



Novel titanium dioxide/iron (III) oxide/graphene oxide photocatalytic membrane for enhanced humic acid removal from water



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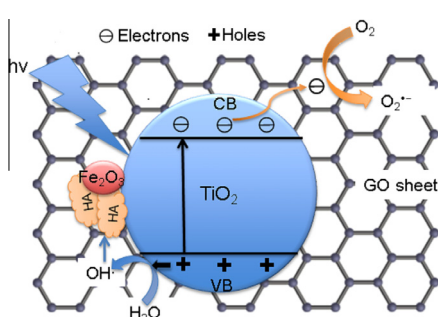
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HIGHLIGHTS

- Membrane made of TiO₂ nanowires/Fe₂O₃ nanoparticles/GO sheets was fabricated.
- Fe₂O₃ nanoparticles improved adsorption of humic acid onto membrane surface.
- GO sheets improved charge transfer from TiO₂ and membrane photocatalytic activity.
- Superb humic acid degradation and membrane antifouling ability under solar radiation.

GRAPHICAL ABSTRACT



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ABSTRACT

Membrane fouling caused by natural organic matters such as humic acid has been one of the major obstacles inhibiting the wide application of membrane technologies for water treatment. In this work, a novel membrane made of interconnecting TiO₂ nanowires, Fe₂O₃ nanoparticles, and graphene oxide (GO) sheets was prepared via a simple hydrothermal, colloidal blending, and vacuum filtration method. Membrane performance of humic acid removal under simulated solar irradiation and in the dark were compared for membranes with different Fe₂O₃/TiO₂/GO compositions. It was demonstrated that enhanced humic acid removal was achieved due to the greater adsorption of humic acid by Fe₂O₃ nanoparticles and the improved photocatalytic activity of TiO₂ by the GO sheets that can facilitate separation of photo-induced electron-hole. An optimal Fe₂O₃:TiO₂:GO weight ratio of 50:100:10 was identified, and over 98% humic acid removal was achieved in a short-term test (2 h) and 92% removal in a 12 h test under solar irradiation. By contrast, only 51% humic acid removal was obtained by the same membrane in dark in the 12 h test. A lower pressure drop across the membrane was also observed under solar irradiation (20 kPa) compared with that in the dark (50 kPa). This nanomaterial-based novel membrane contributes to the development of a more effective water treatment technology.

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1. Introduction

Membrane technology has been widely used for potable water production and wastewater reuse. However, membrane fouling caused by organic foulants such as humic acid was commonly

observed and has been a significant challenge for membrane filtration technologies [1,2]. Membrane fouling can cause severe flux decline, deteriorate quality of water product, shorten membrane life, and increase the operating and maintenance costs of the treatment process [1]. Removing foulants on membrane surface requires periodic chemical cleaning, which not only increases the cost but may also lead to irreversible membrane fouling and damages to the membrane [3,4]. Therefore, pretreatment of the

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feedwater before entering into the membrane module is typically applied to reduce the foulant concentration in the bulk solution [3]. Although adsorptive removal of humic acid by adsorbents such as activated carbon is effective, adsorbent regeneration is needed when the maximum adsorption capability is approached [5]; therefore, photocatalyst-type adsorbent is gaining increasing interest because of its ability to photodegrade the foulants once exposed to light irradiation. However, suspending photocatalyst particles inside the feedwater may cause light shielding from the particles thus decrease the photocatalytic activity [6]. Also, the particles have to be separated from the treated water via additional operations, such as coagulation, flocculation, and sedimentation and the uncollected nanoparticles may transport with water and cause contamination [7]. Therefore, unconventional photocatalytic membranes were fabricated and reported in the literature [8–10]. By confining the photocatalysts by means of a membrane, not only the above drawbacks of suspended nanoparticles can be overcome, it may also save energy, reduce the size of installation for catalyst separation, and reuse the photocatalyst in further runs [7].

Among the photocatalysts, titanium oxide (TiO_2) is most frequently studied because it is highly photoactive, relatively cheap, easily available, and chemically stable [11]. Upon ultraviolet (UV) light irradiation, TiO_2 can generate electron-hole pairs that originate the formation of active radicals (OH and O_2^-), which, together with the hole itself, can oxidize the organic foulants from the feedwater and thus mitigate membrane fouling for TiO_2 based membranes [12]. However, TiO_2 is neutrally or negatively charged in natural water (zero point charge of commercial TiO_2 is 5.5–6.5 [13]), and thus it is ineffective to adsorb aquatic humic acid, majority of which is also negatively charged ($\text{pK}_{a1} \sim 4$ and $\text{pK}_{a2} \sim 8$ [14]). In our previous work, iron (III) oxide (Fe_2O_3) nanowires were added into the TiO_2 membrane matrix that improved adsorption and subsequently the photo-degradation of humic acid under solar irradiation [9].

