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Fabrication of a novel octadecylamine functionalized graphene oxide/PVDF dual-layer flat sheet membrane for desalination via air gap membrane distillation

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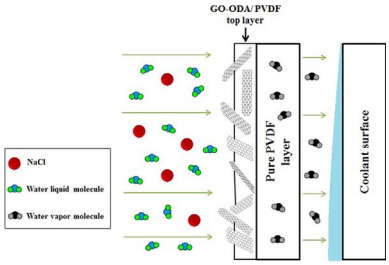
GRAPHICAL ABSTRACT



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ABSTRACT

In the present research, a novel dual-layer membrane was prepared by coating a very smooth layer of octadecylamine functionalized graphene oxide (GO-ODA) on the surface of polyvinylidene fluoride membrane. The GO and GO-ODA were characterized by XRD, TGA and FE-SEM and pure PVDF (unmodified) and dual-layer (modified) membranes were also characterized by contact angle, pore size distribution, liquid entry pressure (LEP), FT-IR, SEM, AFM, and ATR-FTIR. Modified membranes in comparison with unmodified membrane showed a superior performance in terms of surface roughness, hydrophobicity, water flux and NaCl rejection. In air gap membrane distillation (AGMD) experiments using a 3.5 wt% NaCl solution as feed at 80 °C, unmodified, M1 (low GO-ODA loading), and M2 (high GO-ODA loading) modified membranes showed water fluxes of 18.2, 13.8, and 16.7 kg/m^2·h and salt rejections of 88.5%, 96.3%, and 98.3%, respectively. This improvement in membrane performance was attributed to the existence of GO-ODA on the top layer of modified membranes that formed interconnected nano-channels with high surface area for high NaCl rejection and fast flow of water. Furthermore, GO-ODA with high hydrophobicity and low thermal conductivity on the surface of modified membranes contributed to reduce pore wetting, temperature polarization and heat diffusion across the membrane.

1. Introduction

Global demand for fresh water has been increasing because of decreasing sweet water supplies and growing populations and this demand will become greater as technology, population, and economies of countries progress. 98% of water supplies are sea or brackish water, so

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desalination of water with cost effective and low-energy consumption procedures has become very imperative [1].

Membrane distillation (MD) is a non-isothermal separation process driven by a vapor pressure difference that is due to temperature difference across membrane. In this process hydrophobic membrane prevents liquid feed to pass through porous membrane and only vapor molecules can transport through membrane, furthermore simultaneous mass and heat transfer happen in this application [2,3].

MD compared to other conventional separation operations has many advantages. It can be used at low temperature so its heat can be supplied by solar and geothermal energy. In comparison to pressure driven membrane process such as reverse osmosis (RO) lower pressure is needed. Moreover, high solute rejection, less demanding membrane mechanical properties, being less sensitive to feed variations like pH, and also suffering little from fouling make MD more attractive than other separation processes. But beside these benefits, because of some obstacles such as low permeate flux compared to other separation operations, membrane pore wetting, high thermal energy consumption, as well as flux decay, MD has obtained little approval from commercial stance [3–5].

The appearance of nanotechnology has provided new opportunities to promote water desalination technologies. Nanostructured materials, such as TiO_2, zeolites, graphene, and carbon nanotubes (CNTs) have enabled scientists to fabricate size selective pores and well defined membranes with stable salt rejection and high permeate flux. These nanostructured materials can ensure the development of next-generation desalination membranes with significant performance [6,7]. Application of natural zeolite membranes have been reported for desalination in pervaporation. These membranes showed high flux and effective ion rejection for seawater that signify their potential for use in desalination applications [8]. PVDF membranes coated with TiO_2 to create superhydrophobic surfaces for membrane distillation. These modified membranes displayed reduction in pore wetting, improvement in salt rejection, and membrane desalination stability [9]. Recently functionalized CNTs immobilized on porous polypropylene support have been used for membrane distillation [10]. It has been suggested that high flux in carbon nanotubes is attributed to molecular ordering phenomena inside the nanopores of CNTs and atomic scale smoothness of CNTs walls [11].

