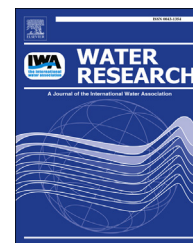


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# Graphene oxide based ultrafiltration membranes for photocatalytic degradation of organic pollutants in salty water

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## ABSTRACT

Flat sheet ultrafiltration (UF) membranes with photocatalytic properties were prepared with lab-made TiO<sub>2</sub> and graphene oxide-TiO<sub>2</sub> (GOT), and also with a reference TiO<sub>2</sub> photocatalyst from Evonik (P25). These membranes were tested in continuous operation mode for the degradation and mineralization of a pharmaceutical compound, diphenhydramine (DP), and an organic dye, methyl orange (MO), under both near-UV/Vis and visible light irradiation. The effect of NaCl was investigated considering simulated brackish water (NaCl 0.5 g L<sup>-1</sup>) and simulated seawater (NaCl 35 g L<sup>-1</sup>). The results indicated that the membranes prepared with the GOT composite (M-GOT) exhibited the highest photocatalytic activity, outperforming those prepared with bare TiO<sub>2</sub> (M-TiO<sub>2</sub>) and P25 (M-P25), both inactive under visible light illumination. The best performance of M-GOT may be due to the lower band-gap energy (2.9 eV) of GOT. In general, the permeate flux was also higher for M-GOT probably due to a combined effect of its highest photocatalytic activity, highest hydrophilicity (contact angles of 11°, 17° and 18° for M-GOT, M-TiO<sub>2</sub> and M-P25, respectively) and higher porosity (71%). The presence of NaCl had a detrimental effect on the efficiency of the membranes, since chloride anions can act as hole and hydroxyl radical scavengers, but it did not affect the catalytic stability of these membranes. A hierarchically ordered membrane was also prepared by intercalating a freestanding GO membrane in the structure of the M-GOT membrane (M-GO/GOT). The results showed considerably higher pollutant removal in darkness and good photocatalytic activity under near-UV/Vis and visible light irradiation in continuous mode experiments.

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## 1. Introduction

The scarcity of clean water and increasing environmental pollution are critical issues in large and industrialized cities as

well as in less developed regions. In this context, efficient water purification technologies with low energy consumptions are needed (Shannon et al., 2008). Membranes play a key role in water purification, seawater and brackish water desalination as well as in wastewater reclamation and reuse

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(Pendergast and Hoek, 2011; Peters, 2010). The preparation of appropriate membranes is an important step, and different materials, such as polymers, ceramics and carbon nanotubes, have been successfully employed (Baek et al., 2014; Das et al., 2014; Ulbricht, 2006; Xu et al., 2013b). Fouling is one of the major problems affecting the performance of these membranes.

In recent years, membranes prepared with photocatalytic nanoparticles have attracted great attention due to their superior characteristics (e.g., anti-fouling and photocatalytic properties) when compared to conventional membranes (Kim and Van der Bruggen, 2010). Titanium dioxide ( $\text{TiO}_2$ ) is one of the most widely used photocatalysts due to its low cost, chemical and thermal stability and excellent photoactivity (Chen and Mao, 2007). Up to date, various  $\text{TiO}_2$ -based photocatalytic membranes have been studied (Albu et al., 2007; Pan et al., 2008; Zhang et al., 2006, 2014b). However, the suppression of the recombination of photo-generated charge carriers, as well as the effective utilization of visible light, are some of the main challenges before these membranes become economically feasible.

Graphene and its derivatives, such as graphene oxide (GO), have attracted huge attention in photocatalytic applications (Tu et al., 2013). GO is a material that can be easily produced by chemical oxidation and exfoliation of graphite. In addition, it can be easily manipulated and its oxygen-containing functional groups (hydroxyl and epoxy groups on the basal planes, and carboxyl and carbonyl groups on the edges) facilitate the interaction of GO sheets with a wide variety of organic and inorganic materials (Dreyer et al., 2010; Pastrana-Martínez et al., 2014). GO- $\text{TiO}_2$  composites are efficient photocatalysts under both near-UV/Vis and visible light irradiation, overcoming one of the main limitations of bare  $\text{TiO}_2$  (Amalraj Appavoo et al., 2014; Fan et al., 2011; Huang et al., 2014; Long et al., 2013; Pastrana-Martínez et al., 2013a; 2014; 2012). However, these materials are usually employed as suspended particles (slurries) in batch reactors and, thus, a second step is required for catalyst separation from the treated water, limiting its recovery and reuse.

