Ultrathin graphene oxide membranes for the removal of humic acid

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Abstract

In this study, multiple layers of graphene oxide (GO) were coated on a commercially available polyether-sulfone ultrafiltration membrane via simple vacuum filtration of a GO suspension. The effect of GO coating on the membrane performance and fouling resistance was examined, in terms of water flux, natural organic matter (NOM) rejection, and flux decline due to NOM fouling. The results showed that the water flux change of the permeate was minimal (less than ±10%), while NOM rejection was improved significantly by the GO coating (31%, 51%, and 67% for the GO-5 nm, GO-10 nm, and GO-30 nm membranes, respectively). The GO-coated membranes also enhanced membrane recovery and antifouling capabilities, due mainly to increased hydrophilicity of the GO-membrane surface. These observations suggest that the GO-coated membrane, prepared by a facile filtration process in the laboratory, facilitates removal of NOM from water and minimizes the associated membrane fouling.

1. Introduction

Membrane treatments are used widely in water purification and wastewater treatment. However, membrane fouling remains a major limiting factor in membrane filtration processes, because it negatively affects membrane performance by decreasing permeate flux and membrane selectivity, leading to increasing capital and operating costs [1,2]. Natural organic matter (NOM) is one of the major contributors to membrane fouling, especially for organic polymeric membranes [3,4]. While NOM is rejected during ultrafiltration (UF), it also clogs membrane pores or forms a cake layer on the membrane surface [5,6]. Thus, various approaches have been investigated to reduce membrane fouling caused by NOMs, such as pre-treatment of the feed water, membrane surface modification, and membrane cleaning processes [4,7–12].

Recently, the application of graphene and its derivatives, such as graphene oxide (GO), has been of increasing interest in the field of water treatment processes [13–15]. GO nanosheets, in particular, have emerged as a promising material for manufacture of high-performance membranes for water purification due to the exceptional surface and transport properties and ease of covering membranes [16–27]. The nanochannels between GO sheets may allow water to pass through, while rejecting larger contaminants, similar to the sieving mechanism of membranes. However, there can be a strong trade-off between water permeability/flux of GO-coated membrane and solute removal. For example, a previous study reported that the water flux of a GO-coated thin-film composite polyamide membrane decreased significantly, to >75%, while the rates of rejection of NaCl, Na2SO4, and organic dyes increased to 6–18%, 24–46%, and 44–95%, respectively [19].

To date, few studies have reported that GO-coated membranes enhance membrane performance and resistance to fouling. In addition, no evaluation of GO-membrane performance to reduce membrane fouling by NOM has yet been reported. In this study, a commercially available UF membrane was modified with single-layered graphene oxide (SLGO). GO was deposited on the surface of the polyethersulfone (PES) UF membrane via simple vacuum filtration of dilute GO suspensions to obtain ultrathin GO membranes with 5, 10, and 30 nm thicknesses. The membrane structure and properties were characterized using field emission scanning electron microscopy (FE-SEM), X-ray photoelectron spectroscopy (XPS), Fourier-transform infrared (FTIR) spectroscopy, atomic force microscopy (AFM), and water contact angle measurements. Membrane tests were conducted to examine the effect of the GO coating on membrane performance in terms of water flux and NOM rejection during membrane filtration. We also examined the effects of the GO coating on membrane fouling by NOM and membrane recovery capabilities.

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2. Methods and materials

2.1. GO-membrane synthesis

A commercially available flat-sheet PES UF membrane having a nominal molecular weight cutoff (MWCO) of 10 kDa was obtained from Koch Membrane Systems Inc. (Wilmington, MA, USA), and was used as a support membrane. The UF membrane was washed with deionized (DI) water at least five times, and then soaked in DI water for subsequent GO deposition. SLGO powder, prepared by the modified Hummer method, was purchased from Cheap Tubes, Inc. (Brattleboro, VT, USA) and used as the raw material for GO deposition.

The membrane was modified by depositing a GO multilayer onto the surface of the PES membrane support (referred to here as “GO-membrane”) via vacuum filtration of the SLGO suspension. Fig. 1 shows the overall GO-membrane synthesis procedure. The as-received SLGO powder was first dissolved in DI water by a 1 h sonication (Branson 2510R-DTH) a frequency between 40 and 50 kHz and then centrifuged (Bio Lion XC-H165; 10,000 rpm, 1 h) to remove large aggregates. The resulting GO dispersion was used as a stock GO solution. Its concentration was determined by UV–vis spectroscopy (Shimadzu UV-PC2010) following a method described previously[28]. To control the thickness of the GO membrane, a series of stable SLGO suspensions (~20 mL in volume) with desired concentrations were prepared via dilution of the stock GO suspension. GO deposition was completed by filtering the SLGO suspension through the PES membrane using the Millipore filtration system with an active filtration area of 9.6 cm\(^2\). In this study, PES membranes with 5, 10, and 30 nm GO thicknesses were prepared and are denoted as GO-# nm, where # is the thickness of the GO coating. After GO deposition, the membranes were immediately soaked in DI water and were ready for use.

2.2. Characterization of GO-membranes

The properties of pristine membrane and GO-coated membranes were characterized by AFM, XPS, FTIR spectroscopy, FE-SEM, and contact angle measurements. FE-SEM (Zeiss UltraPlus, Germany) images at low and high magnifications were captured from the surfaces of the pristine membrane and GO-coated membranes. To improve image quality, a low voltage, 2–5 kV, a low working distance, <4 mm, and a small capture size, <20 mm, were used to obtain satisfactory images. AFM (NanoScope Illa MultiMode, Brucker, England) was used at a scan size of 10 μm\(^2\) when imaged in air to analyze the surface morphology and roughness of the membranes. FTIR spectra were collected on a Nicolet 6700 FTIR spectrometer (Thermo Scientific, Waltham, MA, USA) with a Smart iTR ATR sampling accessory. The spectra were collected over the range 400–4000 cm\(^{-1}\) for both pristine and GO-10 nm membranes. The surface chemical compositions of both pristine and GO-30 nm membranes were analyzed using XPS (Kratos Axis Ultra DLD instrument equipped with a monochromated Al K\(\alpha\) X-ray source and hemispherical analyzer, capable of an energy resolution of 0.5 eV). The peaks of the XPS binding energies were deconvoluted with Gaussian peak shapes using the Origin software package. Water contact angle in air measurements were taken using a VCP Optima system (Optima XE). Water droplets (~1 μL) were dropped carefully onto the pristine or GO-coated membranes. All membrane samples were dried at room temperature prior to characterization.

2.3. GO-membrane performance tests

The performance of the GO-membranes was evaluated by measuring pure water flux, NOM rejection, and flux decline due to NOM fouling. A dead-end stirred cell filtration system (Sterlitech Corporation, Kent, WA, USA) with 300 mL volume and an effective membrane surface area of 14.2 cm\(^2\) was used. DI water was used to test the pure water flux of the GO-membranes and a pristine membrane.

For the membrane fouling tests, Suwannee River humic acid (SRHA) standard, as a model NOM, was purchased from the International Humic Substance Society (St. Paul, MN, USA) and was used as received. Experiments were conducted with an initial feed concentration of SRHA of 10 mgC/L. The pH and ionic strength...