Surface & Coatings Technology 279 (2015) 171–179

Contents lists available at ScienceDirect

Surface & Coatings Technology

journal homepage: www.elsevier.com/locate/surfcoat

Surface modification of reverse osmosis membranes with zwitterionic coatings: A potential strategy for control of biofouling

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ARTICLE INFO

Article history:
Received 6 May 2015
Revised 14 August 2015
Accepted in revised form 18 August 2015
Available online 29 August 2015

Keywords:
Surface modification
Reverse osmosis membranes
Antifouling zwitterionic coatings
X-ray photoelectron spectroscopy
Molecular force mapping

ABSTRACT

In this article we report enhanced antifouling properties of reverse osmosis (RO) membranes surface-modified with zwitterionic copolymer films of poly(4-vinylpyridine-co-ethylene glycol diacrylate) (p(4-VP-co-EGDA)). The copolymer films were deposited onto the surface of RO membranes via an initiated chemical vapor deposition technique (*i*CVD) followed by a quaternization reaction with 3-bromopropionic acid. XPS analysis revealed that zwitterionic moieties were highly surface-enriched; concentrated in the top ~5 nm of deposited films. Resistance to fouling of the zwitterionic coatings was investigated by determining the extent of biopolymer adsorption via quartz crystal microbalance with dissipation monitoring. The surface-modified quartz sensors exhibited superior resistance to the adsorption of two biopolymers; bovine serum albumin (BSA) and humic acid (HA). Biofouling propensity of the modified RO membranes was further investigated using two bacterial strains abundantly present in seawater. The results showed ~98% lower attachment of both *Pseudomonas aeruginosa* and *Bacillus licheniformis* bacteria onto the surface of modified membranes as compared to virgin membranes. Molecular force mapping (MFP) was employed to investigate and quantify interaction forces between model foulant BSA and both bare and modified RO membrane surfaces. The results of MFP revealed that the adhesive force between the foulant (BSA) and membrane surface was at least an order of magnitude lower for the modified membranes when compared to virgin membranes.

1. Introduction

Careful statistics indicate that every third person in this world is deprived of clean drinking water [1]. The fact that almost 98% of the world's water supply comes from seawater or brackish water has made desalination to be an important method to solve the global scarcity of fresh water. Seawater or brackish water desalination via reverse osmosis (RO) is proving as a leading technology for overcoming the stress on the global fresh water supply. Full utilization of the RO technology is however challenged by membrane fouling. Fouling results in several problems associated to membrane processes such as flux decline, high operating pressure and increased cleaning frequency resulting in a shortened lifespan of the system, and the overall effect of all these factors is an increased cost of the desalted clean water [2].

Among various types of fouling, biofouling is the most serious in nature and the most difficult to prevent and control. Biofouling has been reported as the most critical problem in nanofiltration (NF) and reverse osmosis (RO) membrane filtration processes [3]. Biofouling is caused by adhesion and accumulation of microorganisms, and subsequent biofilm formation by a variety of bacterium species found in seawater. Biofouling is known as the "Achilles heel" of membrane processes because of extremely high multiplication and growth of microorganisms over time [4]. According to a recent survey conducted in the USA, 70% of the seawater RO desalination plants suffered the serious membrane biofouling problem [5,6].

Presently, several chemical pretreatment methods are used to remove the marine biota and specially bacteria from the feed. These methods are not only energy-intensive (accounts for more than 36% of the total energy consumption of a desalination plant) but also pose environmental risks to marine life [7]. Therefore there exists an urgent need for developing novel strategies to enhance the fouling resistance of RO membranes so as to lower the energy usage, enhance process reliability and minimize the environmental impact of seawater desalination.

Membrane surface modification is an environment-friendly and effective technique which is being very actively pursued for the control and prevention of organic and biofouling. A thin film composite (TFC) RO membrane is essentially a stack of three layers: the bottom layer is made up of highly porous polyester, on top of it is a strong polysulfone

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http://dx.doi.org/10.1016/j.surfcoat.2015.08.037

layer and the uppermost layer that performs the rejection and/or permeation is composed of polyamide and is known as the barrier (or the active) layer. The active layer of commercial RO membranes is modified by deposition of ultra-thin (~30 nm) films of various polymers known for their antifouling characteristics. However, zwitterionic polymers are a class of material that has attracted recent attention due to their excellent antifouling properties and stability [8–10]. Containing both positive and negative ions, zwitterionic materials strongly bind water molecules via electrostatically induced hydration to produce a hydrated layer on membrane surface that discourages foulant adsorption.

We recently reported the first synthesis of zwitterionic copolymer coatings (containing polycarboxybetaine acrylic acetate ((pCBAA) units) via initiated chemical vapor deposition (*i*CVD) technique [11]. The surface-modified RO membranes were found more hydrophilic (compared to counterpart bare RO membranes). The optimized chemistry of copolymer ((p(85% 4-VP-co-EGDA)) coatings was found stable onto the surface of RO membranes for multi-hour exposure to DI water at higher pressure (800 psi). Furthermore, RO membranes surface-modified with the optimized zwitterionic films were found to exhibit excellent antifouling properties without significantly affecting their performance (permeate flux and salt rejection).

In this article, we focused on evaluating the surface characteristic and antifouling performance of optimized zwitterionic coatings under rigorous fouling conditions. We first demonstrate that a high surface concentration of zwitterionic moieties can be produced at the membrane surface that is essential for achieving ultralow fouling properties. This was explained by the angle resolved X-ray photoelectron spectroscopy (ARXPS) of thicker coatings deposited on Si substrates. We also demonstrate the enhanced resistance to reversible bacterial adhesion of RO membranes modified with optimized zwitterionic films. This was done by exposing membranes to two different bacterial species, namely *Pseudomonas aeruginosa* and *Bacillus licheniformis*, both of which are abundantly present in seawater. Antifouling performance of optimized zwitterionic coatings with regard to two different biopolymers (BSA and HA) was also investigated via quartz crystal microbalance with dissipation monitoring (QCM-D). The molecular force probe (MFP) was performed to investigate and quantify the intermolecular interactions (in the form of adhesive forces) between the surface of membrane under study and BSA-functionalized AFM tip.

