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_2 and graphene oxide-TiO_2 (GOT), and also with a reference TiO_2 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^{-1}) and simulated seawater (NaCl 35 g L^{-1}). The results indicated that the membranes prepared with the GOT composite (M-GOT) exhibited the highest photocatalytic activity, outperforming those prepared with bare TiO_2 (M-TiO_2) 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 11º, 17º and 18º for M-GOT, M-TiO_2 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.

Keywords*: Graphene oxide; photocatalytic membranes; filtration; water purification; salty water; anti-fouling.*

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 (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 (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 TiO_2–based photocatalytic membranes have been studied (Albu et al. 2007, Pan et al. 2008, Zhang et al. 2006, Zhang et al. 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-TiO_2 composites are efficient photocatalysts under both near-UV/Vis and visible light irradiation, overcoming one of the main limitations of bare TiO_2 (Amalraj Appavoo et al. 2014, Fan et al. 2011, Huang et al. 2014, Long et al. 2013, Pastrana-Martínez et al. 2013a, Pastrana-Martínez et al. 2014, Pastrana-Martínez et al. 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 (Athanasekou et al. 2014, Gao et al. 2013, Gao et al. 2014, Pastrana-Martínez et al. 2013b). A GO-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-TiO_2 photocatalytic membrane was synthesized by simple layer-by-layer deposition of 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-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 (Athanasekou et al. 2014). GO-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 TiO_2 and GO-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 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 ($C_{17}H_{21}NO \cdot H_2O$, 99%), methyl orange ($C_{14}H_{14}N_3NaO_3S$, 99%), ammonium hexafluorotitanate ($(NH_4)_2TiF_6$, 99.99%) and boric acid (H_3BO_3, 99%), were obtained from Sigma-Aldrich. Sodium chloride (NaCl, 99.5%) was supplied by Panreac. Mixed cellulose ester (MCE) membranes with 0.45 μm pore size, diameter of 4.7 cm and thickness of 140 μm were purchased from Whatman™. The commercial TiO_2 material (P25) was supplied by Evonik Degussa Corporation (P25) and was used as reference material. It is constituted by 80% of anatase phase and 20% of rutile (manufacturer data).

2.2. Synthesis of graphene oxide and GO-TiO_2

Graphite oxide was obtained by the oxidative treatment of commercial graphite (20 μm, 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-TiO_2 (hereafter referred as GOT) was prepared by liquid phase deposition method according to our previous work (Pastrana-Martínez et al. 2012). Briefly, $(NH_4)_2TiF_6$ (0.1 mol L^{-1}) and H_3BO_3 (0.3 mol L^{-1}) were added to a GO dispersion that was then heated at 60 ºC for 2 h under vigorous stirring. Then the resulting powder was treated as 200 ºC under 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 (Pastrana-Martínez et al. 2012). Bare TiO_2 was prepared using the same methodology but without the addition of GO (hereafter referred as TiO_2).~~The photocatalyst from Evonik Degussa Corporation (P25) was also used as reference material~~ The synthesis of GO, TiO_2 and GO-TiO_2 composite are shown in Scheme 1.

2.3. Preparation of photocatalytic membranes

GOT, TiO_2 and P25 catalysts were selected to prepare the corresponding photocatalytic membranes following a methodology adapted from elsewhere (Morales-Torres et al. 2014), in that case for the preparation of CNT buckypapers over a polytetrafluoroethylene commercial membrane. In a typical procedure, the photocatalyst was dispersed in a 2 g L^{-1} aqueous solution during 10 min by using an ultrasonic processor (UP400S, 24 kHz). The MCE membrane was cut into a piece with 1.4 cm of diameter and placed into a filtration device under vacuum. 5 mL of the photocatalyst dispersion was added slowly (ca. 10 mg of photocatalyst). When the filtration was completed, the membrane was dried under N_2 flow for 10 min, a homogeneous deposition of the photocatalyst being obtained with an effective area

of ca. 1.54 cm^2. The membranes prepared with GOT, TiO_2 and P25 were labelled as M-GOT, M-TiO_2 and M-P25, respectively.

