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Development of anti-biofouling feed spacers to improve performance of reverse osmosis modules

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ABSTRACT

This study investigates the biofouling resistance of modified reverse osmosis (RO) feed spacers. Control spacers (made of polypropylene) were functionalized with a biocidal coating (silver), hydrophilic (SiO_2 nanoparticles) or superhydrophobic (TMPSi-TiO_2 nanoparticles) anti-adhesive coatings, or a hybrid hydrophilic-biocidal coating (graphene oxide). Performance was measured by adhesion assays, viability tests, and permeate flow decline in a bench scale RO system. The control spacers proved to be one of the better performing materials based on bacterial deposition and dynamic RO fouling experiments. The good anti-adhesive properties of the control can be explained by its near ideal surface free energy (SFE). The only surface modification that significantly reduced biofouling compared to the control was the biocidal silver coating, which outperformed the other spacers by all measured indicators. Therefore, future efforts to improve spacer materials for biofouling control should focus on engineering biocidal coatings, rather than anti-adhesive ones.

1. Introduction

Due to a growing global population, expanding economies, and a broadening international middle class, by 2030, the United Nations projects the world will face a global water deficit of 40% (UN water 2015). In order to meet the rising demand for freshwater, utilities around the world are turning to non-traditional sources such as seawater and wastewater. The high salinity of seawater and, to a lesser degree, wastewater, means that these alternative feedwaters must be desalinated for domestic, industrial, or agricultural uses (Wade Miller, 2006). Desalination via reverse osmosis (RO) using thin-film composite (TFC) membranes is the industry standard for desalination due to RO's high energy-efficiency compared to other large-scale desalination technologies (Fritzmann et al., 2007). However, RO desalination is still burdened by substantial economic and environmental costs, both of which must be addressed to ensure the sustainability of this increasingly important water treatment process.

Biofouling, or the attachment and proliferation of microorganisms on a surface, reduces the efficiency of RO and contributes to the high economic and environmental costs of operating RO systems. The formation of biofilms, a heterogeneous assembly of microbial cells and extrapolymeric substances (EPS), in membrane modules increases the hydraulic resistance in the feed channel, and therefore the energy required to move water through the membrane (Chong et al., 2008). Biofouling in membrane modules requires extensive chemical cleaning procedures, which increases costs associated with chemical use, reduces the membrane lifetime, and forces downtime in water production (Flemming, 1997; Madaeni et al., 2001). Due to biofilm-enhanced osmotic pressure at the membrane interface, biofouling can also negatively impact the quality of the permeate (Herzberg and Elimelech, 2007). Altogether, the impact of fouling leads to significant economic impacts, with previous work estimating the costs of biofouling and biofouling control to be as high as 30% of the plant's total operating costs (Flemming, 1997).

Significant research efforts have been made towards designing biofouling resistant membranes and reducing the costs associated with biofilm formation (Rana and Matsuura, 2010; Kochkodan and Hilal, 2015). The most common strategy is to modify membranes

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with biocidal or anti-adhesive properties to reduce deposition of bacteria or inhibit their proliferation (Bogler et al., 2017). Membranes that express biocidal properties are often coated with toxic substances so that microorganisms are impaired and/or removed from the surface. Membranes coated with biocidal materials such as silver, copper, graphene oxide, and selenium have been shown to outperform control membranes in terms of flux decline and biofilm formation (Akar et al., 2013; Perreault et al., 2014; Yin et al., 2013; Ben-Sasson et al., 2014). On the other hand, anti-adhesive coatings aim to minimize the attachment of microorganisms to the surface. This is typically achieved by altering the surface characteristics that makes a membrane prone to fouling, namely hydrophobicity, roughness, surface charges, and surface free energy (Kato et al., 1995; Vrijenhoek et al., 2001; Asatekin et al., 2007; Salta et al., 2010; Zhao et al., 2015).

Most research on fouling control in membrane processes has focused on membrane modifications (Vrouwenvelder et al., 2009). However, modifying the polyamide layer of RO membranes can be challenging since the anti-adhesive modifications often alter the membrane performance or are hard to implement in the current roll-to-roll fabrication process at the industrial scale (Rana and Matsuura, 2010; Kochkodan and Hilal, 2015). Conversely, feed spacers, which provide a channel for water to flow through and induce turbulence to reduce concentration polarization, are passive surfaces that can be easily functionalized without affecting the membrane permeability (Araujo et al., 2012; Ronen et al., 2013, 2016). More importantly, spacers have been shown to have a disproportionately high impact on the feed channel pressure drop when fouled. For example, fouled feed spacers led to a 4 times higher increase in feed channel pressure drop compared to the same amount of biomass fouling on the membrane (Vrouwenvelder et al., 2009; Bucs et al., 2014). Additionally, biofilms on spacers can shear off and redeposit on membranes, resulting in increased membrane fouling (Radu et al., 2014). Research by Yang et al. further confirmed the importance of spacers in fouling, as RO modules with nanosilver-coated spacers outperformed nanosilver-coated membranes in terms of permeate flux (Yang et al., 2009). However, most of the research efforts have focused on antimicrobial spacer designs, and the optimal approach for biofouling mitigation on feed spacers is yet to be established (Bucs et al., 2014; Radu et al., 2014; Ronen et al., 2016, 2013). To date, no studies have compared the efficacy of anti-adhesive spacers versus antimicrobial ones for biofouling control in desalination systems.

