



Thin film composite membranes embedded with graphene oxide for water desalination



Mohamed E.A. Ali^{a,c}, Leyi Wang^b, Xinyan Wang^b, Xianshe Feng^{a,*}

^a Department of Chemical Engineering, University of Waterloo, Waterloo, Ontario N2L 3G1, Canada

^b Zhaojin Motian Co., Ltd., Zhaoyuan, Shandong, China

^c Water Desalination & Treatment unit, Hydrogeochemistry Dept., Desert Research Center, Cairo, Egypt

HIGHLIGHTS

- Thin film composite membranes embedded with graphene oxide were prepared.
- Membranes exhibited improved water flux, mechanical strength.
- Membranes were stable in acidic and alkaline solutions.
- The presence of graphene oxide increased chlorine and fouling resistances.

ARTICLE INFO

Article history:

Received 29 September 2015

Received in revised form 24 February 2016

Accepted 25 February 2016

Available online 4 March 2016

Keywords:

Membranes

Thin film composite

Graphene oxide

Chlorine tolerance

Fouling resistance

ABSTRACT

This work deals with thin film composite membranes prepared from m-phenylenediamine and 1,3,5-benzenetricarbonyl chloride by interfacial polymerization on the surface of a polysulfone substrate, and graphene oxide was embedded into the membrane during membrane formation to improve the membrane performance. The desalination performance of the membranes was evaluated in terms of water flux and salt rejection, along with a baseline membrane containing no graphene oxide. The membrane morphology and surface properties were also studied using contact angle measurements, FT-IR, XRD and SEM. Incorporating a small amount of graphene oxide into the membrane was shown to improve the water flux, mechanical stability, and chlorine and fouling resistances of the membrane. At 15 bar, a water flux of 29.6 L/m²·h and a salt rejection of ≥97% were obtained for a saline solution (2000 ppm of NaCl) when the amine reactant contained 100 ppm of graphene oxide during membrane fabrication. The membranes were found to be stable in acidic and alkaline solutions.

© 2016 Elsevier B.V. All rights reserved.

1. Introduction

The shortage of clean and fresh water has become one of the critical problems for sustainable development to meet the growing social, economic and environmental needs of the society [1]. The desalination of brackish and sea water based on thermal processes and membrane technologies holds great promises to address these issues [2,3]. Especially, the development of thin-film-composite (TFC) membranes comprising of a substrate and an interfacially polymerized polyamide (PA) skin layer has significantly advanced the membrane technology for water desalination [4]. In the thin film composite membranes, the substrate provides mechanical strength to the membrane against the operating pressure applied across the membrane, whereas the PA active

layer is responsible for rejecting salt while allowing water to pass. The PA skin layer also determines the membrane resistances to fouling and chlorine [5]. Ideally, the membranes should be chemically and mechanically stable over a long period of operation at high pressures, while maintaining their desired water flux and salt rejection characteristics. Unfortunately, the current generation of membranes faces two main challenges: chlorine sensitivity and fouling propensity [6]. The amide groups in PA skin layer are vulnerable to chlorine attack even at a low chlorine dosage in the feed water [7], and membrane chlorination normally leads to reduced salt rejection that compromises the quality of the permeated water. In addition, the surface fouling of the thin film composite membranes is often a serious problem because frequent cleaning will not only increase the operating cost but the service life of the membrane will also be shortened if harsh cleaning agents are needed [8].

Therefore, many efforts have been made to modify the membrane surface in order to improve water flux, salt rejection, and fouling and

* Corresponding author. Tel.: +1 519 888 4567.

E-mail address: xfeng@uwaterloo.ca (X. Feng).

chlorine resistances of the membrane. One common approach is the development of hybrid organic–inorganic membranes with tailored surface properties. Over the last two decades, various hydrophilic nanomaterials (including alumina, silica, titanium dioxide, zeolites, and carbon nanotubes) have been used to improve the performance of TFC membranes [9]. In general, a small amount of such nanofillers is often insufficient to alter the membrane permselectivity significantly, while the uniform dispersion of nanofillers in the membrane will be affected because of nanoparticle aggregation if too much nanofillers are used. Nanoparticles with unique structures and functional groups (e.g., hydrophilicized graphene oxide nanosheets) that enhance their compatibilities with the polymer matrix of the membrane are of particular interest. Because of the oxygen-containing functional groups in graphene oxide (GO) nanosheets (e.g., hydroxyl and epoxy groups on the basal plane and carboxyl groups at the edge), they generally have a better dispersibility in water or polar solvents than other nanoparticles [10,11]. It may be mentioned that a great deal of work has been done on the synthesis of various polymer-carbon based hybrid materials through different approaches to enhance mechanical, electrical, catalytic or other properties (see, for example [12–21]). GO nanosheets have recently attracted significant attention in membrane development because of their unique nanostructures and physical and mechanical properties [22–24]. Because of the different functional groups (e.g., hydroxyl, carboxyl, and epoxide) in graphene oxide, there is a good compatibility between the nanosheets with the host (polymer) materials through covalent or non-covalent attachments [25]. When graphene oxide nanosheets are embedded into a membrane matrix, the surface hydrophilicity of the membrane will be enhanced, which are helpful to enhance water permeability and fouling resistance. In addition, because of the intermolecular hydrogen bonding between the amide groups of PA and the functional groups of graphene oxide, the active amide groups in PA vulnerable to chlorine attack are shielded by the nanosheets, resulting in improved membrane resistance to chlorine [26]. Moreover, the embedded GO nanosheets in the membrane matrix also increases the mechanical strength and enhances the membrane stability against high transmembrane pressures [27].