The membrane presenting the highest photocatalytic activity was also modified by intercalating a freestanding GO membrane between the MCE membrane and the photocatalyst layer. First, 2 mL of GO dispersion (1.5 g L^{-1}) was filtered thought a MCE membrane, and a homogeneous GO layer was obtained above the MCE membrane (labelled as M-GO). Then, a uniform multi-layer membrane was prepared by adding 5 mL of the GOT composite suspension (2 g L^{-1}) on top of the M-GO membrane (M-GO/GOT).

2.4. Characterization techniques

The morphology and roughness of the membranes were analysed by scanning electron microscopy (SEM) using a FEI Quanta 400FEG ESEM/EDAX Genesis X4M instrument. The membranes were frozen and broken under liquid nitrogen. The microscope was equipped with a special multiple sample holder, in which the broken membranes were vertically positioned to analyze their cross-sections.

The overall porosity (ε) of the membranes was determined by the gravimetric method (Cui et al. 2013). After measuring the dry weight of the membranes, they were immersed in distilled water overnight to assure solvent penetration into the membrane pores. Then, their wet weight was registered. The porosity was calculated by applying the following equation:

$$\varepsilon\ (\%) = \frac{(m_w - m_d)/\rho_w}{(m_w - m_d)/\rho_w + m_d/\rho_p} \times 100 \qquad (1)$$

where m_w and m_d are the weights of the wet and dry membranes, respectively, and ρ_w and ρ_p are the water (0.997 g cm^{-3}) and polymer (1.520 g cm^{-3}) densities, respectively (Maim et al. 1947). Four different membranes were used to determine an average value of the porosity, and the standard deviation found was always lower than ± 1%.

N_2 adsorption-desorption isotherms at -196 ºC were obtained in a Quantachrome NOVA 4200e multi-station apparatus. The apparent surface area (S_{BET}) was determined by applying the Brunauer–Emmett-Teller (BET) equation (Brunauer et al. 1938). The volume of N_2 adsorbed at a relative pressure of 0.95 (V_p) was obtained from the adsorption isotherms, which corresponds to the sum of the micro- and mesopore volumes according to Gurvitch's rule (Rouquerol et al. 1999). The the Barrett-Joyner-Halenda (BJH) method (Barrett et al. 1951) was applied to the desorption branch of the N_2 isotherms to determine the average mesopore diameter (d_{pore}).

The hydrophilicity of the membrane surface was determined by contact angle (θ) measurements using an Attension apparatus (model Theta) that allowed image acquisition and data analysis. The measurements were performed at room temperature (25 ºC) using the water drop method on dry membranes. The contact angle was measured at least in 5 different locations to get the average value.

The optical properties of the samples were analyzed by UV/Vis diffuse reflectance spectroscopy using a JASCO V-560 UV/Vis spectrophotometer, equipped with an integrating sphere attachment (JASCO ISV-469), barium sulphate being used as reference. The reflectance spectra were converted to equivalent absorption Kubelka-Munk units by the instrument software (JASCO). The band-gap was determined by plotting the transformed Kubelka-Munk values as a function of the energy of light.

