



# Polyimide-graphene oxide nanofiltration membrane: Characterizations and application in enhanced high concentration salt removal



Nadiah Khairul Zaman<sup>a</sup>, Rosiah Rohani<sup>a,\*</sup>, Abdul Wahab Mohammad<sup>a</sup>, Arun Mohan Isloor<sup>b</sup>

<sup>a</sup>Department of Chemical and Process Engineering, Faculty of Engineering and Built Environment, Universiti Kebangsaan Malaysia, 43600 UKM, Bangi, Selangor, Malaysia

<sup>b</sup>Chemistry Department, National Institute of Technology Karnataka, Surathkal, Mangalore 575 025, India

## HIGHLIGHTS

- PI mixed matrix membranes (MMM) with synthesized GO nanosheets has NF properties.
- PI/GO MMM has better rejection in diluted and concentrated salt solution than pure PI.
- XRD analysis shows consistent changes in membrane structure in various salt concentrations.
- Various salt concentrations influence MMM structure thus the membrane performance.
- Optimum amount of GO in MMM ensure high rejection for various salt concentrations.

## ARTICLE INFO

### Article history:

Received 17 July 2017

Received in revised form 1 November 2017

Accepted 21 November 2017

Available online 22 November 2017

### Keywords:

Graphene oxide

Polyimide

Nanofiltration

Mixed matrix membrane

Desalination

## ABSTRACT

A membrane usually suffers from a reduction in membrane rejection performance when exposed to a concentrated salt solution. A fabricated polyimide (PI)/graphene oxide (GO) mixed matrix membrane (MMM) was prepared at different GO/PI concentrations (ranging from 0 to 3.5 wt%) to investigate membrane performance in diluted and concentrated salt solutions. Results showed that the MMM possess nanofiltration (NF) properties with high water permeability and excellent salt rejection (99%) in diluted conditions regardless of the applied filtration pressure. The water and permeate permeability increased with the increase in GO content. Interestingly, for concentrated salt solutions, PI/GO MMM only showed at most 4% reduction in rejection, unlike in pure PI membrane, which experienced 16% reduction. A higher amorphous region of the MMM compared to the pure PI in salt solutions was found through XRD. The ionization of GO increases the amorphous structure thus enhances the effective thickness of membrane maintaining the MMM rejection performance. 0.9 wt% GO/PI in MMM showed the highest rejection (98%) in 0.15 M Na<sub>2</sub>SO<sub>4</sub>. The presence of GO with its unique properties and highly porous structure was found to retain the membrane rejection properties, especially in concentrated solution.

© 2017 Elsevier Ltd. All rights reserved.

## 1. Introduction

Membrane separation processes, involving different types of membranes including microfiltration (MF), ultrafiltration (UF) and nanofiltration (NF), are considered as being among the most environmentally friendly methods currently available. In salts separation and recovery processes, NF membranes work best as they exploit the characteristics of both ions and membranes. As the selectivity and recovery of salts depend on ions' hydrated sizes and ions' charge densities, membrane performance can be easily enhanced by membrane modification such as improving the membrane's surface charge (Lin et al., 2007; Van der Burggen et al.,

2004). In salt separation using NF membranes, there are two major mechanisms involved, including sieving and solution-diffusion, and both depend on membrane charge effects. Membrane charge effects work by separating ions of divalent from monovalent through Donnan forces, where the membrane will retain ions with a higher charge. Meanwhile, ions with a lower charge will be transferred to the permeate side to establish electroneutrality on both sides of the membrane. This has even resulted in a negative rejection value of monovalent ions when filtering mixed salt solutions (Paugam et al., 2004; Mulder et al., 2005).

Despite the excellent properties of NF membranes in salts selectivity and recovery, NF membranes usually suffer from a reduction in rejection performance when a concentrated salt solution is used. At high salt concentrations, the membrane charge due to the ionization of membrane functional groups is highly affected, and the

\* Corresponding author.

E-mail address: [rosiah@ukm.edu.my](mailto:rosiah@ukm.edu.my) (R. Rohani).

electrostatic repulsion effects between charged solutes and membranes no longer work effectively. In the recent past, exploitation of membranes via membrane modification was found to be the best solution to tackle this problem. Different modification approaches have been employed using coating or grafting functional material (Kang et al., 2011; Wei et al., 2010), incorporating nanomaterials into membranes (Lee et al., 2013) or fabricating new membranes with tailored chemistry (Park et al., 2008). Among these techniques, the incorporation of nanomaterials into membranes has been extensively researched due to the availability of a variety of organic and inorganic nanomaterials such as titanium dioxide (TiO<sub>2</sub>), silicon dioxide (SiO<sub>2</sub>), silver and carbon nanotubes (CNTs) with excellent properties of highly negatively charged (Suttiponparnit et al., 2011) antimicrobial (Lee et al., 2013) and anti-fouling (Lee et al., 2013; Choi et al., 2013) properties. The resultant modified membranes usually demonstrated unique features rendered by the nanomaterials presence.

Recently, graphene oxide (GO) has drawn attention due to its superior properties resulting from its structure of an arranged honeycomb lattice with oxygen-rich functional groups in a form of carboxyl, hydroxyl and epoxy groups (Dryer et al., 2010; Huang et al., 2011; Hummers and Offeman, 1958). GO becomes highly negatively charged when dispersed in water due to the ionisation of the carboxyl groups on the edges of the GO sheets. In addition to that, the carbon atoms bonded to the oxygen atoms in the oxygen-containing groups at the basal plane also experience distortion from the high proportion of sp<sup>2</sup> C–O bonds, resulting in the formation of amorphous regions creating nanoscale wrinkles and structural defects in the basal plane. This provides a frictionless flow for water transport through GO-modified membranes (Huang et al., 2014). Previous studies have focused on GO-modified membranes for water permeation improvement and anti-fouling and antimicrobial effects, as GO shows an extensive high negative surface charge of approximately –30 to –58 mV compared to TiO<sub>2</sub> nanoparticles and CNTs with –15 and –8.3 mV (Suttiponparnit et al., 2011; Lee et al., 2007; Cote et al., 2010), respectively. However, less research has been conducted on studying the effect of GO's unique structure and properties on the rejection performance of NF membranes, especially involving high salt concentrations.