Currently, the application of graphene oxide (GO), in water purification and desalination has attracted considerable attention. GO is a graphene derivative with a unique architecture that has many functional group such as epoxide, carboxyl, and hydroxyl that provide reactive sites and hydrophilic properties. It had been reported that after addition of graphene oxide, membrane properties such as mechanical strength, selectivity, antifoulings, and water flux improved. Xu et al. synthesized functionalized graphene oxide (GO) by covalent functionalization with 3-aminopropyltriethoxysilane (APTS) and added different ratios into PVDF solution for ultrafiltration application. They reported strong interfacial interaction between f-GO and PVDF. Furthermore PVDF/f-GO membranes exhibited higher water flux, antifouling, hydrophilicity, and bovine serum albumin (BSA) rejection than PVDF and PVDF/GO membranes [12,13]. Bhadra et al. immobilized GO on PTFE membrane by cast drop and used for membrane distillation. They reported enhancement in water flux due to the nanocapillary effect for selective sieving of water from brackish water, selective sorption of water vapors, reduction in temperature polarization, and as well as existence of polar functional groups in graphene oxide. Hegab et al. used a novel surface modification method and coated a thin layer of graphene oxide functionalized with chitosan on the surface of polyamide membrane and the fabricated membrane showed higher hydrophilicity, NaCl rejection, water flux, and antifouling property than unmodified membrane [14,15].

Therefore the objective of this study was to functionalize graphene oxide chemically with octadecylamine (ODA). The ODA-functionalized GO (GO-ODA) with different ratios blended with PVDF and coated on the top surface of PVDF membranes that acted as the substrate and then applied for desalination in air gap membrane distillation. ODA has a long hydrocarbon chain which reduces the surface energy of GO-ODA and increases membrane hydrophobicity. Many features such as surface structure, wettability, hydrophobicity, thermal and mechanical stability, and desalination performance of modified membranes were evaluated and in comparison to unmodified membrane significant improvement achieved.

2. Experimental

2.1. Materials

Polyvinylidene fluoride (PVDF) (761 grade, Kynar), the polymer used in this study, was supplied by Arkema (USA). Octadecylamine (ODA) was purchased from Sigma-Aldrich (USA). *N*,*N*-dimethylformamide (DMF) (AR grade, > 99.8%) as the solvent, ethanol (AR grade, > 99.9%), isopropyl alcohol (IPA) (AR grade, > 99.8%), sodium chloride (NaCl) (AR grade, > 99.5%) and lithium chloride (Licl) (AR grade, > 99%) as the non-solvent additive, all were from Merck (Germany).

2.2. Preparation of graphene oxide and functionalized-graphene oxide

Graphite oxide was prepared by improved Hummer's method [16]. For functionalization of GO first 100 mg of Graphite oxide and 400 mg of ODA were mixed in 100 ml of ethanol and sonicated for 2 h. Then the solution of GO-ODA was centrifuged at 5000 rpm with ethanol to remove the excess ODA. The obtained GO-ODA was dried and heated at 150 °C for 1 h in vacuum. At the end of procedure GO-ODA was redispersed in ethanol and filtrated to fabricate the superhydrophobic GO-ODA [17]. A schematic illustration of functionalization process has been presented in Fig. 1.

2.3. Preparation of membranes

In brief, PVDF (10 wt%) was dissolved in Dimethyl Formamide (10 ml) and Licl (3 wt%) was also used as the additive into the solution. Then the solution was stirred for 24 h at 50 °C to form a transparent solution and the casting solution was degassed over 24 h to remove bubbles. Then the polymer solution was casted with thickness of 200 μm on a glass plate and immediately was immersed into ethanol coagulating bath. After 1 day the precipitated membrane was removed from the coagulation bath and washed with ethanol to remove residues of solvent and Licl from the membrane. Then the resultant membrane was dried in air for 1–2 days.

After synthesis of substrate, a specified amount of GO-ODA in 5 ml Dimethyl Formamide was sonicated for 2 h. Then 0.3 g of PVDF was added to the solution as a binder material and the resulting solution at 50 °C was stirred for 24 h to obtain a completely dissolved and homogenous solution for casting. The GO-ODA/PVDF solution was placed at room temperature for 24 h to remove air bubbles and this solution was casted with thickness of 100 μm on the substrate and immediately was immersed into ethanol coagulating bath. After 1 day the precipitated membrane was removed from the coagulation bath and washed with ethanol to remove residues of solvent from the membrane. Then the resultant membrane was dried in air for 1 day. In this study the proportion of GO-ODA to PVDF in GO-ODA/PVDF solution were 1:3 (low) M1 and 5:3 (high) M2, respectively. As it was told our aim is to consider the performance of prepared dual-layer membranes with different GO-ODA loading on the top layer for AGMD process. Fig. 2 shows a schematic drawing of fabricated dual layer membrane for AGMD process.