The materials point of zero charge (pH_{PZC}) was determined following a pH drift test described elsewhere (Pastrana-Martínez et al. 2013b). Briefly, solutions with varying initial pH (2-12) were prepared using HCl (0.1 mol L^{-1}) or NaOH (0.1 mol L^{-1}) and 50 mL of NaCl (0.01 mol L^{-1}) as electrolyte. Each solution was contacted with 0.15 g of the material and the final pH was measured after 24 h of continuous stirring at room temperature. The pH_{PZC} of the material

198 was determined by intercepting the obtained final-pH *vs.* initial-pH curve with the straight
199 line final-pH = initial-pH.
200
201 *2.5. Evaluation of membranes performance*
202 The photocatalytic activity and permeability of the membranes were studied in dead-end
203 filtration mode at ambient temperature (25 ºC) and pressure under near-UV/Vis and visible
204 light irradiation, using a lab-scale set up represented in Figure 1. The system consists of a
205 glass made cylindrical reactor with the membrane attached by using a Viton® o-ring
206 (maintaining the effective area of ca. 1.54 cm^2). A reservoir containing the fresh pollutant
207 solution was magnetically stirred and continuously purged with air flow. DP (3.40×10^{-5} mol
208 L^{-1}) and MO (3.05×10^{-5} mol L^{-1}) were used as model pollutants in distilled water (DW) at
209 natural pH conditions (pH_{DP} = 5.9 and pH_{MO} = 6.1). Experiments were also performed using
210 simulated brackish water (SBW, 0.5 g L^{-1} of NaCl) and seawater (SSW, 35 g L^{-1} of NaCl).
211 The pollutant solution was continuously introduced in the reactor at a flow rate of ca. 0.25 mL
212 min^{-1} using a peristaltic pump. This flow rate allows an adequate residence time into the
213 reactor and was selected from preliminary studies at different flow rates. In a typical run, the
214 solution was passed through the reactor for a long time (up to 180 min) before turning on the
215 lamp, to saturate the membrane with the tested pollutants (ca. 60 min needed) and to achieve
216 the initial pollutant concentration in the reactor outlet (i.e. $C_{180\ min\ in\ dark} = C_{0\ min\ under\ radiation}$). In
217 the particular case of the M-GO/GOT membranes a total of 48 h dark period was needed
218 before turning on the lamp.
219 The irradiation source consisted of a Heraeus TQ 150 medium-pressure mercury vapour lamp.
220 A DURAN® glass water cooling jacket was used to obtain irradiation in the near-UV
221 irradiation ($\lambda > 350$ nm) and to control the operating temperature. A cut-off long pass filter
222 was used ($\lambda > 430$ nm) for visible light experiments. The photon flow entering the reactor was

ca. 33 mW cm^{-2} and 2.8 mW cm^{-2} under near-UV/Vis and visible light irradiation, respectively, as determined by integrating the irradiance spectra obtained by using a UV/Vis spectroradiometer (USB2000+, OceanOptics, USA). In the photocatalytic experiments, two dark/bright cycles were carried out in order to evaluate the anti-fouling properties of the membranes. 2 mL of sample were systematically collected from the exit of the photocatalytic membrane reactor (i.e. before the permeate reservoir) at intervals of ca. 20 min, in order to measure the pollutant concentration. Blank experiments were also performed in the absence of catalyst in order to characterize direct photolysis and the filtration capacity of the commercial MCE membrane.

The concentration of DP was determined by HPLC with a Hitachi Elite LaChrom system equipped with a Hydrosphere C18 column. The concentration of MO was determined by UV-Vis spectrophotometry at 464 nm in a Jasco V-560 spectrophotometer. The total organic carbon (TOC) was determined for selected samples using a Shimadzu TOC-5000A analyzer. Chloride ions were monitored by ion chromatography (Metrohm 881 Compact IC) using a Metrosep A Supp 7-250 column.

The permeate flux (L m^{-2} h^{-1}) was calculated according to the following equation:

$$F = \frac{V}{A \, x \, t} \qquad (2)$$

where V (L) is the volume of the solution permeated during the experiment, A represents the effective membrane area (m^2), and t denotes time (h).

