



Preparation of graphene oxide modified polyamide thin film composite membranes with improved hydrophilicity for natural organic matter removal



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HIGHLIGHTS

- TFC membranes with GO embedding in active layer were prepared via IP reaction.
- Natural water was used to study the separation performance of GO membranes.
- TFC membranes with addition of 0.004 wt% GO offered highest pure water flux.
- GO membranes exhibited excellent hydrophilicity and anti-fouling properties.
- Higher GO loadings led to higher removal rates of NOM.

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ABSTRACT

The incorporation of nano-materials in thin film composite (TFC) membrane has opened an alternative opportunity to enhance the membrane permeation and anti-fouling properties in many water treatment processes. In this study, graphene oxide (GO) was incorporated into the polyamide active layer of a TFC membrane via interfacial polymerization (IP) reaction. The structure, composition and hydrophilicity of the membranes were characterized by FT-IR, FE-SEM and water contact angle measurements. The separation performance for natural organic matter (NOM) and the anti-fouling properties of the GO modified TFC membranes were investigated with real natural water sampled from a local river. The permeate water samples were analyzed with ultraviolet absorbance (UV), dissolved organic carbon (DOC), fluorescence excitation–emission matrices (FEEMs) and molecular weight distribution (MWD). Within the range of GO loadings assessed in this study, it was found that the TFC membrane incorporated with GO offered not only higher water flux and NOM removal rate, but also better anti-fouling properties, which was ascribed to the favorable change in membrane hydrophilicity, surface morphology and surface charge by the addition of appropriate amount of GO, indicating great potential of such membranes in water industry.

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1. Introduction

Graphene oxide (GO) is a two-dimensional single layer material bearing sp^2 -bonded carbon [1,2]. Its exceptional physical properties together with its flexibility in chemical functionalization owing to the large numbers of covalent oxygen-containing functional groups—carboxyl, hydroxyl and epoxide present in GO [3], makes GO the candidate of choice for a wide range of applications, including super-capacitors [1,4,5], energy production [5], electronics [6,7], and biological and medical areas [8]. Nowadays the

production of GO in large industrial scale has been enabled which not only significantly lowered the cost of such materials but also showed its great potentials in the areas where large quantity of these materials are required [9].

Thin film composite (TFC) membranes have gained much interest in the applications of water treatment to remove both conventional and emerging contaminants [10–12]. A typical TFC membrane consists of a thin selective polymeric layer (polyamide as the most commonly used polymer material) on the top of a micro-porous support substrate and is often produced by interfacial polymerization (IP) reaction [13–15]. Currently most of the industrial scale nanofiltration (NF), reverse osmosis (RO) and forward osmosis (FO) membranes were produced in the form of TFC

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owing to its good separation performance and wide pH tolerance range. However, its relatively low water flux and poor anti-fouling property has become major concerns which impede their further advance in industrial implementation. In this regard, the research efforts in both academic and industrial sectors have been directed to the searching of appropriate surface modification approach to fine-tune not only the membrane morphology but also its hydrophilicity, thus minimizing the undesired membrane fouling without sacrificing the water flux [16].

In this line of development, the incorporation of nano-sized porous materials either in the top layer polymer matrix or in the polymeric substrate to facilitate higher water flux due to their large pore size and porosity has become a focal point in research. For instance, porous zeolite has been successfully incorporated into the top layer of a polyamide (PA) TFC membrane, with greatly improved water permeability and marginal loss of salt rejection observed as a result [17]. Emadzadeh et al. investigated the addition of different loadings of titanium dioxide (TiO₂) nanoparticles in the polysulfone (PSf) substrate of a TFC membrane, and the results revealed that both the hydrophilicity and porosity of the substrate were increased with the addition of TiO₂ [18,19]. More recently, the incorporation of GO in various membrane types for water treatment to improve their performance, in particularly their anti-fouling properties, has attracted considerable attention [7,20]. For instance, the addition of GO in poly(vinylidene fluoride) (PVDF) ultrafiltration (UF) membrane to improve water flux and anti-fouling properties [21], the incorporation of GO in PSf UF membrane to manipulate the micro-structure and surface charge of the membrane, thus suppressing the fouling behavior [22].

