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Reverse osmosis membranes surface-modified using an *initiated* chemical vapor deposition technique show resistance to alginate fouling under cross-flow conditions: Filtration & subsequent characterization

A. Matin [a,b,*], H. Shafi [c], M. Wang [d], Z. Khan [c], K. Gleason [d], F. Rahman [e]

[a] *Center for Engineering Research, Research Institute, King Fahd University of Petroleum & Minerals, Dhahran 31261, Saudi Arabia*
[b] *Center of Excellence for Scientific & Research Collaboration with MIT, King Fahd University of Petroleum & Minerals, Dhahran 31261, Saudi Arabia*
[c] *Department of Mechanical Engineering, King Fahd University of Petroleum & Minerals, Dhahran 31261, Saudi Arabia*
[d] *Department of Chemical Engineering, Massachusetts Institute of Technology, Cambridge, MA 02139, USA*
[e] *Center for Refining & Petrochemicals, Research Institute, King Fahd University of Petroleum & Minerals, Dhahran 31261, Saudi Arabia*

HIGHLIGHTS

- Amphiphilic copolymer films were deposited on RO membranes using an *initiated* CVD technique
- Coated membranes show lower flux decline and less foulant deposition in fouling tests
- Post-fouling analyses confirm the presence of the copolymer film on the membrane

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ABSTRACT

The surface of commercial reverse osmosis (RO) membranes was modified by the deposition of 2-hydroxyethyl methacrylate-co-perfluorodecyl acrylate (HEMA-co-PFDA) copolymer films using an *initiated* chemical vapor deposition (*i*CVD) technique. Antifouling characteristics of the modified and unmodified membranes were evaluated under cross-flow permeation conditions using sodium alginate as a model organic foulant. The permeate flux decline was lower in the surface-modified membranes as compared to the virgin ones while salt rejection remained almost unaltered in both virgin and coated membranes. The presence of the HEMA-co-PFDA copolymer on the fouled membrane surface is confirmed by simultaneous analyses with Attenuated Total Reflectance–Fourier Transform Infra-Red (ATR-FTIR) and X-ray Photoelectron Spectroscopy. Field Emission Scanning Electron Microscopy (FESEM) images showed a dense and continuous foulant layer on the virgin samples as opposed to a porous and discontinuous one for the coated membranes. The water contact angle values for the coated membranes registered a decrease indicating the more hydrophilic nature of the adsorbed alginate. To conclude, although fouling appears inevitable, it is considerably slowed down by this surface modification strategy.

1. Introduction

Degradation of membranes due to fouling remains a critical issue in membrane-based water purification processes such as seawater desalination using reverse osmosis. Depending on the feed water quality and operating conditions, RO membranes can be fouled by mineral precipitation [1], attachment of colloids and dissolved organics [2], and growth of microbes on the membrane surface [3].

Amongst these, fouling by organic matter and microorganisms, present in brackish and seawater, is the most critical concern in desalination [4]. Organic and biofouling, which are closely related to each other, result in permeate flux decline as well as increase in salt passage across the membrane. The consequences are significant: increasing the energy cost, shortening the membrane life and compromising the permeate quality [5]. Unlike colloidal and particulate fouling, which can be mitigated through pre-filtration, organic and biofouling require much more complex mitigation strategies.

Organic macromolecules such as proteins, polysaccharides and humic substances, which are almost always present in seawater, form a conditioning film on any kind of surface immersed in water, thus rendering the surface viable to microbial attachment [6]. Bacteria of

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* Corresponding author at: Center for Engineering Research, Research Institute, King Fahd University of Petroleum & Minerals, Dhahran 31261, Saudi Arabia.
E-mail address: amatin@kfupm.edu.sa (A. Matin).

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various species then attach to the surface, grow, reproduce and produce extracellular polymeric substances (EPS) [7], which ultimately results in the formation of a biofilm that is difficult to remove. This biofilm significantly deteriorates the membrane performance by causing enhanced concentration polarization and hydraulic resistance to the flow of water.

In general, the pursuit to combat the organic and bio-fouling of RO membranes falls into three categories [8] : (i) synthesize chlorine-tolerant membranes, (ii) fabricate membranes that resist initial biopolymer adsorption and bacterial attachment, and (iii) fabricate membranes that inactivate bacteria, rendering them no more than inert deposits of organic matter. The recent findings on chlorine aggravating the biofouling problem rather than mitigating it [9], have increased the focus of researchers worldwide on the latter options.

Membrane surface modification is an environmentally friendly and effective technique which is being very actively considered for the control and prevention of organic and biofouling [10].

Deposition of antifouling coatings is a simple way of membrane surface modification and has recently been the focus of several research groups. For example, Meng et al. synthesized a salt-responsive thin-film composite (TFC) reverse osmosis (RO) membrane by tethering a zwitterionic polymer poly(4-(2-sulfoethyl)-1-(4-vinylbenzyl) pyridinium betaine) (PSVBP) onto a commercial RO membrane. They found that the membrane was able to restore 90% of its initial flux after rinsing with brine [11].

