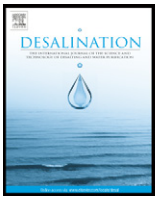
Desalination 369 (2015) 37–45

Contents lists available at ScienceDirect

Desalination

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



Biofouling resistance of polysulfobetaine coated reverse osmosis membranes

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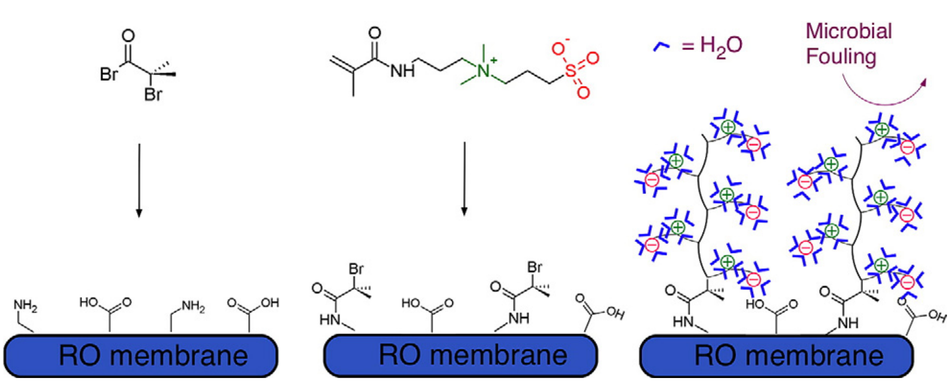
HIGHLIGHTS

- The polymer brushes were successfully grafted from the surface of RO membranes.
- The modification with pSBMA provides densely packed, regular length polymer chains.
- Very stable hydration shell on the monomer segments within the polymer chain was formed.
- Modified membranes showed a minimum of at least 4 times biofouling improvement.
- Modified membranes still maintaining competitive permeation flux and rejection properties

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 23 March 2015
Received in revised form 21 April 2015
Accepted 22 April 2015
Available online 4 May 2015

Keywords:
Reverse osmosis membranes
Membrane fouling
Surface modification
Polysulfobetaine
Cross-flow filtration

ABSTRACT

Although reverse osmosis technology appears to be maturing, several major challenges remain including membrane fouling. The most problematic type of fouling is biofouling because even small amounts of microorganisms that escape pretreatment processes can colonize the system, multiplying the problem at the membrane surface. To address this issue we have created an industrially attractive process suitable for the grafting of polysulfobetaine onto commercially available reverse osmosis membrane surfaces to create an anti-fouling coating. Attachment of coating components was confirmed using X-ray photoelectron spectroscopy (XPS), Fourier transform infrared spectroscopy (FTIR) and thermogravimetric analysis (TGA). Water contact angle (WCA) and transmission electron microscopy (TEM) then illustrated that the polysulfobetaine coating increased both the hydrophilicity and smoothness of the membrane surface. This modification resulted in at least 80% reduction in microbial abundance at the surface in both aquaria-based static tests and hydrodynamic cross-flow filtration tests while exhibiting flux and salt rejection comparable to controls. The potential applications of this technology include sea water reverse osmosis membranes and alternative feed water sources.

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http://dx.doi.org/10.1016/j.desal.2015.04.024

1. Introduction

Freshwater is a fundamental resource whose limited supply is being strained by the demands of population growth and the resultant increases in agricultural production and industrialization throughout the world [1–3]. Of the water in the hydrosphere the vast majority (97.5%) is saline [4], and so desalination provides opportunity to relieve the pressure on fresh water supplies [3]. Most desalination occurs either by reverse osmosis (RO) or thermal distillation; reverse osmosis technologies being the most efficient way to desalinate water in the majority situations [3,5]. Despite the widespread adoption of reverse osmosis technology several major challenges remain, one of the most significant being membrane fouling [3,6]. Fouling of membrane filtration systems has a number of sources including inorganic fouling, colloidal fouling, organic fouling and biofouling [7,8]. Biofouling is the result of algal and bacterial biofilm formation and causes reduced membrane lifetime and selectivity and is the most widespread and difficult to address fouling problem for membrane filtration systems [8,9]. Thus, the development of biofouling resistant RO membranes has attracted wide attention in recent years. The methods developed to address biofouling include: (i) the improvement of the interfacial polymerization process and the development of new monomers for interfacial polymerization; (ii) the exploration of new hybrid organic/inorganic RO membranes; and (iii) the surface modification of conventional RO membranes [10].

Surface modification is an attractive route to improve fouling resistance of RO membranes [2,8,10,11]. In particular thin film composite (TFC) reverse osmosis membranes are prone to biofouling due to the very rough and charged surface of the polyamide active layer. As such, coating materials should: (i) be hydrophilic [12]; (ii) have a low surface roughness (microscale) [13]; (iii) be charge-neutral [14]; and (iv) have stable surface hydration [15]. Physical adsorption of materials such as surfactants [16], polyethylene imine [17], polyether ether ketone [18], polyvinyl alcohol [19] and dendrimers [20] does improve hydrophilicity and membrane antifouling characteristics, but non-covalent attachment leads to a weak boundary layer and leaching of the coating layer during long-term operation. Chemical modification of the TFC polyamide layer through free carboxylic acid and amine groups is an alternative that provides more stable surface modification [10].

