Journal of Membrane Science 425–426 (2013) 1–10

Contents lists available at SciVerse ScienceDirect

Journal of Membrane Science

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

High-flux and fouling-resistant membranes for brackish water desalination

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ARTICLE INFO

Article history:
Received 22 May 2012
Received in revised form
3 September 2012
Accepted 12 September 2012
Available online 24 September 2012

Keywords:
Reverse osmosis
Brackish water desalination
Hydrophilic additive
Polyethylene glycol
Fouling resistance
Surface modification

ABSTRACT

Novel high-flux and fouling-resistant reverse osmosis membrane were synthesized and characterized under brackish water desalination conditions using 2000 ppm NaCl solution at 225 psi (1.55 MPa) and 25 °C. The *o*-aminobenzoic acid-triethylamine salt was added into *m*-phenylenediamine (MPD) solution to react with trimesoyl chloride (TMC) during the interfacial polymerization between MPD and TMC. The membrane synthesis conditions including MPD concentration, TMC concentration, and interfacial polymerization time were optimized. The membrane synthesized under the optimal conditions was post-treated with aqueous solutions containing glycerol, sodium lauryl sulfate, and camphorsulfonic acid-triethylamine salt to further increase the water flux. The resulting membrane showed a flux of 2.22 m^3/m^2/day (54.4 gallons/ft^2/day (gfd)) and a salt rejection of 98.6%. The fouling-resistant property of the synthesized membrane was enhanced by physically coating a cross-linked polyethylene glycol (PEG-200) layer on top of the thin film. The membrane coated with 10 wt% cross-linked PEG demonstrated a very high flux of 2.46 m^3/m^2/day (60.4 gfd) and outperformed the state-of-the-art commercial membrane. Using dodecyltrimethylammonium bromide, a cationic foulant, and tannic acid, an anionic foulant, as model foulants, the coated membrane exhibited much reduced flux decline. The surface morphologies of the modified and unmodified membranes were analyzed using scanning electron microscopy and atomic force microscopy. The results showed a smoother membrane surface by coating the PEG layer.

1. Introduction

The worldwide water crisis has become an inevitable issue due to the lack of proper wastewater management and exponential growth of global population over the past decades [1]. Desalination has been considered as one of the important solutions to this problem, which produces clean water by removing the salts and other compounds from saline waters, such as brackish water and seawater [2].

Reverse osmosis (RO) is a well-developed and the most promising technology for water desalination process [3–16]. Since its invention by John Cadotte in 1981 [4], the polyamide (PA) thin film composite (TFC) membrane has become the state-of-the-art RO membrane for water desalination, which predominates the current commercial RO applications [3,4,7,17]. Particularly, the most widespread PA TFC membrane in industry is synthesized via interfacial polymerization between *m*-phenylenediamine (MPD) and trimesoyl chloride (TMC) on a nanoporous polysulfone support [4,7,17]. The aromatic polyamide structure obtained from MPD and TMC is shown in Fig. 1 [7,18]. However, there are two prominent drawbacks in this kind of RO membrane: the insufficient hydrophilicity of the highly cross-linked network (Fig. 1) and the vulnerability to fouling from bacteria, colloids, humic acid, silt, scaling, and iron rust [19,20]. The first drawback leads to a significantly limited water flux and the second drawback results in a requirement of critical pre-treatment conditions. Both of them increase the capital and energy cost of this technology for water desalination, which limits the further utilization of brackish water and seawater as the fresh water resources.

The hydrophilicity of PA TFC membrane can be improved by the substitution with more hydrophilic monomers or by the incorporation with hydrophilic additives. Yu et al. [21] synthesized a polyamide-urethane TFC membrane by the interfacial polymerization of 5-chloroformloxy-isophthaloyl chloride with MPD. The resulting membrane exhibited an improved desalination performance under brackish water conditions. Chen et al. [22] incorporated sulfonated cardo poly(arylene ether sulfone) in the MPD solution, and the water flux of PA TFC membrane was significantly increased due to the hydrophilic poly(arylene ether sulfone). The desalination performance of PA TFC membrane could also be improved after a post-treatment with the solution containing glycerol, sodium lauryl sulfate, and camphorsulfonic acid-triethylamine (CSA-TEA) salt, which increased the membrane hydrophilicity [11].

Membrane surface morphologies and properties including surface roughness, charge, and hydrophilicity have remarkable effects on membrane fouling phenomenon [23,24]. Generally, a smoother [24]

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http://dx.doi.org/10.1016/j.memsci.2012.09.018