In the present study, we investigated the biofouling resistance of a suite of modified feed spacers containing a broad range of anti-adhesive or biocidal surface chemistries, with the objective of identifying the surface properties that contribute most to spacer's biofouling resistance. Nanosilver was used as the biocidal coating, silica nanoparticles (SiO_2 NPs) and trimethoxypropyl silane coated titanium dioxide nanoparticles (TMPSi-TiO_2 NPs) were used as hydrophilic and superhydrophobic anti-adhesive coatings, respectively, while graphene oxide (GO) was applied as a combined anti-adhesive and antimicrobial coating. Commercial polypropylene feed spacers were used as control samples in order to compare performance against the industry standard for desalination modules and provide useful guidelines for feed spacers' material design. The performance of the spacers was measured by deposition assays and flux decline measured via biofouling experiments in a bench-scale RO system. Our findings indicate that surface free energy (SFE) was the dominant factor in predicting the materials' propensity to foul and that a biocidal coating appears to be the best strategy for biofouling control.

2. Materials and methods

2.1. Materials

All chemicals and supplies were obtained from Fisher Scientific (Hampton, NH), except as noted below. Control spacers (34 mils, polypropylene) were provided by Conwed Plastics LLC. Graphite powder (SP-1 grade, 325mesh) was obtained from Bay Carbon (Bay City, MI). Colloidal silica (Ludox HS-40), was obtained from Aldrich Chemistry (St. Louis, MO). Titanium oxide (Aeroxide P25) was obtained from Acros Organics (New Jersey). The LIVE/DEAD Baclight bacterial viability kit was obtained from Invitrogen (Molecular Probes, Carlsbad, CA). A Dow SW30XLE (FILMTEC Flat Sheet) membrane was used for all RO experiments (Midland, MI). The bench scale RO was constructed using Swagelok (Salon, OH) materials. UV/Ozone treatments were done in a BIOFORCE Nanosciences UV/Ozone ProCleaner unit. Unless specified, all chemicals were dissolved in deionized (DI) water obtained from a GenPure UV xCAD plus ultrapure water purification system (Thermo Scientific, Waltham, MA).

2.2. Spacer modification

Control spacers (Conwed Plastics, 34 mils) were cut into 0.5 cm × 2 cm pieces for the static deposition assays and 4.5 cm × 8.25 cm for the RO experiments. They were used as is (pristine spacers) or functionalized with anti-adhesive or biocidal coatings. Before use, spacers were cleaned with DI water and compressed air. Nanomaterials were dispersed using a 3800 bath sonicator (Branson Ultrasonics, Danbury, CT). Spacers modified with AgNPs were produced according to the polydopamine-mediated silver nucleation reaction described by Tang (Tang et al., 2015). Spacers coated with GO were produced following the functionalization procedure of (Romero-Vargas Castrillón et al., 2015), which first coat the surface with polydopamine to promote GO attachment via hydrogen and $\pi-\pi$ interactions between GO and polydopamine. The GO sheets were produced following a Modified Hummer's procedure (Tung et al., 2009). Spacers functionalized with superhydrophilic silica particles were produced by contacting UV/O_3-treated spacers, which have negatively charged oxygen-containing functionalities, with positively charged N-trimethoxysilylpropyl-N,N,N-trimethylammonium choride-functionalized SiO_2 NPs produced according to a previously described procedure (Fang et al., 2010). Superhydrophobic spacers were obtained by dipping control spacers in a hot xylene, trimethoxypropyl silane (TMPSi), and TMPSi-TiO_2 NPs solution for 3 s, which produced a rough TMPSi-TiO_2 coating on the spacer's surface (Contreras et al., 2014). The functionalization procedures are fully detailed in the Supplementary Information (SI).

2.3. Spacer characterization

Contact angles were taken using an Attension Theta by Biolin Scientifin (Gothenburg, Sweden) using a 1001 TPLT Hamilton syringe (Reno, NV) and flat polypropylene sticks functionalized as described in section 2.2. Contact angle (CA) data was used to determine the hydrophilicity and SFE of each material. Nanopure water was used for water contact angles (WCA), while the solvents used to solve for the SFE were nanopure water, diiodomethane, and glycerol. For both WCA and SFE at least 6 different measurements were taken. For each measurement, the Attension Theta software recorded ~200 data points over 10s. Any significant outliers or improperly measured data points were discarded, and the contact