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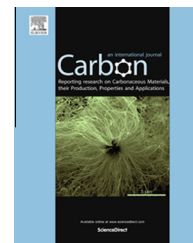
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Graphene oxide and titania hybrid Nafion membranes for efficient removal of methyl orange dye from water

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ABSTRACT

Hybrid Nafion membranes are prepared, using various fillers, such as anatase-type TiO₂ nanoparticles, graphene oxide (GO) and organo-modified graphene oxide (abbreviated as GO_{SULF}) for water purification applications. Scanning electron microscopy analysis confirms the homogeneous dispersion of the fillers. The photocatalytic properties of the hybrid membranes are evaluated using the azo dye methyl orange (MO) in aqueous solutions. The two main effects contributing to the decolourization of the dye, adsorption in the membrane and degradation in solution, are investigated in detail. Among the Nafion membranes under investigation, Nafion–GO_{SULF} for the first time used for water purification purposes, shows the most promising results in MO adsorption and photocatalytic degradation.

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1. Introduction

In the last decades the development of efficient and ecologically-friendly methods to remove contaminants from water has become of fundamental importance, since pollution is increasing drastically. Recent advances in nanotechnology suggest that many of the issues involving water quality could be resolved or greatly ameliorated using nanoparticles, nanofiltration or other products resulting from the development of nanotechnology [1–5]. Among the methods of water purification, advanced oxidation processes (AOPs) are object of increasing attention [6]. These water treatment processes can be performed at room temperature and normal pressure and they are based on the *in situ* generation of a powerful oxi-

dizing agent at a sufficient concentration to effectively decontaminate water. In particular, they constitute promising, efficient and environmentally friendly methods to remove persistent organic pollutants (POPs) from waters. Semiconductor nanomaterials can promote AOPs. Indeed, irradiation with light of proper wavelength excites electrons from the photocatalytic semiconductor valence band to its conduction band, generating electron–hole pairs. Both carriers can migrate to the surface of the semiconductor particles and react with water and dissolved oxygen to form various oxidizing species, such as hydroxyl radicals (•OH) that are able to effectively decontaminate water from organic compounds [2,4,7–8]. Among the semiconducting materials with photocatalytic properties, a lot of research effort has been dedi-

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cated to TiO_2 , due to its inexpensiveness, the catalyst inert nature and photostability [9–13]. Titania in the anatase phase has a band gap E_g of about 3.2 eV [14], hence only light with wavelength below 380 nm can be absorbed and produce e^-/h^+ pairs [15].

Other nanomaterials that have recently showed off in the water purification field are carbon nanostructures, in particular carbon nanotubes and graphene: they own a high surface area and they have been used as high capacity and selective sorbents for organic solutes in aqueous solutions [16]. Recently, photocatalytic properties have also been reported for graphene oxide (GO) [17] with the advantage that visible light can be absorbed and give rise to photocatalytic processes, due to the tunable bandgap of the material. Graphene oxide is composed of graphene flakes containing oxygen functional groups (hydroxyl, epoxy, carboxylic and carbonyl groups) at the surface and at the edges. The presence of such groups makes the GO an hydrophilic material and also favours the functionalization for selective absorption of contaminants through specific chemical treatments.

Several papers in the literature show the use of TiO_2 powder, carbon nanomaterials or a combination of both [18–20], dispersed directly in the solution that is going to be treated. After the photocatalytic process the photocatalyst has to be removed [21–23] by processes not always easy and fast. Furthermore the catalyst cannot be easily used again. A possible solution is to incorporate the photocatalytic nanoparticles in polymeric membranes, that can be removed from water and regenerated for further use after purification processes.