Hydrophilic surfaces are known to be less prone to microbial attachment and hence to biofouling [12]. Hydrophilic surfaces bind a water buffer layer through hydrophilic interactions, effectively minimizing the hydrophobic interactions responsible for adhesion of hydrophobic foulants to the membrane. Many researchers have used different techniques to make the surface more hydrophilic, such as plasma treatment [13], surface immobilization or solution phase coating of hydrophilic polymers [14]. Very recently, a novel random terpolymer with the hydrophilic hydroxyethyl methacrylate (HEMA) was synthesized via free radical polymerization and used as the coating material on the polyamide thin film composite (TFC) reverse osmosis (RO) membrane to improve its chlorine resistance and antifouling performance with a high degree of success [15].

Amphiphilic surfaces represent another interesting category of antifouling chemistry that does not rely on surface hydrophilicity [16]. Their compositional heterogeneities at a molecular length scale (amphiphilic nanodomains) create a degree of chemical ambiguity, which may lower both the entropic and enthalpic driving force for biopolymer adsorption [17]. Surfaces of such characteristics are usually obtained by incorporating components with very different surface energies.

The hydrophilic 2-hydroxyethyl methacrylate (HEMA) and the hydrophobic 1H,1H,2H,2H-perfluorodecyl acrylate (PFDA) are two components that may give rise to an amphiphilic surface. Surfaces of pure poly(HEMA) and poly(PFDA) have static water contact angles of 17° and 130°, respectively, reflecting their very different surface energies [18]. HEMA is hydrophilic due to its pendant hydroxyl while PFDA is extremely hydrophobic due to the fluorinated alkyl side chain, which has a very low surface energy [19].

Recently, Baxamusa et al. synthesized and deposited random amphiphilic copolymer films of the hydrophilic HEMA and the hydrophobic PFDA of varying chemistries on Si wafers using an *i*CVD technique [20]. Adsorption studies with a model protein, bovine serum albumin (BSA), showed that an intermediate chemistry of ~40% PFDA was most resistant to protein adsorption.

Encouraged by the above findings and the unique nature of the *i*CVD technique which allows thin-film deposition at ambient temperatures, we investigated deposition of a HEMA-co-PFDA film as potential antifouling coatings on RO membranes [21]. Subsequent characterization and performance evaluation confirmed the conformity, smoothness and stability of these coatings under high-pressure conditions [22]. Moreover, static bacterial adhesion tests performed with *Escherichia coli* showed a significant decrease in bacterial adhesion on RO membrane after deposition of the copolymer [23].

However, evaluation of the literature and the reporting of some experimental results [24] reveal that short-term, batch tests with pure microbial/organic cultures alone are not sufficient to accurately predict the efficacy of any membrane surface modification strategy. Although the modified surface may resist hydrophobic interactions with biomacromolecules or microbial cells, especially after short times, diminished adhesion has been shown to be a poor indicator of biofilm formation. Microbial/organic adhesion and biofilm formation are related but influenced by very different factors [25].

Applying a surface modification to reduce adhesion, therefore, does not necessarily guarantee organic/biofouling prevention or limitation. Moreover, the presence of various biopolymers in feed waters [26], even if microorganisms adhere in reduced numbers relative to an unmodified surface, may result in the development of a conditioning film, making the surface more susceptible to further adhesion. Once some biopolymers and/or microbial cells are able to adsorb to the modified surface, even in reduced numbers, further adhesion atop this conditioning layer is facilitated and biomass accumulates [27].Many laboratory studies on organic/biofouling control in membrane systems have been reported under non-representative conditions for practice. A fouling control approach effective under non-representative laboratory conditions may not be predictive for industrial practice.

In light of the above, long-term flow-through tests in the presence of a representative foulant are essential. Therefore, after the success of preliminary studies, it was deemed necessary to conduct fouling tests of the modified membranes in conditions that are more reminiscent of an industrial RO plant. For this purpose, the samples were tested in cross-flow, high pressure and salinity conditions and in the presence of a common organic foulant. Sodium alginate is a polysaccharide commonly produced by marine microorganisms containing repeating mannuronic and guluronic acids and is a suitable choice to model EPS fouling during filtration [28].

For comparison purposes, both modified and unmodified membranes were subjected to long-term fouling tests under identical conditions. This was followed by an in-depth surface characterization of fouled samples using updated techniques to develop a correlation between the filtration performance and the foulant adhesion. To the best of our knowledge, this is the first time that surface modification with an amphiphilic copolymer film using the *initiated* CVD technique has registered some success in the control of organic fouling under cross-flow conditions.

2. Materials and methods

2.1. Chemicals

Monomers PFDA and HEMA together with initiator tertbutyl peroxide (TBPO) were purchased from Sigma-Aldrich and used as received. The organic foulant used for this study was sodium alginate. Sodium alginate was purchased from Sigma Aldrich (St. Louis, MI) and used as received. Feed Water for the long-term permeation tests was obtained from an in-house MilliQ water unit (Millipore, Billerica, MA) with resistivity greater than 18.2 MΩ-cm. Sodium chloride was purchased from Sigma-Aldrich and used as received.

2.2. Membranes

Following our previous studies [21,23], TFC-HR from Koch Membrane Systems were used. The membranes were purchased from Sterlitech Corp. (Kent, WA) as flat sheets. For comparison purposes and also to study the effect of permeate flux on fouling, a commercial seawater reverse osmosis (SWRO) membrane, TF-RO-AD, was also selected for the cross-flow tests. This membrane is manufactured by GE Osmonics Inc. and has been extensively studied and characterized by