Surface modification of seawater desalination reverse osmosis membranes: Characterization studies & performance evaluation

CrossMark

Asif Matin [a,*], H.Z. Shafi [a], Zafar Khan [a], Mazen Khaled [b], Rong Yang [c], Karen Gleason [c], Faizur Rehman [d]

[a] Depatment of Mechanical Engineering, King Fahd University of Petroleum and Minerals, Dhahran, Saudi Arabia
[b] Department of Chemistry, King Fahd University of Petroleum and Minerals, Dhahran, Saudi Arabia
[c] Department of Chemical Engineering, Massachusetts Institute of Technology Cambridge, MA, USA
[d] Research Institute, King Fahd University of Petroleum and Minerals, Dhahran, Saudi Arabia

HIGHLIGHTS

- thin film deposition using all-dry technique at ambient temperature.
- minimal compromise on membrane performance.
- presence of coating confirmed by multiple techniques.

ARTICLE INFO

ABSTRACT

In this work we report surface modification of commercial reverse osmosis membranes by depositing ultrathin copolymer coatings, which could potentially enhance the biofouling resistance of RO membranes. Hydrophilic monomer hydroxyethyl methacrylate (HEMA) and a hydrophobic monomer, perfluorodecyl acrylate (PFDA) were copolymerized directly on the active layer of commercial aromatic polyamide reverse osmosis (RO) membranes using an *initiated* Chemical Vapor Deposition (iCVD) technique. Attenuated total reflective Fourier transform infrared spectra (ATR-FTIR) verified the successful modification of the membrane surfaces as a new FTIR adsorption band around 1730 cm^{-1} corresponding to carbonyl groups in the copolymer film appeared after the deposition. X-ray Photoelectron spectroscopy (XPS) analysis also confirmed the presence of the copolymer film on the membrane surface by showing strong fluorine peaks emanating from the fluorinated alkyl side chains of the PFA molecules. Contact angle measurements with deionized water showed the modified membrane surfaces to be initially very hydrophobic but quickly assumed a hydrophilic character within few minutes. Atomic Force Microscopy (AFM) revealed that the deposited films were smooth and conformal as the surface topology of the underlying membrane surface remained virtually unchanged after the deposition. FESEM images of the top surface also showed that the typical ridge-and-valley structure associated with polyamide remained intact after the deposition. Short-term permeation tests using DI water and 2000 ppm NaCl water showed that the deposited copolymer coatings had negligible effect on permeate water flux and salt rejection.

© 2013 Elsevier B.V. All rights reserved.

1. Introduction

Seawater desalination by reverse osmosis (SWRO) is becoming increasingly popular due to its ease of operation, lower operational and maintenance costs, and environmental friendliness [1,2]. The heart of the process is a thin-film composite membrane composed of a nonwoven fabric, a porous support layer and a nonporous ultrathin selective layer [3,4].

However, despite possessing several advantages over contemporary techniques, the reverse osmosis process faces a major challenge of membrane fouling [5]. Fouling, which is defined as the irreversible adsorption of solutes on the membrane surface and pores, results in a significant decline in permeate water flux as well as deterioration of permeate water quality. The economic consequences of membrane fouling are a substantial increase in both operation and maintenance costs due to the need for applying higher pressures as well as frequent membrane cleaning and replacement [6].

Among the different fouling types, organic and biofouling have been identified as the most problematic and hence the most common [7,8]. In fact, biofouling is commonly referred to as the Achilles heel of membrane processes [9]. Fouling due to organic and inorganic components and microorganisms can occur simultaneously, and results in the formation of a biofilm that causes operational problems [10–12].

Membrane surface modification is an attractive technique for the control and prevention of bio fouling. The main idea behind this

approach is to modify the membrane surface characteristics to lower the affinity of foulants to the surface of the selective layer. Deposition of antifouling coatings is a simple way of membrane surface modification and has recently been the focus of several researchers. Kim and Lee [13] coated nanofiltration and reverse osmosis membranes with neutral polyvinyl alcohol (PVA) polymer and showed that the modified membrane had significantly reduced fouling levels. Louie et al. [14] used a hydrophilic polyethylene-polyamide block copolymer and found very encouraging results. Yu et al. [15] used the thermo responsive copolymer poly(N-isopropylacrylamide-co-acrylic acid) to modify commercial polyamide membranes.

Amphiphilic copolymers are another class of material that have been explored in the context of membrane fouling. Asatekin et al. [16] grafted a comb-like amphiphilic copolymer on PAN ultrafiltration membranes that consisted of hydrophilic brushes attached to a hydrophobic backbone. These membranes showed excellent resistance to biopolymers as well as bacterial adhesion [17]. Similarly, Park et al. [18] grafted of the hydrophobic polysulfone and the hydrophilic polyethylene glycol copolymers on polysulfone membranes with considerable success.

In the comb-like amphiphilic copolymers, localization of the additive at the membrane surface during immersion precipitation casting results in the formation of a dense hydrophilic "brush" of copolymer side chains, while the hydrophobic backbone intermixes with the membrane base component, serving as an anchor for the additive. The antifouling properties come mainly from the hydrophilic part (PEO/PEG) that is an integral part of the copolymer. PEO, for example, has been shown to be a very effective material to prevent adhesion of biomacromolecules and bacterial cells due to its hydrophilicity, large excluded volume, and unique ability to coordinate surrounding water molecules in an aqueous medium [19,20]. Similarly, PEG provides resistance to protein adsorption and cell adhesion by lowering the polymer-water interfacial energy [21,22].

