coating Preparation

The synthetic scheme for the preparation of the polymers is shown in Fig. 1. The parent polysulfone (PS), TMPS, was prepared by the condensation of 4-fluorophenyl sulfone with TMBPA. In order to drive the reaction to high molecular weights, the product water was removed by azeotropic distillation with toluene. As previously noted, the weight average molecular weight for the batch of TMPS used to make the coatings in this study was 132,000 with a polydispersity of 2.1.

Insert Figure 1

The benzylic methyl groups on TMPS were brominated using *N*-bromosuccinimide (NBS) as a source of bromine and benzoyl peroxide as an initiator. The degree of functionality (DF) is defined as the number of bromomethyl groups per polymer repeat unit and thus has a maximum possible value of 4. All of the PS-QA polymers prepared for this study were made from a batch of Br-TMPS with a DF of 1.44 (ion exchange capacity $1.9 \text{ mmol QA/g dry polymer}$). This value was chosen in order to allow for the maximum density of QA groups without rendering any of the polymers soluble in water.

The substitution reaction to form the quaternary ammonium groups took place at room temperature by mixing the desired tertiary amine with a DMAc solution of Br-TMPS. In all cases the neat amine was used, except for trimethylamine, which was an aqueous

solution. When the QA groups were initially formed, the counter ions were bromide ions. Later during the work-up, the polymers were precipitated in 1 *M* HCl at which time the bromide ions were exchanged for chloride ions. In the chloride form, the PS-QA polymers were not very soluble in alcohols, so an excess of sodium laurate was added to help them dissolve. Exchange of the chloride ions for laurate ions caused the long, flexible chains to become closely associated with the polymer chains. Although there was no covalent attachment of the laurate ions to the polymers, their presence enabled the PS-QA polymers to be dissolved in methanol, ethanol, or a mixture of both.

2.3. Characterization and Measurements

Gel permeation chromatography (GPC) was performed with a liquid chromatograph equipped with a Viscotek VE2001 isocratic pump and autosampler and a Viscotek VE3580 refractive index detector. The mobile phase was tetrahydrofuran and the system was operated at 25 °C with a flow rate of 1.0 mL/min. The weight-average molecular weights were measured by calibration with polystyrene standards.

A scanning electron microscope (SEM) using a Zeiss Supra 55VP field emitter gun was used to image a PS membrane cross-sectional sample. The contact angle measurements were performed using a VCA-2500 system (AST Products, Bellerica, MA) after a drop (~2.5 μ L) of DI water was placed on each membrane surfaces. Each measurement provided left and right contact angles, and the average of the 10 measurements (20 values) were calculated.

Zeta (ζ) potentials of the prepared membranes were determined from streaming potential measurements using an asymmetric clamping cell (EKA, Brookhaven Instruments, Holtsville, NY). These potentials were measured using an Anton Paar SurPASS Electrokinetic Analyzer and associated software (Anton Paar USA, Ashland, VA). Two membrane samples separated by a spacer were loaded into the clamping cell, creating a channel for electrolyte flow. The cell channel length is L , its cross-sectional area is A , and the electrical resistance is R . A 10 *mM* NaCl solution was used as the background electrolyte for all experiments. The streaming potential was measured as a function of feed pH, streaming potential U_s , solution conductivity κ , applied hydraulic pressure P , permittivity of free space ϵ_o (8.854×10^{-12} C²/J-m); and test solution viscosity η and

permittivity ϵ . The streaming slope potential versus pressure was calculated as $\Delta U_s/\Delta P$, and the Fairbrother-Mastin approximation ($L/AR = \kappa$) was used in the calculation of ζ from streaming potential shown in Equation 1 [30].

$$1) \quad \zeta = \frac{\Delta U_s}{\Delta P} \frac{\eta \kappa}{\epsilon \epsilon_0} \frac{L}{AR} = \frac{\Delta U_s}{\Delta P} \frac{\eta}{\epsilon \epsilon_0} \kappa$$

Before the start of each experiment, the feed pH was manually adjusted to pH 9 using 0.1 M NaOH. A 0.1 M HCl solution was then added automatically during each run, to decrease pH from 9 to 3. Four measurements, two in each flow direction (left to right and right to left), were made at each pH, and the average and standard deviation of these four values are reported. For experiments investigating the effect of charged surfactant on ζ , and 150 mg/L of dodecyltrimethylammonium bromide (DTAB) was added to the electrolyte solution.