The great benefits of adding GO only in the active top layer of the TFC membrane compared to the GO addition in the bulk membrane has been highlighted in some of the previous work, suggesting that the anti-microbial effect can be better facilitated with GO present on the membrane surface rather than becoming unavailable when buried within the bulk polymer matrix [23,24]. Although promising, it was noted that within these studies, only synthetic model water with individual contaminants was investigated. A thorough study on the GO modified TFC membrane with real natural water is therefore essential, not only to provide better understanding of the role of GO in the membrane performance, but also to demonstrate the feasibility of using such membranes under an industry relevant condition.

In this study, the GO modified TFC membranes with different GO loadings were prepared via IP process on the PSf UF membrane substrates. Fourier transform infrared spectroscopy (FT-IR), field emission scanning electron microscopy (FE-SEM) and water contact angle tests were utilized to evaluate the composition, structure and hydrophilicity of the membrane. The water permeation performance and anti-fouling properties of these membranes were systematically studied with real natural water sampled from a local river in urban Shanghai, China. The composition of natural water as well as the permeate water samples were analyzed by UV, DOC, FEEMs and MWD to evaluate the removal efficiency.

2. Materials and methods

2.1. Materials

Graphene oxide in flake form was purchased from Sigma Aldrich. PSf UF membrane (molecular weight cut-off: 100 kDa) was obtained from XINLIMO Tech Co., Ltd., China. 1, 3-Phenylene diamine (MPD) with 99% purity supplied by Aladdin and 1, 3, 5-Benzenetricarbonyl trichloride (TMC) purchased from Sigma Aldrich were used as interfacial reaction monomer. *N*-hexane used

as the solvent was purchased from Sinopharm Chemical Reagent Co., Ltd, China. All chemicals were used as received without further purification. The de-ionized (DI) water was produced by a Milli-Q system (Millipore) with a resistivity of 18 MΩ cm. Natural water used for the filtration test was obtained from Sanhaowu river, a local river located in urban Shanghai, China. Prior to the filtration test, the natural water was pre-treated to remove colloids and suspended solids.

2.2. Fabrication of GO modified polyamide TFC membranes by the interfacial polymerization reaction

TFC membranes with PA and GO in the top layer and PSf UF membrane as substrate were prepared through interfacial polymerization reaction, as shown in the Supporting Information, Fig. S1 [15,18]. PSf UF membranes were immersed in DI water for 24 h before use. Different contents of graphene oxide (0, 0.004, 0.008 and 0.012 wt%) were added in 2% (w/v) MPD aqueous solution. The PSf UF membrane was placed into a frame to allow for the coating only on the top surface. An aqueous solution containing MPD/GO with different ratios was poured onto the membrane, and kept for 2 min, and then the excess solution was removed from the membrane surface using an air knife. Subsequently, 0.1% (w/v) TMC solution in *N*-hexane was poured onto the membrane, and kept for 1 min. The membrane was then soaked in 0.2% (w/v) sodium carbonate solution for 5 min and was thermal treated in a vacuum oven at 60 °C for 8 min. All the membrane samples were stored in a DI water bath prior to further testing.

2.3. Characterization of the in-house fabricated membranes

The presence of GO and the interaction between GO and PA were evaluated by using Fourier transform infrared spectroscopy (Thermo-Nicolet-iS5, America), with three replicates. Field emission scanning electron microscopy (Ultra55, ZEISS, German) was used to provide the surface and cross-section morphologies of the membranes. The cross-sections of the dried membranes samples were prepared by freeze-fracturing in liquid nitrogen. The surface hydrophilicity was measured by using the water contact angle meter (Attension Theta Lite, Biolin Scientific Co. Ltd., Sweden) equipped with video capture at room temperature, and an average value of at least five measurements was calculated.

2.4. Membrane filtration test

The filtration experiments on the in-house fabricated membranes were performed with a nanofiltration cross-flow system, as depicted in the Supporting Information, Fig. S2, with real natural water previously described in Section 2.1. The filtration system consists of one closed loop for the feed solution stream. A bypass pipe of the closed loop was connected to a hydraulic pressure gauge and the pressure was controlled by the adjustment of a needle valve. The cross-flow membrane cell was custom built with an effective membrane area of 46.07 cm². On one side of the cell, the feed solution was pumped through the membrane using a peristaltic pump. Whilst on the other side, the change in permeate flow rate was monitored through a digital balance connected to a computer. The tests were conducted at room temperature at the feed pressure of 8 bar and each was repeated three times. Prior to the filtration test, each membrane was rinsed with DI water for 24 h to remove un-reacted monomers and then compacted at 8 bar with the feed solution of DI water for 1 h to obtain a stable flux. The flux was calculated by using the following Eq. (1):

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