3. Results and discussion

3.1. Membranes characterization

The cross-section and top view of the prepared membranes were analysed by SEM. The corresponding images of M-TiO_2 and M-GOT at different magnifications are shown in

247 Figures 2a-c and 2d-f, respectively. The total thicknesses of the membranes are gathered in
248 Table 1.
249 Cross-sectional images of M-TiO_2 and M-GOT membranes (Figures 2a-b and 2d-e,
250 respectively) show that the corresponding photocatalytic materials (top) were homogeneously
251 deposited on the MCE membrane (bottom) without appreciable presence of cracks, holes or
252 another defects, even if considered that these membranes were fractured for SEM analysis.
253 Both membranes (M-TiO_2 and M-GOT) showed some differences in the packing and
254 morphology of the deposited material. M-TiO_2 (Figures 2a-b and Table 1) presented a good
255 distribution of TiO_2 particles on the substrate membrane with a uniform thickness of TiO_2
256 around 35 μm, while the overall thickness of the M-TiO_2 membrane was ~ 175 μm (ca. 140
257 μm for MCE only). The top view of the M-TiO_2 membrane (Figure 2c) shows spherical
258 particles forming larger aggregates with anatase crystallites of around 4-5 nm in size
259 (Pastrana-Martínez et al. 2012).
260 The cross-sectional images of the M-GOT membrane (Figures 2d-e) show a uniform GOT
261 layer deposited on the MCE membrane with a thickness of ~ 65 μm, almost twice as that
262 observed for TiO_2 in the case of M-TiO_2. The amount of photocatalyst deposited in both
263 membranes was the same. Therefore, the larger thickness observed for M-GOT can be
264 attributed to the lower density of the GOT catalyst (resulting from the arrangement of the
265 GOT platelets, as shown in Figure 2f inset), which differs from that of TiO_2 spherical
266 particles. The top view of the GOT composite (Figure 2f) indicates a good TiO_2 distribution
267 on both sides of the GO sheets, i.e. a good self-assembly of the TiO_2 nanoparticles on GO
268 (Pastrana-Martínez et al. 2012).
269 Regarding the M-P25 membrane (images not shown), a homogeneous layer of P25 with a
270 thickness of ~ 39 μm (more similar to M-TiO_2 than to M-GOT) was observed over the MCE
271 membrane, with a typical morphology of joined P25 nanoparticles.

The total porosity (ε) of the membranes was determined by the gravimetric method and the results are collected in Table 1. The porosity of the modified membranes (65-71%) was lower than that determined for the MCE membrane (74%), but that of M-GOT was the nearest to MCE (71%). The BET surface area (S_{BET}) values were comparable for M-GOT (117 m^2 g^{-1}) and M-TiO_2 (118 m^2 g^{-1}), and both are higher than that of M-P25 (65 m^2 g^{-1}). The total pore volume (V_p) was significantly higher for M-GOT when compared to M-TiO_2, evidencing that a pronounced porosity is created when GO sheets and TiO_2 are in contact. The contact angles, also shown in Table 1, were very low for all membranes (<18º), indicating the high hydrophilicity of the membranes' surface. In particular, M-GOT presents the lowest contact angle (11º), which can be of relevance to treat high water fluxes.

3.2. Removal of pollutants in dark phase

Figure 3 shows DP and MO removals under dark conditions in filtration experiments performed using both DW and SBW at natural pH and 25 °C. The results are given for a period where saturation of all membranes was observed (60 min), and before starting to increase the concentration of pollutants in the reactor outlet.

These results indicate that there is a low removal of the pollutants (ca. 0.2%) when using the commercial MCE membrane in the dark regardless the liquid media (i.e. DW or SBW, respectively labelled as Blank_DW or Blank_SBW in Figure 3). Regarding the experiments with DW, DP removal was significantly higher for M-GOT (12%), M-TiO_2 (9%) and M-P25 (3%) than for MCE. The same tendency was observed for MO, i.e. the highest MO removal was obtained with the M-GOT membrane (8%), lower DP removals being obtained with the other membranes, namely 6% with M-TiO_2 and 5% with M-P25. The removal of these pollutants can be related with two different phenomena occurring under dark conditions, adsorption or retention (Xu et al. 2013a). In order to discriminate between both, some