Interaction forces with a negatively charged particle probe were measured by atomic force microscopy (AFM) (Digital Instruments, Santa Barbara, CA) as described on our previous study (Elimelech *et al.* [31]). A silica particle (Interfacial Dynamics Corp., Portland, OR), 3 μm in diameter, was glued to the end of a commercial 0.06 N/m SiN tipless cantilever (Veeco Metrology Group, Santa Barbara, CA). Force measurements were performed in 1 mM NaCl solution at a tip speed of 1 $\mu\text{m/s}$. The force was normalized to the radius of the particle, R. For a given system, F/R should be a good indicator of the membrane fouling potential (Lee *et al.* [32]).

Bacterial cell attachment assay followed the modified method suggested by Campbell *et al* [33]. Briefly, two pieces (1 cm $\times$ 1 cm) of each membrane were placed in 100 mL of M63 media supplemented with 20 mg-glucose/L, and incubated for 1 hr at 37 °C with *E. coli* cells (1×10^6 cells/mL) that were harvested in the exponential growth phase. After the incubation, membrane coupons were gently washed with M63 media to remove loosely bound cells, then stained with propidium iodide (PI) for 15 minutes followed by SYTO®9 for 5 minutes to examine the viability of *E. coli* cells attached on each membrane surface. Metabolic activity of bound cells were further analyzed using 5-cyano-2,3-ditoyl tetrazolium chloride (CTC). After incubation with cell suspension, the

membrane coupons were washed and incubated again in M63 media supplemented with 0.2 % (w/v) glucose and 4 mM CTC for 1 h at 37 °C. The viability of the attached *E. coli* on the PS-QA coated membrane surfaces were measured by staining the cells with PI and CTC. PI stained only cells that had severe cellular damage or inactivated cells, while CTC stained metabolically active cells. Experimental procedures for viability and metabolic activity tests were explained in detail in our previous publication (Kang *et al.* [34]).

A cross-flow system was used to evaluate the most promising QA coating on a membrane and as a thin film on a porous support. [35]. Tests were run on brackish water RO desalination polyamide membranes (GE Sepa_AG). Five liters of dechlorinated, prefiltered tap water from a groundwater source was transported from the feed tank through a pump to a cross-flow membrane test cell (modified Sterlitech CF042) with an active surface area for transport of 42 cm². Temperature was controlled at 25 °C and a fixed pressure of 300 psig for all tests. Salt rejection was monitored to evaluate the coating impact on membrane performance without the presence of *E. coli*.

3. RESULTS AND DISCUSSION

3.1. Membrane surface characterization

Surface characterization was performed on a reverse osmosis membrane (GE Sepa_AG) coated with PS-QA. A 10 mg/in² mass per membrane area was used to create controllable thin films via airbrush spraying (Fig. 2a). A typical SEM cross-sectional image of a coated membrane clearly shows a uniform PS-QA1 layer with a consistent thickness of 9 µm on a porous polysulfone membrane. All sprayed films yielded a smooth and uniform surface as shown in Fig. 2b. It was observed that PS-QA films did not delaminate from the RO membrane surface after extensive testing or time. Due to possible interactions may be attributed to hydrogen bonding between the QA group and thin film composite containing amide groups. This attribute may be due to mechanical adhesion between the QA coating and membrane surface created by the spraying technique. This initial study focused upon thick coatings in order to ensure a continuous coating without defects. Ultra thin coatings may lead to defects such as dewetting of the polymer solution, and incomplete or uneven surface coverage. These heterogeneous surfaces would create areas

where the RO membrane would not be properly covered and a change in roughness may influence the biofouling process. In this study, it is appreciated that the film's thickness is an order of magnitude too thick for commercial applications. This increased film thickness will decrease water flux that will be discussed in a subsequent section, and will be explored as a separate study in a future effort.

