



Surface nano-structuring of reverse osmosis membranes via atmospheric pressure plasma-induced graft polymerization for reduction of mineral scaling propensity

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ABSTRACT

Surface nano-structuring of polyamide desalination membrane with a hydrophilic poly(methacrylic acid) was shown to reduce the membrane mineral scaling propensity as demonstrated with calcium sulfate dihydrate (gypsum). A two-step approach was employed, whereby the active polyamide (PA) layer of a thin-film composite (TFC) synthesized membrane was activated with impinging atmospheric plasma, followed by a solution free-radical graft polymerization (FRGP) of a water soluble methacrylic acid (MAA) monomer, at 60 °C and initial monomer concentration of 5–20% (v/v), onto the surface of the PA-TFC membrane. The approach of creating a layer of end-grafted poly(methacrylic acid) (PMAA) surface chains was first developed and evaluated using a surrogate polyamide membrane layer interfacially polymerized onto a thin poly(ethyleneimine) (PEI) film coated onto a silicon wafer. The resulting PMAA-PA-PEI-Si surrogate membrane surface was hydrophilic with a water contact angle range of 10–17°. Structuring of the PA-TFC membrane at equivalent FRGP reaction conditions resulted in membranes of higher permeability (by a factor of 1.3–2.26) relative to a commercial RO membrane of a similar surface roughness (~70 nm) and salt rejection. Flux tests of membrane mineral scaling demonstrated that membrane mineral scaling propensity can be measurably reduced, relative to commercial membrane of the same salt rejection, while yielding equivalent or higher water permeability. The onset time for gypsum scaling for the optimal membrane surface (prepared at 10% (v/v) initial MAA concentration) was retarded by a factor of 2–5 relative to the commercial RO membrane. Current work is ongoing to further optimize the surface structure in order to increasing scaling resistance and assess the impact of surface structuring on nucleation of mineral salt crystals.

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1. Introduction

Mineral salt scaling of polyamide thin-film composite (TFC) reverse osmosis (RO) and nanofiltration (NF) membranes is a major impediment to achieving high product water recovery when desalting brackish water [1–3]. Mineral salt scaling occurs when mineral salt ions concentrate near the membrane surface, leading to solution supersaturation and subsequently salt crystallization at the membrane–solution interface [4–8]. Surface scaling results in both permeate flux decline and potential membrane damage. It is known that the membrane surface topography and chemistry have a direct impact on membrane fouling (e.g., colloidal and biofouling) [9,10]. Recently, surface graft polymerization of RO/NF membranes with hydrophilic polymers has been proposed as a means of retarding biofouling in saccharose ($M_w = 342$, 5.5 g/l) solutions [11,12] and

reducing protein (BSA at pH 4.8) adhesion [13] via modification of the native substrate surface chemistry and topographical surface structure. The end-grafted polymer chains have significant mobility when exposed to a good solvent. Therefore, it is reasonable to expect that these protective polymer layers can reduce the propensity of foulants from adhering to the membrane surface as reported in numerous studies [14–18]. The possible benefit of membrane surface structuring with end-grafted hydrophilic polymer chains to reduce membrane mineral scaling propensity has not been previously explored.

Mineral scaling on membrane surfaces is a process that results from the deposition of nuclei and bulk formed crystals onto the membrane surface or direct nucleation onto the membrane surface, and subsequent crystal growth by a diffusion-reaction mechanisms [8,19]. The hypothesis of the present approach is that a sufficiently dense coverage by terminally anchored hydrophilic water soluble polymer chains on the active (polyamide) layer of the RO/NF membrane surface should reduce the membrane-scaling propensity under super-saturated solution conditions. Such reduction in

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scaling propensity could possibly be due to a reduction of the rate of nucleation and/or adhesion of mineral crystals to the surface. Also, the water soluble polymer grafted layer could be beneficial to maintain the water permeability of the RO/NF membrane provided that the surface structuring does not result in surface blockage. The above strategy was demonstrated in the current study, with respect to mineral scaling by calcium sulfate dihydrate (gypsum) which is often encountered in inland water brackish water desalination, via nano-structuring RO/NF membranes by atmospheric pressure plasma-induced free-radical graft polymerization (APPI-FRGP).

In the present work, the end-grafted polymer layer was formed on a low pressure polyamide membrane by a recently developed two-step process of solution graft polymerization of a water soluble monomer onto active surface sites created by treatment with an impinging atmospheric pressure plasma source [20,21]. The atmospheric plasma mixture, followed by surface oxygenation results in the formation of peroxides of surface density that can be adjusted by the plasma source power, exposure period, distance between the substrate and the plasma source, as well as the gas mixture used for the plasma source [20]. In the present work, methacrylic acid, reported in previous studies as an effective membrane antifouling surface modifier [18], was selected as the monomer of choice to develop the nano-structured polyamide RO membrane surface with end-grafted poly(methacrylic acid) (or PMAA) chains. The resulting membranes were then evaluated with respect to their gypsum scaling propensity and general performance.

2. Experimental

2.1. Materials and reagents

Interfacial polymerization to create the active polyamide layer was accomplished using 1,3-phenylenediamine (MPDA, $\geq 99\%$) and 1,3,5-benzenetricarboxylic chloride (TMC, 98%), purchased from Sigma–Aldrich (St. Louis, MO). Ultra-pure deionized water was produced by filtering distilled water through a Milli-Q filtration system (Millipore Corp., San Jose, CA). Mineral salt solutions were prepared using salts of calcium chloride dihydrate ($\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$), anhydrous sodium sulfate (Na_2SO_4), and sodium chloride (NaCl), all reagent grade chemicals purchased from Fisher Scientific (Pittsburgh, PA).

