High-flux reverse osmosis membranes incorporated with NaY zeolite nanoparticles for brackish water desalination

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ARTICLE INFO

ABSTRACT

Thin film nanocomposite (TFN) membranes incorporated with NaY zeolite nanoparticles were prepared via interfacial polymerization (IP) of trimesoyl chloride and m-phenylenediamine on nanoporous polysulfone supports. The isolated zeolite-filled polyamide layer was observed by transmission electron microscopy, and the nanoparticles dispersed in the dense nodular polyamide on the polysulfone side. The effects of IP reaction time and zeolite loading on membrane separation performance were investigated. The results showed that a longer IP reaction time was necessary to form a denser zeolite–polyamide layer for higher salt rejection, and the optimum zeolite loading was determined to be 0.15 wt%. Under the optimum conditions, the water flux increased from 0.95 to 1.78 m^3/m^2/day (23.3 to 43.7 gal/ft^2/day (gfd)) with the incorporation of the zeolite nanoparticles, while providing a high salt rejection of 98.8% (2000 ppm NaCl solution, 225 psi (1.55 MPa), 25 °C). The TFN membranes were then post-treated with aqueous solutions containing glycerol, camphorsulfonic acid-triethylamine salt, and sodium lauryl sulfate to further improve the water flux. By optimizing the post-treatment solution composition, an improved brackish water desalination performance was achieved with 2.06 m^3/m^2/day (50.6 gfd) water flux, which was more than double compared to that of the TFC membrane without the zeolite nanoparticles, along with 98.4% salt rejection.

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1. Introduction

The shortage of fresh water is an increasingly crucial challenge around the world due to the rapid growth in population and the expanding needs of agriculture and energy consumption along with pollution and deficiencies in water management [1]. Seawater and brackish water desalination, which can supply fresh water for drinking, irrigation and industrial development, has emerged as the most sustainable approach to alleviate the water scarcity [2]. Among various desalination technologies, the membrane-based reverse osmosis (RO) process is simple to design and has excellent scale-up capability, and it currently dominates the global desalination market [3]. In the RO desalination process, high performance semi-permeable membranes play the most important role because they determine the product water quality and affect the overall energy consumption [4]. Therefore, high efficiency RO membranes with improved productivity along with good salt rejection are highly desired.

Polyamide (PA) thin film composite (TFC) membranes were developed in 1980s and are now the most widely used desalination membranes due to the high intrinsic water permeability and good stability over a wide range of pH values [5]. A typical TFC membrane consists of a thick, porous, nonselective layer, along with an ultrathin barrier layer on its top surface. This asymmetric structure brings some key advantages to the membranes. Specifically, each individual layer of TFC membranes can be optimized for its particular function, i.e., the thin film layer can be designed for the desired combination of water flux and salt rejection, while the porous support layer can be prepared for good mechanical properties combined with minimum resistance to permeate flow [6]. A number of recent studies have been carried out in terms of the selection and modification of both suitable thin barrier layers and porous substrates towards the goal of enhancing separation performance, fouling resistance and chlorine tolerance [7]. In particular, the modification of the thin film layers can be achieved by the incorporation of hydrophilic additives or by monomer substitution [8–11], while the substrates can be modified with the addition of organic solvents or replaced by other polymers to assist in the preparation of high-performance TFC membranes with improved mechanical and thermal properties [12,13].

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However, the structure of the polymer membrane is difficult to control, and some studies have suggested that it is hard to further increase the water permeability of polymer-based membranes without sacrificing selectivity [14]. Nanotechnology may offer new avenues to develop novel water treatment membranes that can exceed state-of-the-art performance [15]. A number of recent studies have focused on the incorporation of inorganic materials into both the thin film layer and the support layer of organic RO TFC membranes [16,17].

Notably, a new class of thin-film nanocomposite (TFN) membranes with dramatically improved water permeability was developed by incorporating nanoparticles within polyamide films [18]. This concept offers the potential for the next generation of high performance RO membranes and has attracted considerable interest. Different types of nanomaterials have been investigated for such applications including zeolite, silica, carbon nanotubes, mesoporous carbon, pure metal and nanometal oxides [19–23]. The unique functionalities of these materials have introduced new degrees of freedom in the RO membrane design, which combines the essential properties of conventional membrane polymers with the advantages of nanomaterials.

Among various nanoparticles, zeolite nanoparticles are now the most frequently used nano-fillers in TFN membranes that lead to more permeable polyamide active layers. The physical and chemical properties of zeolite are crucially important to the TFN membrane performance and have been widely studied in recent years, such as particle size, adding method, chemical resistance and surface modification [24–28]. Generally, it is hypothesized that zeolite nanoparticles with a tight pore distribution less than the diameter of a hydrated salt ion can exclude the solute to pass through, while also simultaneously providing preferential flow paths for water transport [18]. Besides the molecular-sieving mechanism, it is also believed that the presence of zeolite nanoparticles may change the structure of the polyamide thin film layer by the formation of nano-gaps at the organic–inorganic interfaces, which can reduce the crosslinking density of the polyamide layer [19].

