Development of novel thin film nanocomposite forward osmosis membranes containing halloysite/graphitic carbon nitride nanoparticles towards enhanced desalination performance

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ABSTRACT

In this study, thin film nanocomposite (TFN) membranes were fabricated by incorporating highly hydrophilic halloysite nanotubes (HNTs) and self-synthesized graphitic carbon nitride (g-C_3N_4) nanoparticles into polysulfone-based substrate and interfacially polymerized polyamide top layer, respectively. The TFN membranes were evaluated for their performance in forward osmosis (FO) applications. The XRD, ATR-FTIR, FESEM and TEM results confirmed the successful synthesis of g-C_3N_4 nanoparticles. The effects of nanomaterials incorporation were investigated in terms of membrane surface morphology, hydrophilicity and separation performance. When 0.05 wt/v% of g-C_3N_4 was added to the polyamide layer, the membrane surface contact angle was significantly reduced from 68° in the control membrane (TFN0.0) to < 10° in the TFN membrane (TFN0.05), leading to high water flux of 18.88 L/m²·h (approximately 270% higher than the TFN0.0 membrane). The results have proven the predominant effect of the polyamide layer modification compared to the support modification towards FO performance enhancement. The water flux decline for the TFN0.0 and TFN0.05 membranes after a prolonged time of 1200 min was only 12% for the TFN0.05 while TFN0.0 membrane experienced 24% reduction. In addition, fouling resistance of the membranes assessed by BSA revealed that the flux of TFN0.0 has reduced by 54% after 1200 min, meanwhile TFN0.05 recorded a reduction of approximately 30%. The findings confirmed the effectiveness of g-C_3N_4 as a promising surface modifier for polyamide layer to simultaneously contribute to flux enhancement and increased anti-fouling properties.
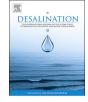
1. Introduction

Due to the increasing demand for the fresh water supply, various strategies and resources have been considered to fulfill the needs. One of the most promising methods is probably through seawater and brackish water desalination. Forward osmosis (FO), as a subset of osmotically driven membrane processes, is an emerging membrane technology which has attracted great attentions for desalination. As this technology requires almost no external hydraulic pressure for the operation, it holds good potential to tackle the limitations that typically faced by reverse osmosis (RO).

Despite the many advantages offered by FO process in terms of low energy consumption and operating cost, excellent anti-fouling resistance and high recovery, efforts have been constantly made in the development of FO membrane to address some challenges such as reverse solute diffusion and severe internal concentration polarization (ICP) phenomenon. The engineering design of thin film composite (TFC) FO membrane is one of the promising strategies to achieve this purpose. Generally, the polyamide (PA) layer produced from interfacial polymerization is responsible for the reverse solute diffusion whereas the structural (S) parameter of the membrane substrate plays a crucial role in dictating the flux and ICP phenomenon. With the decrease of

substrate thickness and tortuosity but enhancement in its hydrophilicity and porosity, the S parameter can be favorably minimized to mitigate the ICP effect as well as to improve the water permeability. In view of the equal importance of both substrate and selective layer, the flexibility and high degree of freedom in the modifications of TFC membrane can significantly optimize the desalination performance.

The characteristics of TFC membranes can be improved by introducing highly hydrophilic nanoparticles into the substrate and/or PA layer to form thin film nanocomposite (TFN) membranes. Remarkably enhanced water flux was reported when nanoparticles such as titanium dioxide (TiO_2) [1], titania nanotubes (TNTs) [2,3], halloysite nanotubes (HNTs) [4], silica dioxide (SiO_2) [5], zeolites [6], carbon nanotubes (CNTs) [7], silver (Ag) [8] and metal alkoxide [9] were embedded within the substrate or the PA selective layer. Our previous published work [4] demonstrated that HNTs can serve as an attractive option to reduce the S parameter of the TFN membranes when they were embedded in the polysulfone-based substrate. The presence of mere 0.5 wt % of hydrophilic HNTs was capable to reduce the S parameter from 0.95 mm in the control TFC membrane to 0.37 mm in the TFN membrane. The drastically reduced S parameter has served as a viable strategy to address the low water flux issue that resulted from the internal concentration polarization (ICP of solutes in the porous substrate). In addition, the results revealed that the addition of HNTs in the substrate of composite membrane has resulted in two-fold improvement in water flux. The enhancement in flux was ascribed to the hydrophilicity of HNTs due to the presence of abundant surface hydroxyl groups. Therefore, it is attempted in this study to modify the properties of the membrane substrate through addition of HNTs since the unique layout of each individual layer of the TFC membrane allows high degree of independent modifications towards further heighten the desalination performance. Such flexibility is valuable especially during the FO membrane synthesis due to equal importance of both substrate layer structure and top PA selective layer.