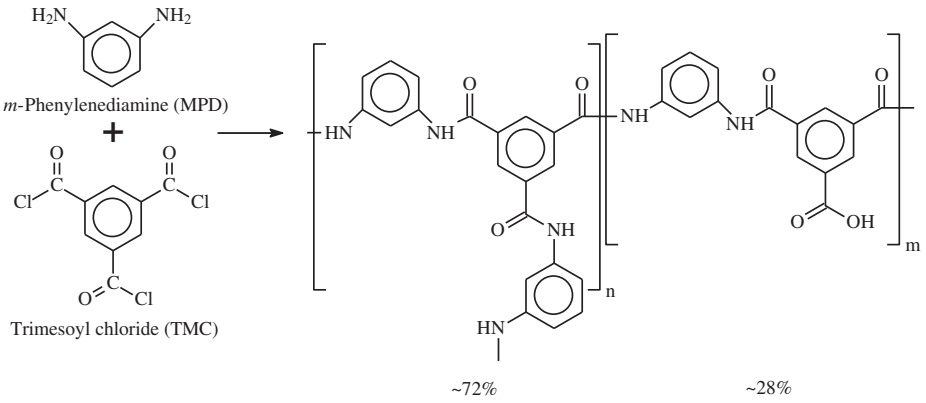
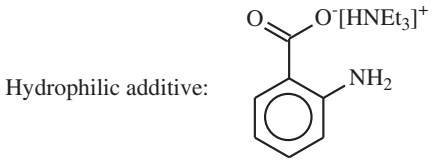


Fig. 1. Aromatic polyamide structure by interfacial polymerization between MPD and TMC.



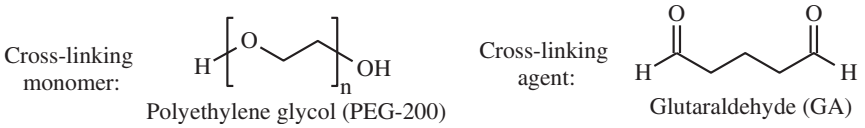


Fig. 2. Chemical structures of hydrophilic additive and cross-linking reactants.

and more hydrophilic [25] membrane surface with stronger electrostatic repulsion [26] to the foulants is expected to have less membrane fouling issue. Therefore, extensive research has been dedicated to the surface modifications to improve the fouling resistance of PA TFC membranes using various polymers as the cover layer. Zhou et al. [26] accomplished the surface modification by depositing polyethylenimine on the membrane surface, which reversed the surface charge and increased the surface hydrophilicity. Louie et al. [23] applied a polyether-polyamide (PEBAX® 1657) coating layer to smoothen the membrane surface. The resulting membrane showed a slower flux reduction rate using an oil/surfactant/water emulsion. Belfer et al. [27–29] modified the commercial PA membrane surface by a redox-initiated graft polymerization of various hydrophilic monomers including acrylic acid, sulfopropyl methacrylate and polyethylene glycol methacrylate (PEGMA), which reduced the surface roughness and contact angle. Sagle et al. [30] grafted PEG-based hydrogels onto a commercial PA RO membrane and obtained improved fouling resistance.

Compared to other polymers, polyethylene glycol (PEG) is extremely hydrophilic and capable of coordinating to adjacent water molecules by hydrogen bonding, which increases membrane fouling resistance without causing a significant water flux reduction. Moreover, the flux reduction caused by the cover layer could be further minimized by the cross-linking of PEG, preventing or minimizing its penetration into the PA thin film.

In this study, *o*-aminobenzoic acid-triethylamine (*o*-ABA-TEA) salt was selected as the hydrophilic additive to enhance the water flux of PA TFC membrane based on the previous work from our laboratory [31,32]. This chemical was commercially available and more cost-effective compared to other additives. Its chemical structure is similar to MPD with one functional amino group and a hydrophilic $-COO^{-}(HNEt_3)^{+}$ salt portion on the benzene ring as shown in Fig. 2. It could be easily dissolved in the aqueous MPD solution and react with TMC during the interfacial polymerization. Furthermore, the hydrophilic salt portion also provides charge repulsion for increasing salt rejection. With the addition of a particular amount of *o*-ABA-TEA, other membrane preparation conditions were evaluated and optimized under brackish water desalination conditions using 2000 ppm NaCl solution at 225 psi (1.55 MPa) and 25 °C by adjusting TMC dipping time, TMC concentration, and MPD concentration. In addition, a post-treatment was applied to enhance the water flux of the synthesized membrane. At last, the cross-linked polyethylene glycol with a molecular weight of 200 (PEG-200) using glutaraldehyde as the cross-linking agent was synthesized and coated onto the synthesized high-flux membrane to improve its fouling resistance. The chemical structures of PEG-200 and glutaraldehyde (GA) are also shown in Fig. 2. The chemical and thermal properties of the synthesized cross-linked PEG were characterized by Fourier transform infrared (FTIR) spectrometry and thermal gravimetric analysis (TGA), respectively. The effects of cross-linked PEG solution concentration on membrane desalination performance were investigated. Dodecyltrimethylammonium bromide (DTAB) and tannic acid (TA) were selected as the cationic and anionic foulants, respectively, for the fouling resistance tests of PEG modified and unmodified membranes. Scanning electron microscopy (SEM) and atomic force microscopy (AFM) were employed to characterize the surface morphology and verify the surface modification.

2. Experimental

2.1. Materials

m-Phenylenediamine (MPD, 99+%), *o*-aminobenzoic acid (*o*-ABA, 98+%), triethylamine (TEA, 99.5+%), (+)-10-camphorsulfonic acid