The immobilization of the photocatalyst into/onto filtration membranes/fibres overcomes this problem, but only a few works have been published on this topic (Athanasakou et al., 2014; Gao et al., 2013, 2014; Pastrana-Martínez et al., 2013b). A GO- $\text{TiO}_2$  microsphere hierarchical membrane was developed by assembling the photocatalyst on the surface of a cellulose acetate filtration membrane, which showed the multifunctionality of water filtration and photodegradation of acid orange 7 and rhodamine B (Gao et al., 2013). A GO- $\text{TiO}_2$  photocatalytic membrane was synthesized by simple layer-by-layer deposition of  $\text{TiO}_2$  and GO on a polysulfone membrane, and the increase in the membrane flux was attributed to the photo-enhanced hydrophilicity and simultaneous degradation of the methylene blue model pollutant (Gao et al., 2014). Recently, we immobilized a highly active GO- $\text{TiO}_2$  composite into alginate hollow fibres by a dry/wet spinning process, and considerable high photocatalytic activity and stability for degradation of diphenhydramine were observed in consecutive light–dark cycles of continuous operation (Pastrana-Martínez et al., 2013b). This composite was also immobilized onto ceramic monoliths via dip-coating and

tested as a hybrid photocatalysis/ultrafiltration process for the removal of methyl orange and methylene blue dyes, the membranes exhibiting enhanced photocatalytic performance under visible light (Athanasakou et al., 2014). GO- $\text{TiO}_2$  composite membranes were also prepared for exclusive use as filtration membranes (i.e. without photocatalysis involved) to remove hazardous dyes, such as methyl orange and rhodamine B (Xu et al., 2013a).

In the present work, three photocatalysts, i.e. lab-made bare  $\text{TiO}_2$  and GO- $\text{TiO}_2$ , as well as the reference material in photocatalysis, Evonik Degussa (P25), were assembled on flat sheet filtration cellulose membranes. The resulting photocatalytic ultrafiltration membranes were tested for the photodegradation and mineralization of a pharmaceutical compound, diphenhydramine (DP), and an organic dye, methyl orange (MO), under both near-UV/Vis and visible light irradiation and in continuous operation mode. In addition, an innovative freestanding GO membrane was intercalated between the cellulose membrane and the photocatalytic layer. Besides studies with the model pollutants in distilled water (DW), the effect of the presence of  $\text{Cl}^-$  anions on the removal of the pollutants was also studied in simulated brackish water (SBW) and seawater (SSW).

## 2. Experimental

### 2.1. Chemicals and materials

Natural graphite (99.9995%), diphenhydramine hydrochloride ( $\text{C}_{17}\text{H}_{21}\text{NO} \cdot \text{H}_2\text{O}$ , 99%), methyl orange ( $\text{C}_{14}\text{H}_{14}\text{N}_3\text{NaO}_3\text{S}$ , 99%), ammonium hexafluorotitanate ( $(\text{NH}_4)_2\text{TiF}_6$ , 99.99%) and boric acid ( $\text{H}_3\text{BO}_3$ , 99%), were obtained from Sigma–Aldrich. Sodium chloride ( $\text{NaCl}$ , 99.5%) was supplied by Panreac. Mixed cellulose ester (MCE) membranes with 0.45  $\mu\text{m}$  pore size, diameter of 4.7 cm and thickness of 140  $\mu\text{m}$  were purchased from Whatman™. The commercial  $\text{TiO}_2$  material (P25) was supplied by Evonik Degussa GmbH (P25) and was used as a reference material. It consists of 80% of anatase phase and 20% of rutile (manufacturer's data).

### 2.2. Synthesis of graphene oxide and GO- $\text{TiO}_2$

Graphite oxide was obtained by the oxidative treatment of commercial graphite (20  $\mu\text{m}$ , Sigma–Aldrich) following the modified Hummers method, as described elsewhere (Hummers and Offeman, 1958; Pastrana-Martínez et al., 2012). The oxidized material was dispersed in water, sonicated for 1 h and centrifugated at 3000 r.p.m. to obtain a suspension of graphene oxide (GO).

GO- $\text{TiO}_2$  (hereafter referred as GOT) was prepared by liquid phase deposition method according to our previous work (Pastrana-Martínez et al., 2012). Briefly,  $(\text{NH}_4)_2\text{TiF}_6$  (0.1 mol  $\text{L}^{-1}$ ) and  $\text{H}_3\text{BO}_3$  (0.3 mol  $\text{L}^{-1}$ ) were added to a GO dispersion that was then heated at 60 °C for 2 h under vigorous stirring. Then the resulting powder was treated as 200 °C under  $\text{N}_2$  flow. The carbon loading (~4.0 wt.%) was selected taking into account the composite presenting the highest photocatalytic activity under UV/Vis and visible light irradiation in our previous work

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