Randomly amphiphilic copolymers are another class of amphiphilic copolymers with differences in chemistry at the molecular-scale level. Such a copolymer has hydrophilic and hydrophobic moieties located next to each other but with a distribution that is random. Due to the random nature, such a surface would be expected to discourage the adsorption of a wide variety of foulants. Baxamusa and Gleason [23] copolymerized the hydrophilic hydroxyethyl methacrylate (HEMA) and the hydrophobic perfluorodecyl acrylate (PFDA) using an *initiated* CVD technique to create such a surface. The films were deposited on silicon wafers and adsorption studies with a model protein, BSA, were also carried out. It was found that less protein adsorbed onto the copolymer as compared to the pure homopolymers and that a minimum adsorption occurred for amphiphilic chemistry (60% HEMA–40% PFDA).

Since protein adsorption and bacterial adhesion are closely interrelated events [24], surfaces that interfere with protein adsorption can be expected to resist the attachment of bacteria as well. Given that bacterial adhesion is a critical early stage event in the overall process of Biofouling [25], this surface may ultimately prove effective in the control/prevention of membrane Biofouling. Also, the technique used for the deposition of these copolymer films, *initiated* CVD, is solvent-free, all dry and carried out at ambient temperatures and thus suitable for RO membranes that are polymer-based.

In light of the above, it was thought to explore the feasibility of these coatings on standard seawater desalination membranes. This is the first part of a series of studies planned to investigate the antifouling potential of these films on RO membranes. The amphiphilic copolymer film was deposited using the *initiated* CVD technique on three different commercial membranes. The modified and virgin membranes were then characterized extensively with FESEM, AFM, FTIR, XPS and contact angle goniometer. Short-term cross flow permeation tests were carried out with a synthetic NaCl solution to determine the effect of the coating on the permeate flux and salt rejection.

2. Materials & methods

2.1. Membranes

Flat sheets (12 in by 12 in) commercial seawater desalination membranes were purchased from Sterlitech Corp. (USA). Table 1 provides the performance details of the membranes as provided by the manufacturer from tests performed using a water feed with NaCl concentration of 32 g/L (pH = 8) at a temperature of 25 °C and a pressure of 800 psi (55 bar).

2.2. Materials

The two monomer species, perfluorodecyl acrylate (97%) and hydroxyethyl methacrylate (99%), and the initiator Ter-butyl-Peroxide (98%), were purchased from Sigma Aldrich, USA and used without further purification.

2.3. Thin-film deposition

The two monomers, perfluorodecyl acrylate and hydroxyethyl methacrylate were heated in separate crucibles to 80 °C and 70 °C respectively, while the initiator was kept at room temperature. Vapors of the two monomers and initiator were metered into the iCVD reactor chamber through mass flow controllers (MKS, 1152). The relative flow rates of the monomer gases and of the initiator were adjusted to obtain a composition of 40% PFA on the copolymer.

The vapors met and mixed at a common manifold prior to entering the reactor. A throttling butterfly valve (MKS, 653B) was used to control the pressure inside the chamber at 200 mtorr (2.7×10^{-3} bar). The filaments in the reactor were heated to approximately 220 °C to promote radicalization of the initiator. The commercial RO membrane samples were placed on the reactor stage with active layer facing up. The membrane sample was adhesively taped on all sides to prevent any deposition on its backside. The membrane sample was held at a 30 °C by keeping its backside in contact with the temperature-controlled stage maintained at the constant 30 °C.

The copolymerization took place directly onto the membrane active layer and resulted in the formation of the co-polymer film with a target thickness of around 20 nm. Film growth was monitored in situ by laser interferometry with the laser focused on a single point on a silicon wafer placed adjacent to the membrane sample. The film deposition was terminated once the laser interferometry indicated attainment of the desired thickness on the silicon wafer.

After the depositions, the film thickness and composition on the silicon wafer were determined by Variable Angle Spectroscopy Ellipsometry (VASE, JA Woollam M-2000). Spectroscopic data were obtained at three different angles (65, 70 and 75°) with the wavelength range of 315–700 nm. A Cauchy–Euler model was obtained to fit the data. The uncertainty in measuring the film thickness is approx. ± 5 nm.

2.4. Membrane characterization

ATR-FTIR spectra were obtained using a Nicolet 8700 FTIR spectrometer coupled to a germanium crystal operated at 45° using OMNIC 6.2 software (Thermo Electron Corp., Hampton, NH). The active layer of the membrane was pressed somewhat tightly against the crystal plate. Carbon dioxide and water vapor were continuously purged out during

Table 1
Manufacturer information for the membranes used in this study.

Manufacturer	Code	Service	Flux (L/m²h)	Rejection (%)
Toray	80B	Seawater RO	27	99.8
GE Osmonics	AD	Seawater RO	26	99.5
Dow FilmTec	SW30HR	Seawater RO	27	99.7