297 screening filtration experiments were performed (not shown) suggesting that the pollutant
298 removal on the photocatalytic membranes may be attributed to DP adsorption.
299 Taking into account the speciation diagrams of both DP and MO (Figures 4a and 4b,
300 respectively), the pK_a of DP and MO are ca. 8.9 (Hein and Jeannot 2001) and 4.2 (de Araujo
301 et al. 2000), respectively. Since the pH in experiments with DW was near to 6.0 (5.9 for DP
302 and 6.1 for MO), this means that DP is positively charged while MO is negatively charged
303 under our experimental conditions. In addition, the pH_{PZC} of both bare TiO_2 and GOT
304 materials are ca. 3.1 and 2.9, respectively (Table 1). Therefore, M-TiO_2 and M-GOT
305 membranes are expected to present negatively charged surfaces at the pH of the experiments
306 (~ 6.0), explaining why the adsorption of DP is higher (electrostatic interactions) than in that
307 of MO (electrostatic repulsions) when both membranes were employed. In the case of M-P25,
308 MO removal was higher than DP removal in DW because the M-P25 membrane surface is
309 practically uncharged (pH_{PZC} ca. 6.3) at the operating pH conditions (~ 6.0). Overall, the
310 lower adsorption capacity for the M-P25 membrane compared to both M-TiO_2 and M-GOT
311 membranes can be ascribed to S_{BET} (Table 1) which is higher for bare-TiO_2 and GOT (118
312 and 117 $m^2\ g^{-1}$, respectively) than for P25 (65 $m^2\ g^{-1}$).
313 The effect of the presence of NaCl (SBW) on the removal of DP and MO under dark
314 conditions is also shown in Figure 3. The results indicate that the presence of NaCl in water is
315 not really affecting the adsorption of these pollutants onto the membranes, probably due to the
316 low amount of Cl^- ions in the SBW prepared solutions (NaCl 0.5 g L^{-1}). In addition, only ca.
317 4-5% of the initial Cl^- concentration was removed during the filtration experiments under
318 dark conditions (data not shown). The Cl^- ions are not retained in the membranes due to their
319 (i) low molecular size (167 pm for the Cl^- ionic radius), (ii) competitive adsorption with the
320 pollutant molecules, together with (iii) electrostatic repulsions in the case of M-GOT and M-
321 TiO_2.

3.3. DP photocatalytic degradation

The efficiency of the membranes for the photocatalytic degradation of DP under near-UV/Vis (closed symbols) and visible light irradiation (open symbols) is shown in Figures 5a and 5b, respectively for DW and SBW, where C_0 represents the DP concentration in the dark after 180 min. It can be observed that the MCE membrane (Blank, cross symbol) did not have any photocatalytic performance by itself under near-UV/Vis (and also under visible light irradiation, not shown), using either DW or SBW, and that DP is a very refractory pollutant when irradiated in the absence of a catalyst, as previously reported (Pastrana-Martínez et al. 2012). For comparison purposes, the experiments were carried out with the same irradiation lamp and pollutants tested by our group in slurry/batch mode (Pastrana-Martínez et al. 2013a, Pastrana-Martínez et al. 2014, Pastrana-Martínez et al. 2012). Although suspended photocatalysts can achieve the highest possible catalytic efficiency, the issue of separating the photocatalysts particles from the treated water was solved with the photocatalytic membranes. M-GOT and M-P25 are very active photocatalytic membranes, presenting comparable efficiencies under near-UV-Vis irradiation in terms of DP removal during the first photocatalytic cycle (ca. 73% in DW and ca. 60% in SBW). The lowest DP removal was obtained for M-TiO_2 (43% in DW and 39% in SBW). The same tendency was observed in terms of TOC removal in 240 min, i.e. M-P25, M-TiO_2 and M-GOT produced TOC reductions of 35%, 18% and 35%, respectively, in DW (Figure 5c).

