Graphene oxide incorporated thin film nanocomposite nanofiltration membrane for enhanced salt removal performance

CrossMark

G.S. Lai, W.J. Lau *, P.S. Goh *, A.F. Ismail, N. Yusof, Y.H. Tan

[a] Advanced Membrane Technology Research Centre (AMTEC), Universiti Teknologi Malaysia, 81310 Skudai, Johor, Malaysia
[b] Faculty of Chemical and Energy Engineering, Universiti Teknologi Malaysia, 81310, Johor, Malaysia

HIGHLIGHTS

- GO nanosheets increased the membrane surface negative charge and hydrophilicity.
- GO incorporated TFN membrane overcame the trade-off effect of TFC membrane.
- TFN 0.3 showed optimum PWP which was 50.9% higher than TFC membrane.
- TFN 0.3 rejected almost 60% of NaCl which was 88.5% higher compared to TFC membrane.

ARTICLE INFO

ABSTRACT

One of the most critical issues encountered by thin film composite (TFC) nanofiltration (NF) membrane in water softening is the trade-off between water flux and salt rejection. A novel thin film nanocomposite (TFN) membrane was fabricated by incorporating graphene oxide (GO) of different quantity (ranging from zero to 0.5 wt.%) into polysulfone (PSf) microporous substrate. Polyamide layer was formed on top of the neat PSf and PSf-GO substrate to produce TFC and TFN membrane, respectively through the interfacial polymerization of piperazine and trimesoyl chloride monomers. With respect to pure water flux, TFN membrane made of 0.3 wt.% GO exhibited the highest water permeability with rejections for Na_2SO_4, $MgSO_4$, $MgCl_2$ and NaCl recorded at 95.2%, 91.1%, 62.1% and 59.5%, respectively. As compared to TFC control membrane, GO incorporated TFN membranes exhibited higher pure water flux, salt solution permeability and salt rejection. This proved that GO plays an important role in increasing both membrane hydrophilicity and surface negativity. Most importantly, TFN membrane made of nanocomposite substrate served as a promising solution to overcome the trade-off effect between water flux and salt rejection of TFC membrane owing to the improved properties of substrate upon incorporation of highly hydrophilic and negatively charged GO nanosheets.

© 2016 Elsevier B.V. All rights reserved.

1. Introduction

In recent years, nanofiltration (NF) membrane has been heavily studied because of its advantages of producing promising water flux at relatively low operating pressure while exhibiting excellent separation rate against divalent salts [1]. The high energy efficiency coupled with excellent divalent salt rejection have made NF membrane a good candidate for water softening and drinking water production compared to reverse osmosis (RO) membrane [2]. Unlike asymmetric NF membrane made via phase inversion method, thin film composite (TFC) NF membrane prepared by interfacial polymerization technique displays significant higher water permeability without compromising good selectivity [3,4].

Typical TFC membrane consists of an ultra-thin selective polyamide (PA) on top of a thick and porous substrate layer. The structure of the top selective layer and the bottom porous substrate can be independently modified to optimize the membrane performance [5,6]. In order to further enhance the TFC membrane filtration performance, inorganic nanomaterials such as titanium dioxide (TiO_2), silicon dioxide (SiO_2), titanate nanotubes (TNTs), silver, carbon nanotubes (CNTs) and halloysite nanotubes have been introduced into the substrate and/ or PA layer of membrane for the production of new type of membrane named as thin film nanocomposite (TFN) membrane [7–12]. The resultant TFN membranes have shown huge potential to overcome the flux-rejection trade-off of TFC membranes owing to the unique features rendered the by inorganic nanofillers. These include improved surface hydrophilicity, greater surface roughness and charge, excellent antifouling properties and antibacterial effect [13–16].

* Corresponding authors at: Advanced Membrane Technology Research Centre (AMTEC), Universiti Teknologi Malaysia, 81310 Skudai, Johor, Malaysia.
E-mail addresses: lwoeijye@utm.my, lau_woeijye@yahoo.com (W.J. Lau), peisean@petroleum.utm.my (P.S. Goh).