Another general concern for photocatalyst materials is the fast recombination of the photo-generated electron-hole pairs, which would lead to the loss of photocatalytic activity [15,16]. Therefore, carbon materials such as carbon nanotubes [17], graphite [18], reduced graphene oxide [19], and graphene oxide [16] were introduced into the TiO_2 membrane matrix to improve the photocatalytic activity of TiO_2 by functioning as electron sink, suppressing the recombination of electron-hole pairs. Among these carbon materials, graphene oxide (GO) – a chemically modified graphene with carboxylic groups at the edge and epoxide and phenol hydroxyl groups on the basal plane [15] – has attracted massive attentions. Besides retarding the recombination of electron-hole pairs on TiO_2 , GO also showed strong adsorption of certain organic compounds in water, which may facilitate the photo-degradation process [15]. In this study, we prepared a novel membrane containing TiO_2 nanowires, Fe_2O_3 nanoparticles, and GO sheets and hypothesized a further improvement of humic acid removal from water comparing to our previous reported $\text{TiO}_2/\text{Fe}_2\text{O}_3$ nanowire membrane [9].

2. Materials and methods

2.1. Materials

Titanium dioxide (P25; particle size of ~ 20 nm) was purchased from Degussa. Sodium hydroxide (NaOH), isopropanol (99.9%), nitrilotriacetic acid (NTA, 98%), ethanol (97%), and hydrochloric acid (HCl, 37%) were obtained from Fisher Scientific. Graphite, sodium nitrate (NaNO_3), potassium permanganate (KMnO_4), hydrogen peroxide (H_2O_2), concentrated sulfuric acid (H_2SO_4), humic acid, and ferric chloride hexahydrate ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, $\geq 98\%$) were purchased from Sigma–Aldrich. Deionized water was used for solution preparation.

2.2. Synthesis of membrane materials (TiO_2 , Fe_2O_3 , GO) and membranes

GO was synthesized by oxidizing natural graphite in the laboratory via the modified Hummers' method [20,21]. Briefly, 1 g of graphite, 1 g of NaNO_3 and 25 mL of concentrated H_2SO_4 were mixed in an ice bath under continuous mixing, after which 3 g of KMnO_4 was slowly added. The mixture was maintained at 40°C for 3 h. Thereafter, 60 mL of deionized water was slowly added and the temperature was increased to 90°C and maintained for 30 min. Finally, 140 mL of deionized water was added, followed by the slow addition of 10 mL of hydrogen peroxide solution (H_2O_2 , 30%). The GO material was separated by centrifugation and washed with 0.1 M HCl and deionized water until pH 7. Finally, the powder was vacuum dried at 60°C for 12 h. TiO_2 nanowires and Fe_2O_3 nanoparticles were synthesized via the methods reported in the literature [9] with a mild modification. To synthesize TiO_2 nanowires, 1.0 g of P25 and 130 mL of 10 M NaOH were mixed inside a Teflon-lined stainless-steel autoclave and kept at 160°C for 16 h under vigorous stirring. After the hydrothermal reaction, the floccules inside the autoclave were washed with 0.1 M HCl solution and deionized water alternately until pH dropped to almost 7. Anatase- TiO_2 nanowires were obtained by filtering and vacuum-drying the materials at 60°C for 12 h followed by calcination at 400°C for 2 h with a ramp rate of $2^\circ\text{C}/\text{min}$. To synthesize the Fe_2O_3 nanoparticles, 0.15 M $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, 65 mL of isopropanol and NTA solution were mixed inside a Teflon-lined autoclave and heated at 170°C for 24 h. After cooling, the floccules were washed with ethanol and deionized water alternately and then vacuum-dried at 60°C for 12 h followed by calcination at 450°C for 3 h with a ramp rate of $2^\circ\text{C}/\text{min}$.

The TiO_2 nanowire/ Fe_2O_3 nanoparticle/GO sheet composite was prepared through a one-step colloid blending method [22]. In a typical process, 100 mg TiO_2 nanowires and proper amounts of Fe_2O_3 nanoparticles and GO sheets were sonicated together inside a 150 mL deionized water for 1 h followed by overnight mixing to form a homogeneous solution. The composite in the solution was then vacuum-filtered onto a glass-fiber filter paper (Type A/E Glass, Pall Corporation) with a nominal pore size of $1\ \mu\text{m}$, thickness of $330\ \mu\text{m}$, and a typical water flow rate of $250\ \text{mL}/\text{min}\cdot\text{cm}^2$ at 0.3 bar (given by manufacturer). The nanocomposites were uniformly assembled on the filter paper surface. The prepared membrane (with filter paper at bottom) was dried overnight in air and hot pressed for 10 min before test. Membranes with different amounts of Fe_2O_3 and GO were prepared to identify the optimal weight ratios that may lead to the highest removal of humic acid.

2.3. Membrane characterization

Membrane morphology was measured using the scanning electron microscopy coupled with energy dispersive spectroscopy (SEM–EDS, Hitachi S570). Samples were loaded onto the adhesive copper tape for elementary analysis using EDS. The crystal structures of the membrane nanomaterials (TiO_2 nanowires, Fe_2O_3 nanoparticles, and GO sheets) were identified by X-ray diffraction (XRD, Scintag XDS 2000) with $\text{Cu K}\alpha$ radiation operated at 40 mA in the 2θ range from 10° to 70° at a scan rate of $1^\circ/\text{min}$. The UV–vis absorption spectrums of the membrane nanomaterials were measured using a UV–vis spectrophotometer (Ocean Optics).

2.4. Photo-degradation experiment

The membrane performance was tested in a dead-end membrane filtration system (with concurrent flow) as shown in Fig. 1. The membrane with an effective surface area of $35.2\ \text{cm}^2$ was placed at the bottom of a stainless steel reactor. Two peristaltic

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