The photocatalytic DP degradation under visible light illumination in DW (Figure 5a) was significantly higher for M-GOT (ca. 28%) than for TiO_2 membranes (ca. 5% with both M-TiO_2 and M-P25) indicating that TiO_2 is not active under visible light illumination, in agreement with previous reports where similar materials were used in the form of powder slurries for the photodegradation of different pollutants (Fotiou et al. 2013, Maroga Mboula et

al. 2013, Pastrana-Martínez et al. 2012). This observation confirms that the addition of GO into the TiO_2 matrix increases light absorption in the visible spectral range, resulting from a decrease in the band-gap energy (2.9, 3.1, and 3.2 eV for M-GOT, M-TiO_2 and M-P25, respectively, Table 1). In our previous studies (Pastrana-Martínez et al. 2012, Pastrana-Martínez et al. 2013b), the high activity of the GOT composite was attributed to the good TiO_2 distribution in the composite containing ca. 4% of GO content, leading to good assembly and interfacial coupling between the GO sheets and TiO_2 nanoparticles (as can be observed in the SEM micrograph of M-GOT, Figure 2f).

Regarding the results with SBW (Figure 5b), it can be concluded that the presence of NaCl (0.5 g L^{-1}) slightly decreases the photocatalytic efficiency for DP under near-UV/Vis (i.e. 60%, 39% and 61% for M-P25, M-TiO_2 and M-GOT, respectively in the first cycle), in comparison with DW (Figure 5a). TOC removal (Figure 5c) follows a trend similar to that observed for DP degradation, i.e. lower mineralizations were also obtained in the presence of NaCl (27%, 12% and 28% for M-P25, M-TiO_2 and M-GOT, respectively).

This effect could be due to the presence of Cl^- ions acting as holes and hydroxyl radical scavengers, affecting the efficiency of the photocatalytic process. The presence of Cl^- anions in SBW could generate less reactive species such as chlorine radicals ($Cl^{\bullet}$) and dichloride anion radicals ($Cl_2^{-\bullet}$) (Eqs. 3-5), which are less reactive than $HO^{\bullet}$ radicals (De Laat and Le 2006). The formation of these less reactive species may decrease the efficiency of the process. These results are in agreement with those published in literature (Sirtori et al. 2010, Yap and Lim 2011), where a negative effect of Cl^- ions was observed for the photocatalytic degradation of other pollutants.

$$Cl^- + h_{vb}^+ \rightleftharpoons Cl^{\bullet} \quad (3)$$

$$Cl^- + HO^{\bullet} \rightleftharpoons ClOH^{\bullet -} \quad (4)$$

$$Cl^{\bullet} + Cl^- \rightleftharpoons Cl_2^{-\bullet} \quad (5)$$

…Membrane cleaning will be an essential part during the photocatalytic degradation of organic pollutants in salty water. Different cleaning methods have been proposed in literature (Shi et al. 2014, Wang et al. 2014) such as physical, chemical and biological/biochemical cleaning according to fouling removal mechanisms or cleaning agents used

3.4. MO photocatalytic degradation

The same type of photocatalytic experiments were performed using MO as model pollutant. The photocatalytic activity of M-P25, M-TiO_2 and M-GOT membranes under both near-UV/Vis and visible light irradiation are shown in Figures 6a and 6b for DW and SBW, respectively. It is observed that MO is poorly removed when the commercial MCE membrane is used (Blank). The M-GOT membrane showed significantly higher photocatalytic activity for MO abatement than the other membranes tested in DW (51% and 5% for M-P25, 39% and 4% for M-TiO_2, 65% and 19% for M-GOT, under near-UV/Vis and visible light irradiation, respectively). The same trend was found concerning the respective TOC removal (Figure 6c). The photodegradation of MO from the first to the second cycle was practically the same for all membranes when using DW as solvent (Figure 6a).