Recently, graphene oxide (GO) has drawn the attention of scientists of various disciplines owing to its superior charged properties resulted from bulk amounts of oxygen functional groups such as hydroxyl, epoxy, and carboxyl [17–19]. These oxygen functionalities are able to form strong hydrogen network with water molecules, creating superior hydrophilic property [20]. Referring to several previous works, it is found that the incorporation of GO in the membrane matrix is more focused on improving water permeation [21], anti-fouling [22] and anti-microbial [23] for ultrafiltration (UF), RO and forward osmosis (FO) application. However, very less research had been conducted to study the effect of the unique characteristics of GO, which is highly negatively charged (approximately −30 to −58 mV at pH 5–8) [24–26], on the performance of NF application. Its charge value is much higher than those of TiO$_2$ nanoparticles (30 to −15 mV at pH 5–7) [27] and CNTs (−8.3 mV at pH 7) [28]. For NF membrane, the solute rejection is strongly depending on both steric hindrance (size exclusion) effect and Donnan exclusion (charge repulsion) mechanism [29–32]. In view of this, the highly negatively charged GO nanosheets have great potential to be used to modify membrane surface charge for the purpose of enhanced salt separation, in addition to improvement in water flux.

The objective of this work is to study the performance of new type of TFN membrane that was made using PSf-GO nanocomposite substrate. A series of characterization were conducted to understand the effect of self-synthesized GO nanosheets on the physicochemical properties of PSf substrate and further TFN membrane characteristics with respect to structural property, surface charge and surface hydrophilicity. NF experiments were also performed to evaluate the performance of TFN membrane in rejecting mono- and divalent salts. The membrane performance of the membrane was evaluated in terms of pure water permeability (PWP), solute permeability and salt rejection. The most suitable PSf-GO nanocomposite substrate was further applied for water softening process.

2. Experimental

2.1. Materials

Polysulfone Udel® P-3500 in pellet form (Solvay), polyvinylpyrrolidone (PVP K29-32, Acros Organics) and 1-methyl-2-pyrrolidinone (NMP, 99%, Acros Organics) were used for fabrication of PSf substrate. Piperazine (PIP, 99% Acros Organics) and trimesoyl chloride (TMC, 98%, Acros Organics) were used as the monomers to establish the PA selective layer on PSf substrate. n-Hexane (99%, RCI Labscan) was used to dissolve TMC. Graphite powder (<20 μm, Sigma Aldrich) was used to synthesize graphene oxide which was later used to modify PSf substrate. Sulphuric acid (H$_2$SO$_4$, 95–97%, Merck), sodium nitrate (NaNO$_3$, Riedel-de Haen), potassium permanganate (KMnO$_4$, >99%, Sigma-Aldrich) and hydrogen peroxide 30% (H$_2$O$_2$, Merck) were used to oxidize graphite to GO. Barium chloride 2-hydrate (BaCl$_2$·2H$_2$O, Riedel-de Haen), hydrochloric acid (HCl, 37%, Merck), acetone (RCI Labscan) and Millipore RO water (ASTM Type III) were used during washing process of synthesized GO. Polyethylene glycols (PEGs, Acros Organics) with molecular weights of 200, 400, 600, and 1000 g/mol were used as the neutral solutes to estimate the molecular weight cut-off (MWCO) of the TFC and TFN membranes. Inorganic salts including sodium sulfate (Na$_s$SO$_4$, Riedel-de Haen), sodium chloride (NaCl, Merck), magnesium sulfate (MgSO$_4$, Merck) and magnesium chloride (MgCl$_2$, Acros Organics) were used as the charged solutes to determine the NF performance of resultant membrane in water softening.

