



High permeance nanofiltration thin film composites with a polyelectrolyte complex top layer containing graphene oxide nanosheets



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ABSTRACT

A graphene oxide (GO) nano-additive was incorporated into a polyelectrolyte complex (PEC) to prepare water selective membranes for a water desalination process. The synthesized thin film composites consisted of a PEC-GO separation layer, a microporous poly(vinylidene fluoride) layer, and a non-woven substrate. The crosslinking agent glutaraldehyde (GA) was used to enhance the stability of the PEC composite membranes. The resulting membranes were investigated in nanofiltration systems to examine their permeance and salt rejection efficiency. The results demonstrated that 100 ppm GO in the PEC exhibited a high desalination efficiency on a 1000 ppm NaCl solution. This composite exhibited permeance values in the range of 69–89 kg m⁻² h⁻¹ MPa⁻¹ for various salt solutions. The Na₂SO₄ solution resulted in the highest rejection ratio of 62.1%, followed by the NaCl rejection (38.6%). The MgCl₂ and MgSO₄ solutions had lower rejections of 12.2% and 22.0%. It seems that the GA-PEC-GO composite was more efficient in removing divalent ions than monovalent ions, while maintaining high filtration flux.

1. Introduction

Water resources have become limited and in great demand globally due to increasing industrial activities and population growth. In recent years, reclaimed wastewater and seawater desalination techniques have become the most important routes to provide pure water in the regions affected by water scarcity [1–3]. Currently, water desalination techniques are receiving noteworthy attention, including multi-effect distillation, multi-stage flash, electro-dialysis, reverse osmosis, and nanofiltration (NF) techniques [4]. The NF process has low energy consumption and high permeate flux and is a simple and successful strategy for separating various contaminants from water streams compared with other filtration systems using semipermeable membranes [5].

NF membranes are classified as charged or neutral NF membranes. Charged NF membranes demonstrate improved permeation, separation, and anti-fouling with salt solutions due to steric hindrance and

electrostatic repulsion compared with neutral NF membranes [6]. A new category of charged NF membrane is based on polyelectrolyte complexes (PECs), which are synthesized by mixing positively and negatively charged polyelectrolyte solutions to form thin layers [7,8]. PECs have ionic interpenetrating structures and are prepared through ionic complexation using an aqueous solution. The phase separation and unique complexation properties of PECs have also marked them as superior materials for highly selective membrane for reverse osmosis, ultrafiltration, microfiltration, nanofiltration and pervaporation [9,10]. The hydrophilicity of PECs can be easily modified by adjusting their constituent polyelectrolyte species [11], charged functional groups [12], charge densities [13] or the ratios thereof [14]. PECs have been used to fabricate NF membranes with high permeate flux and superior solute separation for the treatment of water contamination [15]. Wu et al. prepared a PEC using polymerization techniques to improve the permeate flux (24.8–37.7 kg m⁻² h⁻¹ MPa⁻¹) and achieve a higher salt rejection toward divalent ions than monovalent ions [16]. Deng

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et al. also reported higher permeance values ($76.6 \text{ kg m}^{-2} \text{ h}^{-1} \text{ MPa}^{-1}$) due to the larger pore size and reduced roughness of a PEC membrane [17]. Ba et al. demonstrated PEC membranes having good resistance to activated sludge to improve the permeance and salt rejection when compared with commercial membranes (NTR-7450) for desalination [18]. Nevertheless, the stability of electrostatically assembled PEC membranes will be affected by the existence of alkali, acid, oxidant and salt from the feed solution [19,20].