For the experiments with SBW (Figure 6b), once again the membrane prepared with the GOT composite exhibited the highest photocatalytic activity under near-UV/Vis and visible light irradiation (respectively, 52% and 13% reduction of the initial MO concentration) and also the highest TOC removal (respectively, 31% and 9%, Figure 6c). However, the presence of NaCl leads to a slight decrease in MO degradation, in comparison with DW, regardless of the membranes employed (Figure 6b). The same trend was observed in terms of TOC removal (Figure 6c). As previously observed for DP removal, MO degradation decreases from the first to the second bright cycle, reinforcing the idea that Cl^- ions are scavengers of holes and

hydroxyl radicals.

3.5. Permeate flux and anti-fouling of the photocatalytic membranes

Regardless of the membrane employed, the photocatalytic degradation of both pollutants tested was practically the same from the first to the second bright cycle when using DW as solvent (Figures 5a and 6a for DP and MO, respectively). These results indicate that all membranes are quite stable and that fouling did not take place. This observation also suggests that parent pollutants/intermediate compounds are not irreversibly accumulated on the membrane surface, which guarantees that the membranes can maintain high permeate fluxes for long operation periods (Zhang et al. 2014a).

The permeate flux was monitored for experiments performed with DP. Figures 7a and 7b show the results obtained for DW and SBW, respectively, in 240 min. The flux performance of the MCE membrane (blank) in darkness, UV/Vis and visible light irradiation, did not change during the experiments. In addition, the permeate flux of the lab-made membranes (M-P25, M-TiO_2 and M-GOT) was slightly lower in comparison with that of the blank MCE membrane, probably due to the nanostructured materials that were deposited over MCE and that have influence on the membranes porosity.

The pollutants can stay adsorbed on the membrane surface and can partially block the pores under dark conditions. The permeate flux increased for M-P25, M-TiO_2 and M-GOT membranes under near-UV/Vis irradiation, probably as a consequence of the photocatalytic degradation of DP molecules adsorbed on the membrane surface or to a higher hydrophilicity of the materials under near-UV/Vis irradiation. However, a similar increase of the water flux was not always observed under visible light illumination. Only for M-GOT the permeate flux was higher at such conditions than in the darkness, which can be related to the high photocatalytic activity of this membrane under visible illumination, when compared with the

others (Figure 7), and/or to its higher hydrophilicity (contact angles of 11º, 17º and 18º for M-GOT, M-TiO_2 and M-P25, respectively). Therefore, overall, M-GOT performs better than M-TiO_2 and M-P25.

3.6. Hierarchically ordered M-GO/GOT membrane

A free-standing GO membrane (M-GO) was introduced between the commercial MCE membrane and the GOT layer with the aim to improve the performance of the M-GOT membrane. The resulting membrane was referred as M-GO/GOT and its efficiency was evaluated for the degradation of DP, first in darkness and then under visible and near-UV/Vis irradiation. The experiments were carried out using DW and simulated seawater (SSW - 35 g L^{-1} NaCl).

The cross-sectional SEM micrographs of the prepared M-GO/GOT membrane are shown in Figure 8. Uniform GO layers (ca. 6.5 μm of total thickness) between the MCE membrane and the GOT photocatalyst are observed. The GO membrane consists of several GO sheets (inset of Figure 8b: M-GO) and the GOT catalyst was homogeneously deposited on top of M-GO. The M-GO/GOT membrane has an overall thickness of ~ 200 μm, in which ~ 50 - 55 μm are due to the GOT photocatalyst. The thickness of the GOT layer in M-GO/GOT seems to be smaller than in the case of M-GOT (65 μm), both prepared with the same amount of photocatalyst. This smaller thickness could be due to a stronger packing of the GOT particles during the preparation step, since a longer time of filtration was required to prepare M-GO/GOT.