Chemical modification of TFC membranes with hydrophilic polyethylene glycol (PEG) has improved resistance to nonspecific protein adsorption [21,22]. However, PEG molecules are easily auto-oxidized in the presence of oxygen or transition metal ions [21]. Hydrophilic polyzwitterionic coatings have also been developed based on the natural anti-biofouling properties of cell membranes provided by phosphatidylcholine lipid head groups. This research has been pursued since the 1990s [23], but while phosphorylcholine-based polymers decrease biopolymer adsorption [24], they are fragile as the phosphoester groups are readily hydrolysable [25–27]. Chemically, more stable are zwitterionic betaine polymers such as polyphosphobetaine, polysulfobetaine, and polycarboxybetaine that have been attached to the different surfaces using a range of techniques. Such zwitterionic coatings have been revealed to be among the most effective anti-biofouling materials [28–31], and the fundamental aspects how zwitterionic surfaces can reduce the adhesion of cells and bacteria are well understood [23]. Nonetheless, the translation to membrane filtration is not straightforward and so it has taken time to produce effective coatings [32]. Indeed, even the best methods to coat RO membranes with polyzwitterionic coatings still have some draw backs including reduction in water permeability [31], and the use of complex experimental procedures [33], so there are still improvements to be made.

In this study we investigated the biofouling resistance of membranes modified by reacting surface amine groups with an atom transfer radical polymerization (ATRP) initiator, 2-bromoisobutyryl bromide, followed by surface initiated polymerization of sulfobetaine from the surface using activators regenerated by electron transfer (ARGET) ATRP (Fig. 1).

This ‘grafting from’ process generates polymers of narrow molecular weight distribution without the stringent experimental conditions required for other ATRP processes [34] and enables higher polymer densities than the ‘grafting to’ approach [35]. This industrially favorable process was therefore used to create a stable, durable coating with controllable thickness on commercially available RO membranes and the antibiofouling and filtration properties of the modified membranes were evaluated.

2. Experimental

2.1. Materials

Prior to use, membranes were immersed in isopropanol (IPA) for at least 30 min followed by immersion in pure water for 24 h. This process was required to remove any extractable components and preservatives (e.g., glycerin) from the membrane materials, and then to remove any remaining IPA from the membrane pores. 2-bromoisobutyryl bromide (BiBBr), copper (II) chloride ($CuCl_2$, 97%), ethanol, glutaraldehyde solution (25% w/v in water), paraformaldehyde, phosphate buffered saline (PBS), [3-(Methacryloylamino)propyl]dimethyl(3-sulfopropyl)ammonium hydroxide inner salt (3-SBMA), sodium acetate, sodium chloride, sodium nitrate, sodium phosphate monobasic, sucrose, triethylamine (TEA), tris(2-pyridylmethyl)amine (TPMA), sodium alginate, and $CaCl_2$ were purchased from Sigma-Aldrich, Australia and used as received. IPA, hexane and methanol were purchased from Merck, and used without further purification. Pure water was obtained from a Barnstead E-pure water purification system operating at a resistance of at least 18.0 MΩ. Commercially available RO polyamide membranes were kindly donated by Dow (Filmtec SW30HR), GE (GE-AD), and NanoH_2O.

2.2. Surface modification

2.2.1. Synthesis of ATRP initiator modified polyamide membranes

The presoaked membrane coupon was blotted between absorbent papers to remove excess water, and then subsequently stirred in hexane for 20 min. The membrane coupon was then immersed in fresh hexane

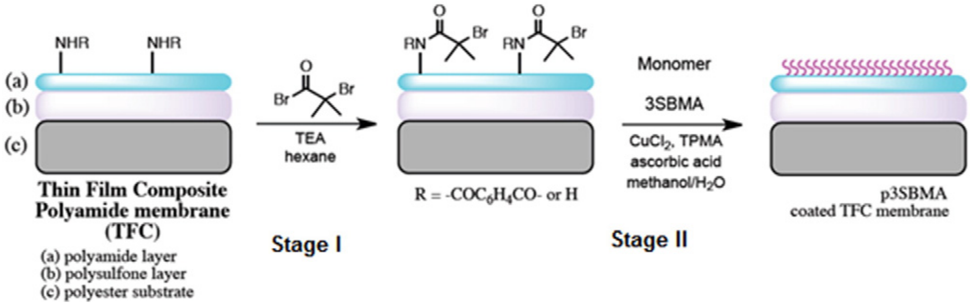

Fig. 1. Reaction scheme for grafting from the surface the polymer brushes of zwitterionic monomers.