As self-standing GO membranes usually demonstrate poor mechanical strength, the unique properties of GO can be best utilised by combining it with other membranes. Previous studies have displayed good membrane performance when GO is incorporated with polymeric membranes. Lai et al. (2016) had fabricated a thin-film nanocomposite (TFN) membrane by incorporating GO into a Psf microporous substrate, which was then layered with polyamide (PA) via in situ interfacial polymerisation. The membrane was reported to exhibit higher pure water flux, salt solution permeability and salt rejection compared to the pristine membrane without GO. Na<sub>2</sub>SO<sub>4</sub> and NaCl retention were recorded at 95.2% and 59.5%, respectively (Lai et al., 2016). Another study by Choi et al. (2013) has also demonstrated an improvement in water flux but the membrane performance remain unchanged when using a PA membrane modified with GO-aminated GO (GO-AGO) via layer-by-layer (LbL) assembly techniques. NaCl retention was recorded at around 96–97% irrespective to the number of GO layers. These studies only focused on the rejection of low concentrations of salt at around 1–2 g/L. No relevant work related to GO has ever reported on using high concentrations of salt(s) so far, which has been an important issue as most of the crude feeds or waste stream from organic or food processes usually contain highly concentrated salt of up to 20% wt/vol.

In this study, polyimide (PI) P84 was used as the membrane-based polymer for GO nanosheets dispersion. PI P84 was chosen among other types of PIs such as Kapton as it demonstrates good chemical stability in acids and solvents, high chemical resistance

properties, and good thermal and mechanical properties (See-Toh et al., 2007). PI was also reported to exhibit high rejection performance towards salts, a high membrane zeta potential and low surface roughness, which makes it a good membrane for long-term application due to low susceptibility towards fouling (Ohya et al., 1996; Myllymaa et al., 2010). One of the advantages of PI compared to other polymers is that PI can be tuned to desired membrane properties of high rejection, high permeation performances and good stability by just manipulating the synthesis parameters during the polymerisation process (Ohya et al., 1996). This allows flexibility in tuning and fabricating the desired membrane for a specific application.

To recapitulate, a new NF mixed-matrix membrane (MMM) fabricated from polymeric PI and GO dope solution was prepared via the immersion precipitation technique under controlled conditions for enhanced high concentration salt removal. Comprehensive characterisations were performed to understand the effect of variation in GO content towards PI/GO membrane performances. The membranes were evaluated based on (i) the morphology and structure and (ii) the physical and chemical properties. Membranes were also tested for pure water permeation, and ionic solute permeation and rejection to understand the behaviour of (iii) water transport and (iv) ionic solute transport for diluted and concentrated salts solutions across the membrane. The performance of the membrane in terms of flux and rejections were correlated with the physicochemical and structural properties of the PI/GO membranes. The results of PI/GO membranes testing were then evaluated and compared to the pure PI membranes.

## 2. Materials and methods

### 2.1. Materials

Polyimide P84 (PI, Good Fellow, UK) was used as the membrane material. N-methyl-2-pyrrolidinone (NMP) was purchased from Sigma-Aldrich and used as a solvent to prepare the cast solution. Graphite (Aldrich) was used to manufacture graphene oxide for the modification of the PI membrane via blending. Sulphuric acid (H<sub>2</sub>SO<sub>4</sub>, R&M Chemical), phosphoric acid (H<sub>3</sub>PO<sub>4</sub>, R&M Chemical), potassium permanganate (KMnO<sub>4</sub>, Sigma-Aldrich) and hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>, R&M Chemical) were used to oxidise graphite to graphene oxide (GO) for exfoliation.

### 2.2. Preparation of GO solution

GO was prepared from natural graphite (Aldrich) using the following chemicals according to the simplified Hummers method (Huang et al., 2011). Phosphoric acid (H<sub>2</sub>PO<sub>3</sub>), sulphuric acid (H<sub>2</sub>SO<sub>4</sub>), potassium permanganate (KMnO<sub>4</sub>) and hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) were used to oxidise graphite to GO. Oxidation of the graphite was carried out by mixing H<sub>2</sub>SO<sub>4</sub>:H<sub>3</sub>PO<sub>4</sub> (320:80 mL). The graphite flakes (3.2 g) were added to the mixture of concentrated acids, and KMnO<sub>4</sub> (18 g) was gradually added to this mixture with stirring. The one-pot mixture was then left for stirring for 3 days to allow the oxidation of the graphite. The colour of the mixture changed from dark purplish green to dark brown. After 3 days, the H<sub>2</sub>O<sub>2</sub> solution was added to stop the oxidation process, and the colour of the mixture changed to brown, indicating a high oxidation level of the graphite. The GO which had formed was then washed with water to dilute acidic remnant from the GO. For each wash, the mixture was centrifuged with a centrifugation force of 7000rpm for 15 minutes and the supernatant decanted and removed. The process was repeated until a nearly neutral aqueous solution was achieved. During the washing process with deionised water, the GO experienced exfoliation, which resulted in the thickening of the graphene solution, forming a GO gel. The GO was then

Download English Version:

<https://daneshyari.com/en/article/6588766>

Download Persian Version:

<https://daneshyari.com/article/6588766>

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