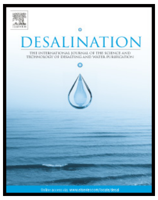
Desalination 404 (2017) 304–312

Contents lists available at ScienceDirect

Desalination

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



Evaluation of thin film nanocomposite reverse osmosis membranes for long-term brackish water desalination performance

Pinar Cay-Durgun [a,b], Cailen McCloskey [a], John Konecny [a], Afsaneh Khosravi [a], Mary Laura Lind [a,b,*]

[a] School for Engineering of Matter, Transport and Energy, Arizona State University, Tempe, AZ 85287, USA
[b] Nanosystems Engineering Research Center for Nanotechnology-Enabled Water Treatment, Arizona State University, Tempe, AZ, 85287, USA

HIGHLIGHTS

- NaA type zeolite nanoparticles embedded in polyamide membranes *via* interfacial polymerization process.
- Hand-cast TFC and TFN membranes were tested for ~3000 h in a cross-flow testing system.
- TFN membranes demonstrated enhanced water-salt permselectivity compared to TFC membranes.
- TFN membranes exhibited desalination performance stability over long term application.

ARTICLE INFO

Article history:
Received 8 June 2016
Received in revised form 18 October 2016
Accepted 27 October 2016
Available online xxxx

Keywords:
Thin film nanocomposite membrane
Reverse osmosis
Nanoparticles
Long-term performance
Desalination

ABSTRACT

Nanoparticle addition in the currently widely used thin film composite (TFC) membranes is a promising technology to advance separation performance and bring novel functionality in membrane desalination processes. These thin film nanocomposite (TFN) membranes boast many advantages over their TFC counterparts such as increased water flux without compromising salt rejection and bacterial resistance. However, the stability of TFN membranes is unknown in industrial, long-term applications. Via interfacial polymerization, we synthesized a series of polyamide TFC and TFN membranes with different nanoparticle content, 0 wt%, 0.15 wt%, 0.30 wt%, in the casting solutions. At the United States Bureau of Reclamation's Water Quality Improvement Center in Yuma, AZ, the membranes were tested for ~3000 h in a lab-scale testing system. We characterized the physico-chemical nature and morphology of the membranes before and after the testing. All membranes exhibited relatively stable long-term separation performances. At the highest zeolite loading tested, in comparison with the TFC membrane, water permeance increased from 3.7 ± 0.6 μm MPa^{-1} s^{-1} to 5.3 ± 0.5 μm MPa^{-1} s^{-1} and solute rejection slightly increased from 97.4 ± 0.3% to 97.9 ± 0.1%. In this study, TFN membranes exhibited long-term desalination stability and improved separation performance compared to TFC membranes.

1. Introduction

Reverse osmosis (RO) is a pressure-driven membrane process which is currently the most dominant technology for water desalination because of its relatively low energy consumption compared to non-membrane based desalination processes (e.g, thermal processes such as multi-stage flash and distillation) [1]. From the first cellulose acetate membranes to the current polyamide thin film composite (TFC) membranes, permeability increased from 1.4 μm MPa^{-1} s^{-1} to 5.5–8.3 μm MPa^{-1} s^{-1} for seawater and 8.3–13.9 μm MPa^{-1} s^{-1} for brackish water with very high rejections (>99%) of ionic solutes, such as sodium and chloride [2,3]. This technology widely uses the thin film composite (TFC) polyamide (PA) membrane which consists of an interfacially polymerized, ultrathin, crosslinked, aromatic PA layer onto microporous polysulfone supported by a non-woven polyester layer. The interfacial polymerization is a complex process involving the condensation reaction of an amine and an acid chloride at the interface of an aqueous and organic solution [4]. This dense PA structure is highly salt selective and the thinness of this layer (~100 nm) enables high water permeance in wide temperature and pH ranges [5,6]. Nevertheless, further performance improvement of polyamide TFC membranes in desalination applications is challenging because of two main factors. First, the "upper bound" permeability/selectivity trade-off observed in polymeric membranes for gas separations [7] also constrains the maximum performance of polymeric desalination membranes [8]. Second, polyamide membranes are susceptible to damage from biological fouling, scaling, and free chlorine (the most common disinfection agent in water treatment) [9,10]. Biofilms on the PA surface increase the resistance of the total membrane, resulting in flux decline and