Insert Figure 2

A streaming or Zeta (ζ) potential surface measurement is a technique to determine a film's surface polarity while it is wet. It is sensitive to changes in surface chemistry, polarizability, wettability, morphology, surface roughness, and solution properties (electrolyte, counter-ion; solution and ion concentration, and pH). In this study, solution concentration, surface film forming technique, QA group's molar concentration, and solution properties were constant variables in order to probe variations in surface polarizability and wetting. At these conditions, all PS-QA coatings with a Br counter-ion had a positive ζ potential (Fig. 3). The magnitude of the positive surface charge decreased as a function of alkyl chain length attached to the QA group (17.2 mV PS-QA1, 7.22 mV PS-QA8, 6.21 mV PS-QA10, and 4.1 mV PS-QA12). This result is in sharp contrast to the uncoated RO membrane that had a strongly negative surface charge of -21.1 mV. The absolute ζ potential difference between QA-PS1 and the RO membrane is 38.3 mV. A 9.98 mV decrease is observed when the alkyl chain-length increases from one carbon to eight. A linear change in potential is noted with increasing QA side-group carbon length. Increasing alkyl chain length improves inductive effects that add electron density charge to the positively charged quaternary ammonium group decreasing its overall charge. Also, it is expected that steric hindrances increase with longer carbon chains that may partially mask the QA group.

Insert Figure 3

Interestingly, because there is a charge difference between the RO membrane and PS-QA coating there will be an electrostatic attraction created between the negatively charged substrate and the positively charged coatings. In particular, the quaternary ammonium group ($-N^+R_3$) basicity is much greater than the amide group ($-NHCO-$) that will lead to

complexation forces between these functional groups. This charge interaction led to good adhesion between PS-QA and polyamide RO membrane surface. Composite film integrity and good film adhesion was empirically evaluated by PS-QA resistance to film delamination from the RO membrane's surface after long periods of exposure to saline water during desalination testing. These complexation forces may provide an efficient route to functionalize surface with sufficient charge differences.

Apparent water contact angle measurements were made at steady-state when the membrane surface, liquid drop, and their liquid/vapor interface were allowed to come to equilibrium at constant temperature and relative humidity. At these testing conditions, PS-QA1 had a contact angle of 73° . This water contact angle increased from 73° to 97° for methyl (PS-QA1) to octyl (PS-QA8), and 119° to 126° for decyl (PS-QA10) to dodecyl (twelve) carbon side-chains. The uncoated RO membrane had an apparent water contact angle of 68° as shown in Fig. 4.

Insert Figure 4

In general, water contact angles smaller than 90° are associated with hydrophilic surfaces and angles greater than 90° are linked to hydrophobic ones. The PS-QA apparent water contact angle measurements revealed that they transitioned from hydrophilic to hydrophobic with increasing alkyl chain length, and the RO membrane's polyamide surface is hydrophilic. A significant water contact angle from 68° to 126° was shown to be a function of increasing alkyl chain length. This is a 46% change in surface properties, which reveals a surface transition from hydrophilic to hydrophobic. The observed hydrophobicity changes are partly attributed to physically shielding of the QA charge due to increasing carbon chain length. This result is consistent with the ζ potential surface charge decreasing from 17.2 mV (PS-QA1) to 4.1 mV (PS-QA-12).

It is important to note that many polymers exhibit hydrophobic surfaces, but surfaces with contact angles greater than 120° are typically associated with highly hydrophobic materials such as fluorinated materials. PS-QA is an ionomer and not in this class of polymer. In order to achieve a higher contact angle with a hydrophilic material, it must have some degree of roughness as shown by Mazumder [36]. In this work, an ionomer

(Nafion) and a series of Pt/carbon/ionomer composites were coated on 3M micro-replicated brightness enhancement films (BEFP) to probe the role of roughness and contact angle of hydrophilic materials. Nafion's apparent water contact increased from 78.4° to 101.5° because of the 10 µm air gap between BEFP coated surface features. This air gap provides an area for the water's vapor pressure to reduce the liquid's contact with the surface yielding a larger contact angle. While surface roughness may be introduced by spraying PS-QA solutions onto the RO membranes; this will be investigated in a future study, but it does reveal a weakness associated with surface property discussions solely based upon a water contact measurement.

In order to further quantify PS-QA ($^+NR_4$) surface charge changes; the interaction forces between the modified and unmodified RO membrane surface and a silanol (R_3SiOH) coated AFM probe tip were measured during retraction (Fig. 5). The uncoated RO membrane had a retraction force per length of -0.82 mN/m. This force increased with QA alkyl length in the following order -2.35 mN/m (PS-QA1), -6.97 mN/m (PS-QA8), -11.40 mN/m (PS-QA10), and -20.84 mN/m (PS-QA-12). As previously stated, this is partially attributed to an increasing electron donating ability of the alkyl chain with length due to inductive effects. This analogous effect occurs between NaOH and KOH giving rise to differences in basicity strength.

