Flux enhancement of thin-film composite membrane by graphene oxide incorporation

Sajjad Jalali¹ · Abdollah Rashidi Mehrabadi¹ · Jalal Shayegan² · Maryam Mirabi¹ · Sayed Siavash Madaeni³

Received: 17 September 2018 / Accepted: 8 February 2019 / Published online: 12 March 2019
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Abstract

Reverse Osmosis (RO) is a rapid-developing desalination technology; however, it suffers from inefficient energy consumption. To reduce energy consumption, in this study, reverse osmosis thin-film composite membrane (TFC) module was prepared and composed of m-phenylenediamine (MPD), graphene oxide, and 1,3,5-benzenetricarbonyl chloride (TMC) by interfacial polymerization on the surface of a polysulfone substrate. The graphene oxide was embedded in the mentioned thin-film composite by adding it to MPD aqueous solution to enhance permeation flux and, thus, reduce energy consumption. This study assessed the performance of the membrane using a lab-scale RO setup and evaluated permeability and salt rejection. The chemical properties of TFC were also analyzed using ATR-FTIR. Incorporating various concentrations (0, 20, 40, 60, and 80 ppm) of graphene oxide into the TFC was shown to improve water flux. Flux improvement of 50% was achieved by using graphene (80 ppm), while 10% of salt rejection was lost. These flux increases resulted from the changes in surface charge, surface roughness, and hydrophilicity due to the embedment of GO nanosheets. The simplicity of the method, compatibility of GO with polyamide membrane, and quite short-time reaction are the highlights of this technique for developing novel TFC membranes for water treatment.

Keywords Thin-film composite · Graphene oxide · Flux enhancement

Introduction

Desalination technology is an effective strategy for producing potable water from saline resources. In particular, thin-film composite membranes consist of a substrate and an interfacially polymerized polyamide (PA) skin layer [1, 2]. Compared to thermal processes, low-energy requirements in Reverse Osmosis (RO) have become one of the most popular techniques in the world [3]. However, relevant findings highlight the considerable gap between the Theoretical Minimum Energy Requirement (TMER) for RO and practical energy measurements [4, 5]. For example, TMER of a feed is 0.84

kWh/m³ with a salinity of 3.43%, a temperature of 25 °C, and 30% recovery, while it is observed to be about 4.5 kWh/m³ for realistic plants [6, 7].

One effective approach to reducing energy consumption is to improve the membrane surface so as to enhance water flux [1]. Embedding nanoparticles in the polyamide thin-film layer is an attractive strategy to ensure the improvement [8]. The incorporation of nanomaterials created an additional “degree of freedom” in designing high-performance RO membrane [9]. Various studies have attempted to use nanostructures (including zinc [10], iron [11], alumina [12], silica [13], titanium dioxide [14], zeolites [15], and carbon nanotubes [16]) for altering the membrane properties [17] such as antifouling, biofouling, and desalination performance. The mentioned nanomaterials are often too inadequate to alter the membrane permeability and selectivity significantly, while the high concentration of nanofillers prepares suitable conditions to aggregate nanoparticles.

One of the emerging nanomaterials that has been used to develop high-performance thin-film composite polymers is graphene oxide [18]. Oxygen-containing functional groups, such as hydroxyl and epoxy groups, on the basal plane and carboxyl groups at the edge in graphene oxide (GO)

✉ Jalal Shayegan
Shayegan@sharif.edu

¹ Department of Civil, Water and Environmental Engineering, Shahid Beheshti University, Tehran, Iran

² Department of Chemical and Petroleum Engineering, Sharif University of Technology, Tehran, Iran

³ Department of Chemical Engineering, Razi University, Kermanshah, Iran

Fig. 1 GO molecule structure

nanosheets (Fig. 1) produce better dispersion in water or polar solvents than other nanoparticles; therefore, there is good compatibility between the nanosheets and polymers [19, 20]. Moreover, the incorporated GO nanosheets in the TFC increased the mechanical properties and improved the membrane stability against high transmembrane pressures [21].

In this research, RO membranes were prepared by embedding graphene oxide in thin-film composite membranes into the interfacially polymerized polyamide skin layer. Therefore, GO was incorporated in the polyamide layer by adding it to the aqueous solution of *m*-phenylenediamine (MPD). The performance of the modified thin-film composite was evaluated with respect to permeation flux and salt rejection; in addition, its chemical structure was evaluated by means of ATR-FTIR spectrum.

Materials and methods

Materials

The graphene oxide powder was prepared from United Nanotech Innovations PVT.LTD. Microporous polysulfone ultrafiltration membranes were supplied by Sepro. Industrial-grade *n*-hexane (a mixture of isomers) was supplied by ICMC Petrochemical Co. Trimesoyl chloride (TMC), *m*-Phenylenediamine (MPD), and NaCl were purchased from Merck & Co.

Thin-film composite preparation

The polyamide membranes with and without graphene oxide were prepared on the surface of the polysulfone substrate by the interfacial polymerization technique. In the first step, the substrate was rinsed with deionized water to remove any unwanted material. Then, the PSF-UF membrane was immersed

into a 2 wt% MPD aqueous solution containing various concentrations of GO (0, 20, 40, 60, and 80 ppm) for 5 min. Excess MPD solution remaining on the PSF-UF membrane surface was removed by a rubber roller. Next, the PSF-UF membrane was immersed in 0.1 w/v% TMC in *n*-Hexane for 1.5 min to form a PA layer via interfacial polymerization. Finally, the membrane was dried in an oven at 60°C for 10 min to reach stability (Fig. 2).