Many PEC composite membranes show moderate efficiency (rejection efficiency $\leq 60\%$) for salt ions and are more effective (rejection efficiency $\leq 90\%$) for organic molecules that depend on permeate flux [21–23]. Therefore, researchers have incorporated graphene oxide (GO) flakes into PEC composite membranes to improve the permeance and salt rejection for water purification [24,25]. GO plays a significant role in numerous pathways, such as the uniform distribution of GO in PEC preventing unnecessary aggregation of PEC chains, decreasing the redundant entanglements of PEC molecules, controlling cracks/defects in the film surface and improving the modulus and hardness of the composite [24,26–28]. In addition, GO coating layers in PECs act as barriers for different salt ions and improve the membrane stability by suppressing membrane degradation [29]. The frictionless surfaces of the GO sheets in a polymeric matrix particularly improve the flow of water molecules through the zigzag pathways to attain higher water fluxes [30]. Wang et al. prepared single-layered GO in a PEC membrane and improved the permeate flux to $24.8 \text{ kg m}^{-2} \text{ h}^{-1} \text{ MPa}^{-1}$ from that of a pristine PEC ($15.6 \text{ kg m}^{-2} \text{ h}^{-1} \text{ MPa}^{-1}$) membrane, resulting in a higher NaCl rejection (37.8%) due to the migration and rearrangement of polymeric chains [24]. When increasing the number of GO layers (10 layers) in a polymeric membrane, Choi et al. demonstrated that the permeate flux decreased ($9.3 \text{ kg m}^{-2} \text{ h}^{-1} \text{ MPa}^{-1}$), but the monovalent salt rejection (96.4%) progressively improved, as did the stability of the composite membrane [31]. Hu et al. used a 15-layered GO composite membrane to obtain high permeate values ($\sim 276 \text{ kg m}^{-2} \text{ h}^{-1} \text{ MPa}^{-1}$) to remove monovalent ions (rejection of $\sim 19.5\%$). When increasing the GO up to 25 layers, the permeate flux ($\sim 190 \text{ kg m}^{-2} \text{ h}^{-1} \text{ MPa}^{-1}$) and salt rejection ($\sim 19\%$) also gradually decreased [32]. Therefore, the addition of GO in PECs may construct different pathways for water molecules and modify the transport channels in the membranes [33]. Hence, the incorporation of GO in PEC membranes has afforded novel materials for the bases of high-performance hybrid NF membranes for water treatment.

The present work aims to develop a novel top separation layer of NF composite membranes using a PEC and GO nanofillers with crosslinking glutaraldehyde (GA). The PEC was constructed using sodium carboxymethyl cellulose (CMCNa) and poly(diallyldimethylammonium chloride) (PDDA) prepared in dilute hydrochloric acid (HCl) aqueous solution and attained in its solid condition. The PEC was then dispersed in aqueous sodium hydroxide (NaOH) to form an ionic-crosslinked structure and was subsequently cast onto a non-woven/poly(vinylidene fluoride) (PVDF) microporous substrate. The effects of adding GO into the PEC and additional glutaraldehyde crosslinker on the filtration performance were examined. The permeance and salt rejections of various salt solutions using these prepared thin film composites were evaluated.

2. Experimental section

2.1. Synthesis of graphene oxide

A modified Hummers' method was used to prepared graphene oxide (GO) from graphite powder (Sigma-Aldrich, St. Louis, MO, USA) [25]. In detail, 2 g of graphite powder was dissolved in 100 mL of concentrated sulfuric acid (H_2SO_4 , 95–98%, Sigma-Aldrich) and maintained below 10°C in an ice bath. Afterwards, 8 g of potassium permanganate (KMnO_4 , Sigma-Aldrich) was added slowly with stirring over 2 h. Then, the mixture solution was continuously stirred for 1 h, and 100 mL of deionized (D.I.) water was added to dilute the solution.