---

[*] Corresponding author.
E-mail address: mllind@asu.edu (M.L. Lind).

http://dx.doi.org/10.1016/j.desal.2016.10.014
0011-9164/

ultimately in lower membrane performance and lifetime [10]. Some fouling and scaling may be minimized through appropriate cross-flow conditions within the RO membrane module to minimize issues with concentration polarization [11,12]. Although free chlorine is a low-cost and effective disinfection chemical for reducing biofilm layers, the PA structure degrades after continuous exposure to trace amounts of chlorine (at amounts three orders of magnitude lower than the effective chlorine present in disinfected water [13]). The PA degradation may result in increasing the water flux and the salt passage [6,13]. On the other hand, water permeance, solute rejection, and operational robustness of the membrane highly affect the energy consumption and operational costs of RO desalination processes [1,5]. Thus, there is a need to address these membrane challenges in desalination processes.

Coatings of porous metals, metal oxides, and zeolites are applied to mesoporous ceramic membranes or metallic membranes formed to develop mechanically enhanced and chemically durable membranes for water purification processes [5,14]. Compared to polymeric membranes, defect-free, versatile zeolitic membranes may enhance desalination performances, however, they have higher membrane production costs [14,15]. Moreover, because of the rigid structure, zeolitic membranes have lower permeation surface area density in a membrane module, which may cause an increase in operational costs [14,16]. These membranes are therefore rarely used for commercial desalination processes [5,15,16].

Mixed Matrix Membranes (MMMs) have emerged as an alternative to pure polymeric membranes or zeolitic membranes [17]. MMMs are composed of an inorganic filler phase dispersed through a continuous polymer phase. Ideally, the MMM retains the desirable characteristics of the individual components while obviating their individual disadvantages. MMMs have been studied extensively for gas separation applications [18,19]. For water separation applications, recent studies of nanoparticles embedded into the thin film polyamide structure during an interfacial polymerization process showed improved membrane performance [20]. In these advanced membranes for water treatement various nanofillers have been studied such as zeolite nanoparticles [21–29], carbon nanotubes [30–33], silica [34–36], silver [30], and metal oxides [37]. Superhydrophilic, nanosized Linde Type A (LTA) zeolites have demonstrated promising results in thin film nanocomposite (TFN) polyamide membranes for RO processes [21,22,24–26]. This zeolite consists of an aluminosilicate framework with a molecular formula of $Na_{12}[(AlO_2)_{12}(SiO_2)_{12}]\cdot27H_2O$ (lowest possible silicon/aluminum ratio in LTA is 2). Because of this aluminum rich structure, LTA is a super-hydrophilic zeolite. However, it may not be stable under acidic environments [28] (dealumination may occur at low pH [38]). LTA (NaA type) has 3-dimensional narrow-pores with a diameter of 4.2 Å [39], which is suitable for selecting water, but excluding hydrated ions and small organic molecules [40,41]. The 3-dimensional structure of the LTA pores ensures access to the pore regardless of how the zeolite is oriented in the polymer (and is much simpler to embed in membrane structure compared to 1-dimensional structures such as carbon-nanotubes which require precise orientation to take advantage of the pore structure). Polyamide membranes with incorporated LTA nanoparticles are hydrophilic and have higher flux and similar rejection when compared with commercial membranes [21,22,24–26]. Furthermore, previous research on TFN membranes has demonstrated an increase in properties (smoother and more hydrophilic surfaces) that limit bacterial adhesion to membrane surfaces in short-term bacterial adhesion tests [26]. However, the performances of TFNs vary as a function of the type, size, and concentration of nanoparticles [21,22,24]. In addition, there may be some "non-ideal effects" [42] in MMMs such as particle aggregation at higher zeolite loadings [43] and void or rigidified polymer formation at the polymer/particle interface [42]. This may result in decreased performance of the membrane. In our publication analyzing the permeance of pure zeolite-4A molecular sieves and nanocomposite zeolite-4A/polymeric MMMs for water separations, we demonstrated that transport may occur both at the molecular sieve/polymer matrix interface and through the molecular sieves [44]. However Turgman-Cohen et al. performed a molecular dynamic simulation study on pressure-driven water transport through thin film membranes of LTA zeolite [45]. Based on this simulation result, they hypothesize that preferential flow may be around the zeolite particles not through the zeolite pores [45].