Characteristics of GO and thin-film membrane

Fourier transform infrared (FTIR) was used to analyze the chemical structure of GO, and ATR-FTIR was applied to analyze GO to enhance thin-film composite polyamide membranes. The samples were scanned in the range of 450–4000 cm^{-1} by ATR-FTIR (Tensor 27, Bruker, USA) and FTIR (Bruker) with a resolution of 2 cm^{-1} for each spectrum.

Membrane performance for rejection and flux

The performance of the membranes for water desalination was measured in terms of water flux and salt rejection using a crossflow permeation cell with an effective area of 18.84 cm^2 . The operating conditions include pressure three bar, NaCl concentration of 2000 ppm in feed water, 35 °C, and a pH of 7. Salt rejection (*R*) and permeation flux (*J*) were determined by means of the following equations:

$$R = \frac{C_{FEED} - C_{Permeate}}{C_{FEED}}$$

$$J = \frac{V}{At}$$

where C_{FEED} is the concentration of feed in mg/l, $C_{Permeate}$ is the concentration of permeate in mg/l, *V* is the volume of

Fig. 2 TFC preparation

permeate in ml, A is the area of membrane in the square meter, and t is the time of accumulation of permeate.

Results and discussion

Graphene characteristics

FTIR spectroscopy was used to study the functional groups of GO. The FTIR spectrum of GO (Fig. 3) indicated the presence of O–H groups (3369 cm^{-1}), C–O stretching vibration in carboxyl groups (1722 cm^{-1}), unoxidized sp^2 aromatic C–C bonds (1623 cm^{-1}), C–O stretching vibration in epoxy groups (1224 cm^{-1}), and C–O stretching vibration in alkoxy groups (1053 cm^{-1}) [22]. A strong band at 3350 cm^{-1} indicates that GO has many free hydroxyl groups, which can form hydrogen bonds and intermolecular forces of GO nanosheet and polyamide groups.

Fig. 3 GO FTIR spectrum

Membrane FTIR characterization

Figure 4 shows the ATR-FTIR spectra of GO-TFC membrane in which the intrinsic peaks of the polyamide layer formed by the interfacial polymerization (IP) process with GO appeared in the ATR-FTIR spectra. The peaks at 3429 cm^{-1} , 1734 cm^{-1} , and 1052 cm^{-1} indicate hydroxyl, carboxyl, and epoxide functional groups of GO, respectively. It is clear that the high concentration of graphene oxide consequently increases the intensity of the hydroxyl peak [23]. For TFC membrane, the characteristic band at 1694 cm^{-1} was attributed to C=O stretching vibration (amide II) of the active polyamide layer, while the band at 1589 cm^{-1} resulted from N–H and C–N stretching vibrations of the amide group (amide II) [24]. The latter band was shown to have lower intensity and a broader width for the TFC/GO membrane, accompanied by a band shifting to 1660 cm^{-1} , suggesting the interaction between PA and GO nanosheets [23].

Fig. 4 ATR-FTIR spectra of GO-TFC membranes

Flux performance

The presence of GO in TFC membranes can affect the permeability of the membrane by modifying the polymer structure and creating nanochannels. Figure 5 shows that the presence

Fig. 5 The effect of GO on flux

of GO in the membrane enhances water transport. The water flux of 80 ppm-GO-TFC membrane was approximately 50% higher than that of 0 ppm-GO-TFC membrane. Permeability increases can be interpreted by GO characteristics such as hydrophilicity and two-dimensionality.

The increase of the membrane hydrophilicity generally results in an increase in water permeability [25]. Thus, the hydrophilic functional groups (hydroxyl, carboxyl, and epoxy) in GO help TFC to enhance permeability. The two-

Fig. 6 The effect of GO on rejection

dimensional structure of GO embedded in TFC membrane can increase roughness. The increase of the membrane roughness intensifies water flux [26].

Desalination performance

Figure 6 illustrates the effect of GO on the salt rejection, which showed a slight decrease in salt rejection when GO was increased. This effect can be interpreted by the aggregation of too much GO in thin-film composite [27, 28], while the interfacial reaction between MPD and TMC occurred in processing. The GO aggregation in the polyamide layer may produce localized “defects” in the aggregates, which tend to reduce salt rejection. On the other hand, due to the nanosheet structure of GO, it is randomly arranged in the membrane skin layer [29]. The GO nanosheets are perpendicular to the membrane surface, which are not effective in blocking the passage of salt while allowing water to permeate.

Conclusions

This study evaluated the embedment of GO sheets in the thin-film composite polyamide layer for desalination applications. It was shown that incorporating GO into the membrane improved the water permeability of the membrane while decreasing salt rejection. Therefore, a trade-off was observed between the improved water flux and desalination performance. The chemical structures of membranes, especially functional groups, were also studied using ATR-FTIR. The results of the FTIR spectrum analysis showed that the GO functional groups in the thin-film composite remained without any structural changes. Future efforts regarding the use of GO in membrane design should introduce a method for improving chemical bonding between polyamide and GO, which can prevent GO aggregation.

Acknowledgments This research is been founded by Iran National Science Foundation.

Compliance with ethical standards

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