2.2. Preparation of GO nanosheets

GO was synthesized from graphite powder using modified Hummers' method [33–35]. In brief, GO was prepared by the oxidation of graphite using KMnO$_4$ as a strong oxidizing agent. 3 g of graphite and 1.5 g of NaNO$_3$ were mixed well in 69 mL of concentrated H$_2$SO$_4$. The mixture was cooled to 0 °C using ice bath and stirred for 15 min. Then

9 g of KMnO$_4$ was added slowly into the mixture while maintaining the temperature below 20 °C to prevent overheating and explosion. After stirring for 2 h, the ice bath was replaced by water bath and the mixture was stirred vigorously for another 30 min at 35 °C. RO water (150 mL) was added and the temperature of the mixture was maintained below 95 °C for 15 min of stirring. Finally, the reaction was terminated by addition of RO water (500 mL) and 30% H$_2$O$_2$ solution (15 mL) to reduce the residual permanganate and manganese dioxide to colorless soluble manganese sulfate. The resulting mixture was filtered, and the filtered product was washed with 5% HCl aqueous solution until sulfate could not be detected by BaCl$_2$. GO was later washed by RO water and centrifuged until the supernatant reached pH 5–6. The GO solution was ultrasonicated for 1 h and the GO mud was obtained by centrifuging at 4000 rpm for 2 h to remove large and not fully exfoliated GO. The GO product was dried in vacuum oven at 60 °C for 12 h. To further purify the GO, the dried GO was dissolved into large amount of acetone and stirred vigorously [36]. At last, the GO solution was filtered and the obtained GO cake was dried in vacuum oven again at 60 °C for 6 h.

2.3. Preparation of PSf and PSf-GO substrates

Four different PSf substrates were fabricated using dope solution formulation as shown in Table 1. The dope solution used for pristine PSf substrate making was an optimized substrate reported in previous work for NF membrane fabrication [37]. To prepare the dope solution containing GO, an appropriate amount of PVP and GO nanosheets were first added to NMP, followed by 30 min ultrasonication to disperse GO and minimize agglomeration. PSf was then added slowly into the mixture under vigorous stirring. To remove air bubbles trapped within the dope solutions, each solution was subject to 1 h ultrasonication followed by at least 24 h storage at room conditions before being used for casting process. The viscosity of the dope solution was measured using a rotational viscometer (Cole–Parmer). The substrate layer with thickness of 110 ± 5 μm was cast on a glass plate using a glass rod. The cast substrate was left for 10 s at ambient temperature before immersing into a water coagulation bath at room temperature for phase inversion process to take place. Once the membrane was peeled off from the glass plate, it was transferred to another water bath and kept for 24 h to remove residual solvent. At last, the obtained microporous PSf substrate layer was washed with RO water and kept in wet condition prior to use. These substrates are hereafter denoted as PSf, PSf-GO 0.1, PSf-GO 0.3 and PSf-GO 0.5 according to the GO loading used in the casting dope.

2.4. Preparation of polyamide selective layer

The PA selective layer of TFC or TFN membrane was prepared via in-situ interfacial polymerization of PIP and TMC. The substrate was first clamped in between a glass plate and Viton frame. 20 mL of 2 w/v% PIP aqueous solution was poured on top of porous substrate made of either pure PSf or PSf-GO and held for 2 min before draining off the excess solution. The residual droplets were rolled off from the amine saturated substrate using a rubber roller. Then, 20 mL of 0.2 w/v% TMC in n-hexane solution was poured onto the substrate surface and drained off from the surface after 1 min contact time. The interaction between two active monomers has resulted in the formation of a thin active PA

Table 1
Properties of dope solutions for microporous substrate making.

Substrates	Dope formulation (wt.%)				Dope viscosity (mPa·s)
	PSf	PVP	GO	NMP	
PSf	15.0	1.0	–	84.0	496.5
PSf-GO 0.1	15.0	1.0	0.1	83.9	515.2
PSf-GO 0.3	15.0	1.0	0.3	83.7	534.3
PSf-GO 0.5	15.0	1.0	0.5	83.5	572.6