Insert Figure 5

The inductive effect enhancement and subsequent basicity decrease should impact the overall positive charge of the quaternary ammonium group. A silanol is considered to be “relatively” acidic with a pKa of 13.6 and changing the quaternary ammonium substituent group with carbon chain length is expected to be marginal with a nominal pKa value of 10.8 [37]. When the R_3Si-OH coated AFM tip comes into contact with the PS-QA film surface, the carbon chain length should attenuate it. This trend is observed with increasing chain length such that a greater retraction force is needed to remove the tip from the surface. These PS-QA film's retraction force changes may be associated with a surface becoming more hydrocarbon-like. Future studies will be done in order to characterize this observation.

3.2. Antimicrobial surfaces

E. coli attachment onto the series of PS-QA coatings were shown to be dependent on the measured surface ζ potential, apparent water contact angle (hydrophobicity), retraction force, and alkyl side-chain length (Fig. 6). However, the uncoated RO membrane results did not correlate well with PS-QA, which is due to chemical functional group differences. In this study, the attached *E. coli* cells/cm² increased in the following order: 16,600 (PS-QA12) > 8,740 (PS-QA10) > 3,420 (PS-QA8) > 2,170 (RO membrane) > 680 (PS-QA1).

Insert Figure 6

A trend is noted for all surface measurements, cell attachment appears to be strongly influenced by the alkyl chain length attached to the QA group (Fig. 6d). This result was counter intuitive because *E. coli* cell has a negative surface charge that should give rise to higher fouling for the more positively charged PS-QA1. However, this coating had the lowest concentration of cells on its surface. Consequently, cell attachment is not simply determined by electrostatics/surface charge. Interestingly, PS-QA surface property measurements appear to suggest that lower *E. coli* fouling is achieved with a surface that is simultaneously positive and hydrophilic (Fig. 6a and 6b). Additionally, this tailored surface must also have a low attractive affinity for biological cells, which is not a simple materials task. As previously noted, *E. coli* cell attachment appears to be strongly influenced by the presence of hydrophobic alkyl chains attached to the QA groups. Our finding was shown in a previous cell interaction effort using an immobilized QA coating having a 12-carbon alkyl chain. Nakagawa *et al.* concluded that cell adsorption was predominantly influenced by hydrophobic forces associated with low QA group concentration (2.7 mmol/g) [28]. While our PS-QA polymer QA concentration is 1.9 mmol/g, cell adhesion properties corresponded strongly with alkyl chain length, which is in agreement with this work.

In Fig. 7, live and dead *E. coli* cells were expressed as a percentage for all coatings. All four PS-QA coatings showed significant biotoxicity, but the uncoated RO membrane did not provide any protection. Initial biofilm staining was done using propidium iodide (PI) that is excluded from viable cells and ones that are still impermeable to the dye. Dead *E. coli* cells with damaged cellular membranes will have their DNA exposed to PI that will

intercalate with nucleic acid pairs. The bound PI molecule gave rise to enhanced excitation that was observed as a fluorescence signal. This signal was used to normalize the *E. coli* concentration, and qualitatively determine that approximately 80% to 90 % of all cells had cellular damage and assumed non-viable. Due to the non-quantitative nature of PI staining, 5-cyano-2,3-ditolyl tetrazolium chloride (CTC) was used to determine the metabolic activity *E. coli* cells. CTC was chosen because of its sensitivity associated with the respiration and subsequent metabolic activity of a viable cell [38]. Viable cells convert CTC into an insoluble fluorescent formazan. As with PI staining, the CTC conversion to a fluorescing molecule was used to determine the concentration of metabolically active *E. coli* cells. Utilizing this technique, no live *E. coli* cells were detected on any PS-QA surfaces. This approach also showed that the uncoated RO membrane's surface was still metabolically active.

Insert Figure 7

Discovering that all four QA coatings had approximately equivalent antimicrobial properties was surprising given the increasing number of attached *E. coli* cells. Interestingly, QA containing polymer's antimicrobial effectiveness against Gram-negative bacteria (such as *E. coli*) was shown by Ikeda and Dizman to be very good [26, 27]. Our results support their conclusion that *E. coli* cells are killed by a QA functionalized polymer. However, these works considered unsymmetrical QA polymers with a general functionality of $-N(CH_3)_2R$ where R is an alkyl chain with a length of two to sixteen carbons. The QA materials evaluated in this work are symmetrical and of the form $-NR_3$. While their chemistries are quite different from our work, a similar conclusion is reached, which is that antimicrobial properties are due to cell adsorption onto a QA surface. Furthermore, variations in surface biotoxicity of *E. coli* are due to carbon side chain length.