Evaluation of the characteristics of the graft polymerized polymer layer (synthesized by graft polymerization) was accomplished by synthesizing the nano-structured surface layer onto surrogate polyamide–poly(ethyleneimine) membrane surface layer interfacially polymerized onto smooth prime-grade silicon (100) wafers (Wafernet, Inc., San Jose, CA) samples measuring $1\text{ cm} \times 1\text{ cm}$. Reagent grade sulfuric acid and aqueous hydrogen peroxide (30 vol%), used for silicon wafer cleaning, were purchased from Fisher Scientific (Pittsburgh, PA). Poly(ethyleneimine) (PEI, $M_w = 750,000\text{ g/mol}$), used to promote adhesion between the polyamide active layer and silicon substrate, for preparing surrogate polyamide membrane test surfaces, was purchased from Sigma–Aldrich (St. Louis, MO). Methacrylic acid, the monomer for grafting polymerization (Sigma–Aldrich, St. Louis, MO) and its aqueous solution was prepared at various volume percents. The polyamide membranes that were subsequently surface nano-structured with poly(methacrylic acid) were prepared by interfacial polymerization on a commercial polysulfone support (Hydranautics, Oceanside, CA).

Gypsum mineral scaling tests were performed with the surface nano-structured polyamide thin-film composite polyamide membrane and four different commercial low pressure reverse osmosis (RO) membranes: LFC1 (Hydranautics, Oceanside, CA), ESNA1-LF (Hydranautics, Oceanside, CA), TFC-ULP (Koch, Wilming-

ton, MA), and ESPA1 (Hydranautics, Oceanside, CA). The ESNA1-LF, ESPA1, TFC-ULP and LFC1 membranes had surface roughness of 55 [22], 123 [17], 42 [23] and 73 nm, respectively, salt rejection of 93% [24], 96% [17], 99% [23], and 95%, respectively, and water permeability of $0.21 \times 10^{-10}\text{ m/s Pa}$ [22], $0.13 \times 10^{-10}\text{ m/s Pa}$ [25], $0.18 \times 10^{-10}\text{ m/s Pa}$ [23], and $1.5 \times 10^{-10}\text{ m/s Pa}$, respectively.

2.2. Preparation of polyamide membrane surfaces

Polyamide–polyethyleneimine–silicon (PA–PEI–Si) membrane test surfaces were prepared with a typical loose RO membrane PA surface chemistry but with low surface roughness to assess the effect of graft polymerization on surface topography. The PA–PEI–Si surfaces were first used to determine the reaction conditions suitable for surface nano-structuring, as well as to evaluate the thickness of the grafted polymer layer. The PA–PEI–Si test surfaces were prepared by creating a relatively smooth thin PA layer interfacially polymerized onto a PEI–Silicon (PEI–Si) substrate ($\sim 7\text{ nm}$ PEI film thickness), followed by methacrylic acid graft polymerization onto the PA surface.

The wafer samples were first cleaned in an acid-etching process with a mixture of 70:30 sulfuric acid to hydrogen peroxide for 10 min at 90°C and then triple rinsed to remove residuals and oven dried (caution: this piranha solution reacts violently with many organic materials and should be handled with extreme care). About 1 mL of a 0.3 wt% aqueous solution of PEI, used to assist in the adhesion of PA to the silicon wafer sample, was initially spin-coated (using spin-coater model PWM32, Headway Research Inc., Garland, TX) on the cleaned silicon surface at 2500 RPM for 30 s in an inert nitrogen environment. About 1 mL of a 2.5 wt% aqueous solution of MPDA was then applied by spin-coating at 2500 RPM for 30 s onto the PEI–Si surface. Once the formation of the MPDA–PEI–silicon surface was accomplished, approximately 1 mL of a 0.13 wt% TMC solution was dispensed (via a syringe) onto the surface to initiate polyamide interfacial polymerization at a controlled chamber temperature of 25°C . The reaction was allowed to proceed for approximately 2 min, at which time the surface was washed with DI water to remove unreacted monomer and the PA–PEI–Si surface was vacuum-oven dried at 80°C for a period of 0.5 h. The PA–PEI–Si surfaces were subsequently nano-structured by graft polymerization as described in Section 2.3.

Poly(methacrylic acid) surface nano-structured PA–TFC (SNS–PA–TFC) membranes, evaluated with respect to their mineral scaling propensity, were prepared by first synthesizing an active PA layer on a polysulfone (PSF) support via conventional polyamide interfacial polymerization technology [26]. Briefly, the PSF support membrane was dipped into an aqueous solution containing MPDA (2.5%, w/w) for 3 min, followed by draining of the excess solution. Subsequently, the membrane was dipped into the organic phase containing TMC (0.13%, w/w) in hexane and allowed to react for $\sim 20\text{ s}$, followed by draining the excess organic solution and oven curing at 80°C for 30 s. The membrane was then rinsed with DI water and stored in a 1% aqueous NaHSO_3 solution. The resulting PA–TFC membrane had nanofiltration membrane performance with a water permeability of $5.2 \times 10^{-10}\text{ (m/s Pa)}$ and 30% NaCl salt rejection measured at 1000 ppm.

2.3. Poly(methacrylic acid) surface nano-structured PA membrane surfaces

Two different sets of poly(methacrylic acid) surface nano-structured polyamide membranes were prepared. The first was a membrane test surface prepared by using the surrogate PA–PEI–Si surfaces (Section 2.2). The second set was prepared using the PA–TFC membrane synthesized to match the desired permeability for the subsequent graft polymerization step.

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