Again, the solution was stirred for 1 h, and 100 mL of D.I. water was added to dilute the solution. Twenty milliliters of hydrogen peroxide (H_2O_2 (30%), Showa Chemical, Tokyo, Japan) was mixed into the solution to oxidize the KMnO_4 . Finally, the solution liberated bubbles, and the color changed to bright yellow. Afterwards, the solution was ultrasonicated (Q700, Qsonica, Newtown, CT, USA) for 1 h. The product obtained was centrifuged (Centrifuge Z326K, Hermle Labortechnik, Wehingen, Germany), and the supernatant was replaced by D.I. water three times to eliminate the metal ions. The resultant product was completely dried in a vacuum oven for 24 h at 60°C .

2.2. Synthesis of the non-woven/PVDF supporting layer

A desirable amount of dried PVDF powder (MW = $\sim 534,000$ Da) was dissolved in N-methyl-2-pyrrolidinone (NMP, Sigma-Aldrich). Then, the polymeric solution (20%) was stirred continuously for 48 h at 60°C to ensure its homogeneity. The solution was cast on a non-woven fabric (grade 3706, Ahlstrom Corporation, Helsinki, Finland) at ambient temperature with a casting knife at $200 \mu\text{m}$ (Elcometer 3580, Elcometer, Manchester, UK). After being exposed in air for 2 h, the casted film was dipped into a D.I. water coagulation bath. The two-layer composite film was removed from the coagulation bath and washed with D.I. water to remove the residual solvent. Finally, the prepared wet membrane was completely dried in a vacuum oven at 50°C .

2.3. Preparation of non-woven/PVDF/PEC

The PEC preparation method was modified from previous work [8]. A 400 mL anionic polyelectrolyte solution was prepared by dissolving sodium carboxymethyl cellulose (CMCNa, Sinopharm Chemical Reagent Co., Ltd, Shanghai, China) in D.I. water to form a 0.01 M solution and adjusted with 0.009 M hydrochloric acid (HCl, J.T. Baker, Phillipsburg, NJ, USA). Another cationic poly(diallyldimethylammonium chloride) (PDDA, Sigma-Aldrich) solution was prepared at 0.01 M and acidified with 0.009 M HCl.

The PDDA solution was slowly mixed with the CMCNa solution using a burette at a fixed rate (6 mL min^{-1}) under stirring at 200 rpm. During the addition of PDDA to the CMCNa solution, turbidity formed immediately, representing the formation of insoluble PECs. The turbidity continued to increase, and finally, macroscopic phase separation was obtained when the endpoint was attained (after approximately 8 mL of PDDA was added). After the PDDA addition was stopped, loose white precipitates were visible at the bottom. The precipitate solution was then filtrated and immersed in D.I. water for 6 h and rinsed with copious D.I. water to remove free ions and soluble impurities until the conductivity of the water effluent remained unchanged. The final product was then completely dried in a vacuum oven at 60°C for 24 h and stored in a nitrogen atmosphere for further use.

To prepare the PEC thin film of CMCNa-PDDA, 0.05 g of PEC precipitate was dissolved in 0.1 M sodium hydroxide (NaOH, Sigma-Aldrich). To enhance PEC stability, pre-crosslinking was also performed by mixing GA (Sigma-Aldrich) and HCl into the PEC in NaOH solution for 10 min. The viscous polymer solution was then cast on the dried non-woven/PVDF layer. The sample was initially placed in a conventional oven at 50°C for 5 h to eliminate most of the solvent and solidify the thin film, followed by drying in vacuum for 24 h at 60°C to produce a pristine PEC composite membrane. The pristine PEC membrane crosslinked with GA was coded as GA_PEC.

For the GO-containing sample, 40 mg or 80 mg of GO was dispersed in the acidified CMCNa solution. These corresponded to GO concentrations of 100 and 200 ppm. Following the above-mentioned procedures, we obtained PEC-GO thin film composites; the resulting crosslinked PEC-GOs were coded as GA_PEC-GO₁₀₀ and GA_PEC-GO₂₀₀, respectively. The synthesized thin film composites consisted of a PEC-GO separation layer, a microporous poly(vinylidene fluoride) layer and a non-woven substrate (shown in Fig. 1). The top layer must be

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