Notably, the nanostructure of polyamide active layers is believed to have two distinct regions: a dense phase of nodular polyamide on the support side and a more open structure of loose polyamide on the surface side. Many studies have suggested that the polyamide dense phase presumably acts as the true separation barrier [29–31]. Therefore, as for zeolite-filled TFN membranes, the distribution characteristics of zeolite nanoparticles in different polyamide regions is especially crucial to bring the function of zeolite nanoparticles into full play. It is reasonable to hypothesize that the zeolite nanoparticles will play a greater role in affecting the membrane properties when the nanoparticles are mainly dispersed in the dense core sub-layer of polyamide. As a result, the study of specific zeolite distribution state is essential to achieve a better understanding of the transport mechanism of TFN membranes.

Zeolite-Y possesses the Faujasite (FAU) framework with a 3-dimensional pore structure similar to Linde Type A (LTA). The pore diameter is relatively large, i.e., 7.4 Å, which is formed by a 12-member oxygen and connected to the inner cavity with a diameter of 12 Å [32]. FAU type zeolite has been shown as a good candidate for the application in seawater desalination by molecular dynamics simulations [33]. Therefore, the incorporation of zeolite-Y nanoparticles in TFN membranes may create more preferential water pathways than zeolite-A (4.2 Å pore diameter) and result in a better membrane separation performance. The effects of adding FAU type zeolites with a NaX composition into polyamide thin layers on membrane separation performance have been reported [34]. However, the increased water flux was achieved at the cost of salt rejection due to the void defects formed in the structure of the thin film layers. Thus, it is important to observe and study the detailed dispersibility and distribution of zeolite nanoparticles in polyamide layers to avoid the non-selective defects. Besides, the post-treatment of TFC membranes by glycerol solutions is an effective way to enhance the membrane separation performance [35]. As a result, the effects of post-treatment process on the properties of zeolite-filled TFN membranes is also worth studying.

In this study, NaY zeolite nanoparticles were synthesized via the hydrothermal method. The framework structure, particle diameter, and elemental composition of the synthesized zeolite nanoparticles were characterized by X-ray powder diffraction (XRD), dynamic light scattering (DLS), and X-ray photoelectron spectroscopy (XPS), respectively. The TFN membranes were prepared by adding NaY zeolite nanoparticles in amine solution in the interfacial polymerization (IP) process. Scanning electron microscopy (SEM) and attenuated total reflectance infra-red (ATR-IR) were employed to investigate the membrane morphology and composition. Transmission electron microscope (TEM) was used to observe the isolated polyamide thin film layer and determine the dispersion and distribution of zeolite nanoparticles in polyamide. Contact angles of deionized water were measured on air-dried samples of synthesized TFN membranes with different zeolite loadings to verify the hydrophilicity of the membranes. The effects of IP reaction time and zeolite loading were evaluated by using brackish water desalination tests with 2000 ppm NaCl solution at 225 psi (1.55 MPa) and 25 °C. After the membrane preparation conditions were optimized, the post-treatment using glycerol solutions containing camphorsulfonic acid-triethylamine salt was investigated to further improve the water flux of TFN membranes. For the post-treatment, the effects of heat-treatment time and solution composition on TFN membrane separation performance were studied.

2. Experimental

2.1. Materials

The polysulfone support (ultrafiltration membrane) with nonwoven polyester fabric backing was purchased from TriSep Corporation. Isopropanol (IPA, > 99.9%, Fisher Scientific) was used for the pretreatment of the polysulfone supports. Chemicals used for the synthesis of the polyamide thin film layer in the aqueous phase included m-phenylenediamine (MPD, > 99%, Sigma-Aldrich), triethylamine (TEA, > 99.5%, Sigma-Aldrich), (+)-10-camphorsulfonic acid (CSA, > 99%, Advanced Asymmetrics) and sodium lauryl sulfate (SLS, > 85%, Fisher Scientific). Trimesoyl chloride (TMC, > 98%, TCI America) and Isopar G® (ExxonMobil Chemical) were used as monomer and solvent in the organic phase, respectively. Chemicals used for the post-treatment process included sodium sulfate anhydrous (Na_2SO_4, > 99.4%, Fisher Scientific), sodium carbonate (Na_2CO_3, > 99.5%, Sigma-Aldrich), glycerol (> 99.5%, Sigma-Aldrich), TEA, CSA, and SLS. The membrane separation performance was tested using sodium chloride (NaCl, > 99%, Sigma-Aldrich). All the chemicals were used as received without further purification. Deionized water was used for the solution preparation and the desalination study.

2.2. Zeolite synthesis and characterization

Zeolite-Y crystals were synthesized hydrothermally from the starting molar composition of 0.37 Na_2O: 1.0 Al_2O_3: 3.13 $(TMA)_2O$: 4.29 SiO_2: 497 H_2O according to previously reported procedures [36]. Typically, the clear synthesis solution was placed in a polypropylene bottle and stirred at 98 °C for 4 days until white crystals were observed. The product was collected by centrifugation and washed to remove excess reactants. The clean product was sodium ion exchanged to remove tetramethylammonium