Reverse osmosis desalination applications are divided into two primary categories based on feed type: brackish water or sea water. Feed water salinity ranges determine the type. In 2010, Kurth et al. published the long-term performance of TFN membranes (with unknown types of inorganic particles) for seawater desalination [46]. However, to our best knowledge, no publications report the long-term performance and stability of TFN membranes for brackish water desalination. The differences in feed water characteristics such as foulants and salinity, in addition to the operating conditions such as pressure and temperature, cause the flux and rejection of the membranes to vary between brackish water and seawater desalination [47].

The objective of our research is to evaluate the long-term effectiveness of mixed matrix nanocomposite membranes for treating brackish water with reverse osmosis (RO) in an operating plant environment. The ultimate impact of this research is to increase the amount of available technology for reclaiming and purifying water supplies with reduced energy demands. This is the first report on long-term performance of TFN membranes with brackish feed waters.

2. Experimental methods

2.1. Materials

Chemicals used in this manuscript are referred to with the following nomenclature. We used a polysulfone coated non-woven polyester ultrafiltration membrane (PSf, NanoH$_2$O) as a support membrane. We prepared monomer solutions of meta-phenylene diamine (MPD, 99%, Sigma-Aldrich) in ultrapure deionized water (milli-Q water, Millipore), and trimesoyl chloride (TMC, 98%, Spectrum) in the organic solvent Isoparrafin-G (Isopar-G, Sigma-Aldrich), for the synthesis of the thin polyamide film. We used freeze dried powdered Linde type A zeolites (LTA, 4A, Na^+, NanoScape) with an ~100 nm mean particle size. The post-cure rinses consisted of solutions of sodium hypochlorite (NaOCl, reagent grade, Sigma-Aldrich) and sodium bisulfite ($NaHSO_3$, reagent grade, Sigma-Aldrich).

2.2. Membrane synthesis

Our casting procedure is based on previously published methods [21,22,25,26]. Thin film composite (TFC) membranes are pure polyamide membranes without nanoparticles. Thin film nanocomposite (TFN) membranes are similar polyamide membranes, with nanoparticles dispersed in the TMC-Isopar-G monomer solution.

First, we prepared the MPD in water and TMC in organic solvent monomer solutions separately. The solutions were magnetically stirred at 300 rpm for at least 3 h prior to use.

For the casting, a sheet of polysulfone coated polyester support membrane was taped on all sides onto a glass plate. Then, we soaked the support into 3.5 wt% MPD in milli-Q water monomer solution for 2 min, with the active side (PSf side) facing down in the solution and the back of the plate not submerged. After lifting the plate from the amine solution, to increase the uniformity of the membrane surface, we removed the excess solution from the surface with a rubber fingerprint ink roller. Then, we immediately placed the MPD coated membrane vertically into a monomer solution of 0.15 wt% TMC in isopar-G for the interfacial polymerization reaction. After 1 min, we removed the plate from the solution and held it vertically for 2 min. We cured the membrane through a series of post-treatment rinses. First, the membrane was placed into a water bath at ~95 °C with active side up for 2 min. Then, the membrane was removed from the glass plate and placed into 1.5 mL L^{-1} NaOCl in deionized water for 2 min. We believe