3.3. Membrane Cross-Flow Desalination Testing

In this study, a fixed pressure of 300 psig was used at a salt concentration of 1800 $\mu S/cm$. PS-QA1 coated on a commercial RO membrane, and a microporous polysulfone (PSf) support were compared to the commercial RO membrane. The PS-QA1 desalination properties were selected for study because of its lower concentration of dead *E. coli* cells

on its surface. Also, the works of Ikeda and Dizman showed that smaller alkyl chains were able to regenerate their biocidal surfaces much better than longer ones [26, 27]. A 9 μm thick PS-QA1 coating on a RO membrane had a water flux of 6.21 L/(m²-hr) and a salt rejection of 98.5%, which is a promising salt rejection result. However, the water flux is nearly an order of magnitude less than the commercial RO membrane having a flux of 44.2 L/(m²-hr). Nevertheless, it is important to recognize that the commercial membrane is 44 times thinner than the PS-QA1 film, and there will be a large mass transfer resistance created between the interface of the RO membrane's polyamide thin film composite (TFC) layer and the PS-QA1. In order to "qualitatively" demonstrate it, an equivalent PS-QA1 layer (9 μm) was sprayed onto a microporous PSf film. The water flux increased to 35.3 L/(m²-hr) with a salt rejection of 74%. This water flux is 20% less than the RO membrane at a thickness 44 times greater than the RO membrane. While significant improvements are still required for this family of PS-QA coatings, it is clear that optimizing its thickness will yield higher water fluxes with surfaces that still possess biocidal activity. Future efforts will be related to optimizing the process of creating ultrathin coatings. One approach to yield thin films will include dip coating to create Langmuir-Blodgett "like" coatings with very dilute solutions.

Insert Figure 8

4. CONCLUSIONS

A series of poly(sulfone)s with quaternary ammonium groups were synthesized and converted into polymer-alcoholic solutions. These solutions were shown that they could be sprayed to coat a surface, QA coatings were durable and survived pressure driven flow, and QA surfaces generate a biocidal layer. The alkyl chain length of the QA group affected its surface charge and hydrophilicity to varying degrees, but all four coatings had excellent antimicrobial activity towards *E. coli* cells. The PS-QA1 coating on a RO membrane did not impact salt rejection, but it did result in a significant decline in water flux. While biocidal activity is noted for these materials, their desalination rates are not competitive with commercial materials. However, the concept of designing a biocidal surface with good desalination properties is demonstrated by this work.

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FIGURES

Fig. 1. Synthesis of poly(sulfone) with quaternary ammonium groups.

Fig. 2. (a) Spray coating RO film to yield a 10 mg/in^2 coating that yielded $9 \text{ }\mu\text{m}$ thin films. (b) SEM cross sectional image of a polysulfone ultrafiltration membrane (PSf) coated with a PS-QA1 coating (PS-QA1-PSf).

Fig. 3. Streaming potential measurements of PS-QA1, PS-QA8, PS-QA10, PS-QA12, and an uncoated RO membrane.

Fig. 4. Apparent water contact angles of PS-QA1, PS-QA8, PS-QA10, PS-QA12, and an uncoated RO membrane.

Fig. 5. AFM retraction force curve measurements using a 3 μm silica colloid probe and RO membranes coated with PS-QA versus uncoated films.

Fig. 6. *E. coli* cell attachment on PS-QA1, PS-QA8, PS-QA10, PS-QA12, and uncoated RO membrane versus (a) zeta potential, (b) water contact angle, (c) retraction force, and (d) alkyl chain length attached to the QA group.

Fig. 7. Cell viability on coated membranes after 1h incubation with 10^6 *E. coli* cells/mL.

Fig. 8. Percent desalination versus water flux (L/(m²-hr) using a fixed pressure of 300 psig for PS-QA1 (9 μm), PS-QA1-PSf (9 μm) coated onto a micro-porous polysulfone membrane (PSf), and a commercial RO membrane (0.2 μm).