The main objective of the present work was to prepare hybrid organic–inorganic thin film composite membranes by incorporating graphene oxide nanosheets into the interfacially polymerized polyamide skin layer. The effects of the addition of GO nanofillers in the membrane on the desalination performance of the resulting membrane were investigated. It was shown that by properly controlling the membrane formation conditions, thin film composite membranes with significantly improved performance (i.e., mechanical stability against high pressure, tolerance for high chlorine dosages, resistance to strong acidic and alkaline solutions) were produced. These membranes compared very favorably with those GO-modified membranes recently reported in the literature [26,28–30]. It may be mentioned that unlike GO-modified membranes where GO was incorporated into the membrane by coating or layer-by-layer deposition [26,30], the composite membranes developed in this work comprised of GO that was embedded in the polyamide skin layer during the interfacial polymerization.

It may be noted that prior work on modification of TFC membranes with GO involved surface coating or layer-by-layer assembly. In one approach, GO was deposited on top of a polyamide active layer by electrostatic self assembly, and the GO coating layer led to an additional resistance to water permeability [14,16]. In another approach, oppositely charged GOs were deposited on a porous substrate by electrostatic self assembly, and the polyamide layer was formed on top of the GO layer by conventional interfacial polymerization [30]. In both cases, the GO layer and the polyamide layer were not interpenetrated, and the stability of the electrostatically assembled GO layer may be a potential concern when used in water desalination because of the ionic solutes involved. Therefore, it is desirable to incorporate GO into the polyamide layer during the

course of interfacial polymerization so as to form a nanostructured hybrid membrane. In the present work, GO nanofillers were dispersed in the aqueous amine reactant phase, which was allowed to react with the organic phase of acyl chloride reactant on a substrate surface to achieve interfacial polymerization, thereby incorporating the GO in situ into the thin polyamide layer during the course of interfacial polymerization.

2. Experimental

2.1. Materials

Graphene oxide was prepared from graphite powder, potassium permanganate, sulfuric acid, nitric acid and hydrogen peroxide; all the chemicals were supplied by Fisher Scientific, except for graphite powder which was supplied by Acros Organics. Microporous polysulfone ultrafiltration membranes supplied by Sepro Membranes were used as the substrate. They had a molecular weight cut-off of 10,000, and a pure water permeability of approximately $90 \text{ L/m}^2 \cdot \text{h} \cdot \text{bar}$. 1,3,5-benzenetricarbonyl chloride (i.e., trimesoyl chloride, TMC) (>98%), m-phenylenediamine (MPD) (>99%), and camphor sulphonic acid (CSA) were supplied by Fischer Scientific. n-Hexane was purchased from Caledon Laboratories. Sodium lauryl sulfate (SLS) was purchased from Matheson Coleman & Bell Chemical. NaCl (EMD Chemical) was used to characterize the salt rejection of the TFC membranes. The chlorine solution was prepared from a commercially available sodium hypochlorite solution (NaClO, 14.5% available chlorine, Alfa Aesar). When needed, the feed solution pH was adjusted to desired values using hydrochloric acid (37 wt%, Sigma-Aldrich) or sodium hydroxide (Caledon Laboratories). Bovine serum albumin (BSA) supplied by Sigma-Aldrich was used as a model foulant in membrane fouling experiments.

2.2. Preparation of graphene oxide

GO was prepared following a modified Hummers' method [31]. Briefly, in an ice bath, 1 g of graphite powder was dispersed in a mixture of 25 ml of cold concentrated sulfuric acid and 1 g of sodium nitrate. Then, 3 g of potassium permanganate was slowly added under vigorous stirring and cooling conditions to keep the temperature below 20°C . Thereafter, the reaction mixture was placed in a water bath at 35°C with continuous stirring for 1 h. Then, 50 ml of deionized water was slowly added, and the reaction mixture was allowed to stay at 98°C for 12 h, producing a bright-yellow suspension. Finally, the reaction was terminated by sequentially adding 140 ml of deionized water and 3 ml of hydrogen peroxide solution (30%). The solid product was filtered out of the solution, rinsed with a dilute hydrochloric acid (3.4 wt.%) until a pH of 7, and vacuum-dried at room temperature.

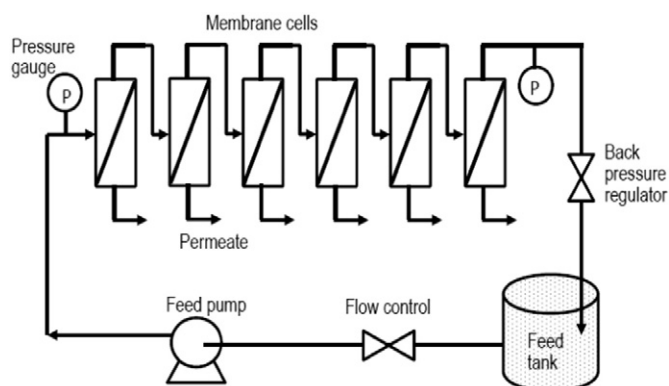


Fig. 1. Schematic diagram of the cross-flow membrane testing unit.

Download English Version:

<https://daneshyari.com/en/article/622871>

Download Persian Version:

<https://daneshyari.com/article/622871>

[Daneshyari.com](https://daneshyari.com)