The PA selective layer properties have also undergone significant improvements upon the addition of nanoparticles which are mainly attributed to the enhanced surface hydrophilicity, increased pore channels and improved antibacterial properties rendered by the nanomaterials. These features have concertedly contributed to higher water permeability as well as greater resistance towards fouling and chlorine attack. Emadzadeh et al. [10] fabricated TFN membranes by incorporating functionalized TNTs into PA selective layer for FO application. Compared to the membranes with no surface modification, they showed that the prepared TFN membranes improved the water flux by two folds without sacrificing the salt rejection. On the other hand, nitrogen-doped graphene oxide quantum dots (N-GOQD) were also used by Fathizadeh et al. [11] and Song et al. [12] as nanofiller for the modification of PA layer for RO process. Both research works showed promising results on the TFN membrane upon N-GOQD modification. The permeate flux was increased up to 50% without compromising the NaCl rejection (98.8%). Metal–organic frameworks (MOFs) have also been utilized for the modification of the TFC FO membranes owing to the molecular sieving and superhydrophilic nature of this kind of nanomaterials [13,14].

Recently, graphite-like carbon nitrite (g-C_3N_4), a class of emerging graphene analog material consisting mainly of carbon and nitrogen, has been extensively explored mainly because of its outstanding chemical and thermal stability, high mechanical strength, surface functionalities, low cost and biocompatibility [15–17]. In addition, the porous and nanosheet structure of g-C_3N_4 has also rendered high specific surface area [18] to promote it as one of the promising materials for surface modification and photocatalysis [19,20]. g-C_3N_4 nanoparticles can be synthesized from low cost urea through a simple and template-free thermal condensation synthetic steps [21]. Due to its hydrophilicity in nature, g-C_3N_4 has been used to facilitate metal/metal oxide nanoparticle dispersion and growth [22–24]. Furthermore, it has been reported that the edge groups of g-C_3N_4 could endow the compound with

negative surface charges [25]. Based on its unique characteristic, g-C_3N_4 can be feasibly used for preparation of high performance membranes for water treatment.

When g-C_3N_4 is incorporated into TFC membranes, the defect-rich planar structure of g-C_3N_4 generated during the thermal condensation process is desirable to shorten the water transport path. The formation of defects with an average size of 3.2 Å enables g-C_3N_4 to be more water permeable [26]. Furthermore, the negatively charge surface is beneficial for the desorption of foulants during membrane cleaning process [26]. Previously, Cao et al. [27] observed a significantly improved permeate flux in ethanol dehydration using mixed matrix membrane incorporated with g-C_3N_4. The enhancement was mainly attributed to the horizontally aligned lamellar structure of g-C_3N_4 which facilitated fast solvent transport rate through the ordered channels. The nanoporous structure of g-C_3N_4 has also favorably rendered sieving effects to improve the separation efficiency. Chen et al. [28] in another work fabricated TFN membrane where the g-C_3N_4 nanosheets were introduced to aqueous solution for the modification of PA active layer. Compared with the water flux of the membrane with no modification (20.9 L/m²·h), for the g-C_3N_4-incorporated membrane showed significant flux improvement (37.9 L/m²·h) when tested at 2 bar. Furthermore, the modified membrane also demonstrated better antifouling properties with salt rejection (Na_2SO_4) maintained at above 84.0%.

Therefore, the objective of this study is to explore the potential of g-C_3N_4 to heighten the performance of TFN FO membrane. A novel TFN membrane was prepared by incorporating commercial HNTs and self-synthesized g-C_3N_4 nanoparticles into the substrate and PA layer, respectively. The effects of these nanomaterials on the resultant FO membranes with respect to morphology, hydrophilicity, S parameter and FO separation performances were evaluated. The fouling behavior of the optimized membrane as a function of time was also investigated. Finally, the performance of the membrane was benchmarked with several commercial FO membranes. To the best knowledge of the authors, this is the first study reporting the development and application of TFN membranes incorporated with HNTs and g-C_3N_4 into different layers of TFN membrane for FO process.

2. Experimental

2.1. Materials

Pellet form polysulfone (PSf) (Udel P-3500, Solvay Advanced Polymers), dimethylacetamide (DMAc, > 99.5%, Merck), polyvinylpyrrolidone (PVP K30, Sigma-Aldrich), HNTs were used for the substrate fabrication. Monomers - 1,3-phenylenediamine (MPD, > 99%, Merck) and 1,3,5-benzenetricarbonyl trichloride (TMC, > 98%, Merck) were used for the interfacial polymerization to form the PA selective layer of the membranes. Bovine serum albumin (BSA, 98%, Sigma-Aldrich) with molecular weight of 67,000 g/mol was used as the model foulant for evaluating the antifouling property of the prepared membranes.

2.2. Synthesis of g-C_3N_4

To synthesize g-C_3N_4, sufficient amount of urea (25 g) powder was placed in a crucible with a cover. The crucible with closed cap was put in a furnace at 550 °C with 5 °C/min heating rate for 2 h to complete the reaction. Later on, the obtained yellowish crystalline solid was washed with ethanol followed by distilled water to remove any impurities before being dried in oven at 80 °C. The as-synthesized g-C_3N_4 was then incorporated into the PA top layer of the TFN membranes.

2.3. Fabrication of TFN FO membranes

2.3.1. Preparation of FO membrane substrate

The substrate of composite membranes was fabricated from a dope