Figures 9a and 9b show the results obtained in terms of DP removal and permeate flux, respectively. The M-GO/GOT membrane exhibited a significantly higher DP removal under dark conditions in DW when compared to M-GOT (i.e, 12 and 42% for M-GOT and M-GO/GOT, respectively). The DP concentration increased after the initial fast DP removal and

447 before turning on the lamp, but a long dark period (up to 48 hours) was needed for the
448 saturation of the M-GO-GOT membrane with the DP pollutant while only 180 min where
449 required in the case of the M-GOT membrane.
450 These results indicate that the adsorption and/or exclusion of pollutants of the M-GOT
451 membrane was increased by the introduction of the free-standing GO membrane, the M-
452 GO/GOT membrane presenting a higher DP adsorption capacity in the filtration process. As
453 expected, the removal capacity was lower when the experiments were performed in SSW
454 (10%) due to the high content of Cl^- anions (35 g L^{-1}) that could reduce the electrostatic
455 interactions between catalysts and pollutants due to a screening effect (Stuart et al. 1991), i.e.
456 the Cl^- anions might pair with the positive DP molecules and reduce the electrostatic
457 interactions with the catalyst surface, and/or could block the active sites of the catalyst
458 (Kamble et al. 2008).
459 Regarding photocatalytic activity, the M-GO/GOT membrane also showed a relatively good
460 activity for DP degradation under near-UV/Vis and visible light irradiation; however, the M-
461 GOT membrane performed better (Figures 5a and 5b respectively). Since the thickness of the
462 GOT layer in M-GO/GOT was smaller (~ 50 - 55 µm) than in the case of M-GOT (65 µm),
463 one possible explanation is that the photocatalyst is more compacted in the case of M-
464 GO/GOT and, therefore, less exposed to the irradiation, an important aspect when dealing
465 with photocatalytic reactors. The longer time of filtration required by the presence of GO is
466 the main synthesis limitation regarding this issue. The permeate flux increased for the M-
467 GOT membrane under near-UV/Vis and visible light irradiation (Figure 7), probably as a
468 consequence of the photocatalytic degradation of DP molecules adsorbed on the membrane
469 surface, or to a higher hydrophilicity of the materials under irradiation. The permeate flux was
470 also monitored for the M-GO/GOT membrane in darkness and under visible and near-UV/Vis
471 irradiation (Figure 9b). As expected, the results showed a decrease of the permeate flux under

dark conditions. However, an increase in permeate flux was subsequently observed under visible light and near-UV/Vis irradiation, as in the case of M-GOT. This effect was more significant for the experiments in DW, and can be attributed to the photocatalytic activity, hydrophilicity and anti-fouling properties of the prepared membranes.

4. Conclusions

Different photocatalytic membranes were synthesized with P25 (M-P25), bare-TiO_2 (M-TiO_2) and GO-TiO_2 composite. The prepared membranes were compared in terms of photocatalytic activity using distilled water and simulated brackish water and seawater. The photocatalyts were homogeneously deposited without appreciable presence of cracks, holes or another defects. All the membranes presented high activity and stability in consecutive light-dark cycles under continuous mode. During the photocatalytic reaction, the permeate flux increased due to the high hydrophilicity of the membranes and larger contaminant removal by photodegradation. The presence of NaCl had a substantially detrimental effect on the photocatalytic performance which may be due to the chloride anions acting as hole and hydroxyl radical scavengers. In general, the M-GOT membrane showed significantly higher photocatalytic activity for the pollutants abatement than the other membranes tested. In addition, an innovative hierarchically membrane referred as M-GO/GOT was prepared by intercalating a GO membrane in the structure of the M-GOT. This membrane showed higher pollutant removal under dark conditions and good performance under visible and near-UV/Vis irradiations. However, the M-GOT membrane performed better, probably due to the higher compactness in the case of M-GO/GOT as a consequence of the synthesis conditions required for its preparation.

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