2. Experimental

2.1. Thin film synthesis and conversion to zwitterions

Thicker copolymer coatings (up to 200 nm) of 4-vinylpiridine-co-ethylene glycol diacrylate (p(4-VP-co-EGDA)) were first deposited on test grade silicon (Si) wafers (Wafer World, USA) without any pretreatment using an iCVD reactor (Sharon Vacuum) described earlier [12,13]. In separate glass jars attached to the reactor, the EGDA monomer (vapor pressure = 0.0939 Torr at 25 °C) and the 4-VP monomer (vapor pressure = 1.68 Torr at 25 °C) were heated and the initiator tert-butyl peroxide (TBPO) was maintained at room temperature, and their vapors were fed into the chamber over heated filament arrays (80% Ni-20% Cr, Good fellow, USA). Copolymer compositions within the deposited films were varied by systematically changing the vapor flow rate of each monomer while maintaining the initiator flow rate fixed. This was accomplished by varying the flow rates of the two monomers 4-VP, EGDA and Ar gas from 6.0–6.4 sccm, 0.24–0.72 sccm and 2.0–2.6 sccm respectively, while fixing the flow rate of TBPO at 2.0 sccm. *i*CVD copolymer films of 4-VP-co-EGDA were thus synthesized to yield varying content of 4-VP (the precursor for zwitterions) from 25 to 85% in the copolymerized films. During thin film synthesis, the filament temperature was maintained at 200 °C while the substrate was fixed at 20 °C. Total pressure in the vacuum chamber was maintained at 0.450 Torr for all depositions. All chemicals were used without further purification.

An ultrathin (35 ± 3 nm) film of the optimized chemistry of zwitterionic copolymer was then deposited on desalination RO membranes. RO membranes (TFC-HR from Koch Membrane System, USA) were considered for this study and hereafter referred to as Koch membranes. Prior to deposition, the Koch membrane surface was cleaned with high purity argon and then treated with oxygen plasma for 5 min. The purpose of oxygen plasma treatment was to create dangling bond in order to have strong interface between the membrane surface and the depositing copolymer film. The Koch membranes used in this study were of thin film composite type polyamide with no prior antifouling coatings on their surfaces.

The conversion of as-deposited copolymer films (films synthesized by *i*CVD) to zwitterions was accomplished by exposing the film to vapors of the quaternizing agent 3-bromopropionic acid (3-BPA). For detailed description of the synthesis of copolymer films, film uniformity, stability onto the surface of RO membranes and quaternizing reaction the reader is directed to our earlier study [11].

2.2. Surface characterization of synthesized films: XPS and ARXPS analysis

X-ray photoelectron spectroscopy (XPS) and angle resolved XPS (ARXPS) were performed using SSX-100 Kratos Axis Ultra Spectrometer (Surface Science Instrument, USA) with a monochromatic Al Kα source (1486.66 eV). Survey scan was obtained at 150 W with pass energy and step size of 160 W and 1 eV, respectively. For high-resolution scans, the pass energy and step size were 20 W and 100 eV, respectively. Pressure during the analysis was maintained at 2×10^{-8} Torr. XPS measurements were taken from an elliptical area of approximately 1×3 mm^2 at two emission angles of 0° and 71° for the angle-resolved XPS (ARXPS). Escape depth corresponding to each emission angle was calculated utilizing the inelastic mean free path (IMFP) of the element under consideration. Samples were kept under vacuum overnight prior to analysis. Casa XPS processing software (CasaXPS Manual 2.3.15, rev 1.3, 2009, Casa Software Ltd., USA) was used to fit the high-resolution spectra with Shirley-type background. The obtained high-resolution spectra (C1s, O1s and N1s) were calibrated with respect to C1s = 284.5 eV to remove any charging effects.

Depth profiling analysis was performed on thicker (~200 nm) copolymer films deposited on Si substrates by removing the coating material (via Ar^+ ions bombardment) at an approximate etch rate of 3–4 nm/s. At least ten etch-cycles were performed removing material (~8–10 nm/etch step) to go deep down to ~90 nm from the surface of film. XPS measurements were taken after every etch step. For reproducibility, analysis were performed on duplicate samples and average reported as the amount of quaternary and protonated nitrogen present in the thickness direction (along the cross section of deposited film) as a function of film depth.

2.3. Fouling resistance testing: QCM-D analysis

Fouling propensities of modified membranes to two different model foulants, namely, bovine serum albumin (BSA) and humic acid (HA) was investigated using QCM-D. This was performed by depositing copolymer coatings on SiO_2 sensors (QSX-303, from Q-Sense) followed by zwitterionicalization of coatings with vapors of quaternizing agent 3-BPA. HA was dissolved in DI water, whereas, BSA was dissolved in phosphate-buffered saline (PBS) at solution concentration of 1 mg/mL for each foulant. Functionalized (zwitterionic) and bare (reference) sensors were placed in flow cells and allowed to equilibrate for at least 30 min at 25 °C by flowing DI water (for HA) and PBS (for BSA) at a flow rate of 100 μL/min. After achieving the stabilized flow, the solution was promptly changed to HA in DI water, or to BSA in PBS, and the frequency shift (ΔF) for each solution was monitored. The adsorbed mass of each foulant