Up to now only a few studies have been conducted on photocatalytic nanocomposite membranes incorporating TiO_2 [24–25] or C nanostructures [26]. Membrane processes such ultrafiltration, nanofiltration and reverse osmosis are becoming the standard water purification and desalination technologies for public utilities and industry because they are flexible, scalable, modular and relatively easy to operate and maintain [1] and nanomaterials are providing novel opportunities to develop more efficient reactive membranes. For this reason the use of hybrid photocatalytic composite membranes would allow one to combine the advantages of membrane technology with nanoparticles and AOPs in the removal of water pollutants, such as bacteria, heavy metals, dyes, etc. Azo dyes constitute about 50% of dyes normally used in the textile industry, hence the effluent streams coming from textile plants must be treated in order to remove the toxic or carcinogenic dye residues and their by-products, that otherwise could be released in the environment [3,27]. The application of heterogeneous photocatalysis for this treatment is a promising alternative to conventional methods [28–29].

In this work we explore the use of Nafion[®](DuPont) membranes containing a common photocatalytic material such as TiO_2 or novel graphene-based materials for water purification. Nafion membrane consists of an anionic perfluorinated polymer with sulfonic groups belonging to ionomer polymers, it is well known for its chemical and photochemical inertia [30] and it is a superacid catalyst and highly permeable to water [31]. Moreover, the high proton conductivity of Nafion membranes could favour the separation of the ionic compounds of the water molecules. This effect is enhanced by

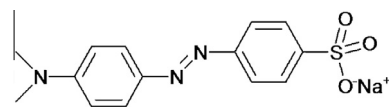


Fig. 1 – Structure of methyl orange.

adding organo-modified GO with sulfonic functional groups, denoted hereafter as GO_{SULF} , into the Nafion matrix [32–33]. In GO_{SULF} the epoxy groups at the surfaces of the GO flakes are replaced with ammine functional groups. Furthermore a larger water uptake is observed for Nafion- GO_{SULF} composite with respect to Nafion alone, due to a larger number of sulfonic functional groups (SO_3H) which are also present in the polymeric Nafion matrix. This can be useful in order to increase the interaction between a contaminant present in water and the composite membrane, and therefore for water purification purposes. To the best of our knowledge, the possibility of using organo-modified graphene oxide as catalyst in water purification has not been explored up to now, whereas it is limited mainly to fuel cells applications [32–35].

The photocatalytic activity of all the prepared membranes was evaluated by measuring the degradation of methyl orange (denoted as MO) under UV/visible light illumination. The structure of the MO molecule is reported in Fig. 1.

2. Experimental

2.1. Materials

Nafion as a 20 wt% dispersion in water and lower aliphatic alcohols was supplied by Aldrich. The preparation of GO by the Staudenmaier's method and the synthesis of the organo- GO_{SULF} by using 3-amino-1-propanesulfonic acid are described in detail in a previous work [32]. Anatase TiO_2 nanoparticles (hereafter np- TiO_2) with a nominal average diameter of 21 nm, and methyl orange (MO, 0.1% in H_2O) were acquired from Sigma-Aldrich.

2.2. Membranes preparation

Hybrid nanocomposite Nafion membranes containing different fillers such as anatase-type TiO_2 nanoparticles, graphene oxide (GO) (Fig. 2a) or organo-modified graphene oxide (GO_{SULF}) (Fig. 2b) were prepared by the solvent casting method. Fillers were directly dispersed in Nafion commercial solution, ultrasonicated for 1 day and stirred for another day at room temperature until a clear solution was obtained. After that, the dispersion was cast on a petri dish at 30 °C overnight to remove the solvents. The hybrid membranes were removed from the petri dish by immersing the glass plate in deionized water for several minutes. To reinforce the membrane, it was sandwiched and pressed between two Teflon plates and placed in oven at 150 °C for about 25 min. All composite membranes produced by casting were subsequently treated by rinsing in: (1) boiling HNO_3 solution (1 M) for 1 h to oxidize the organic impurities; (2) boiling H_2O_2 (3 vol%) for 1 h to remove all the organic impurities; (3) boiling deionized H_2O for 40 min three times; (4) boiling H_2SO_4 (0.5 M) for 1 h to remove any metallic impurities; and again (5) boiling deion-

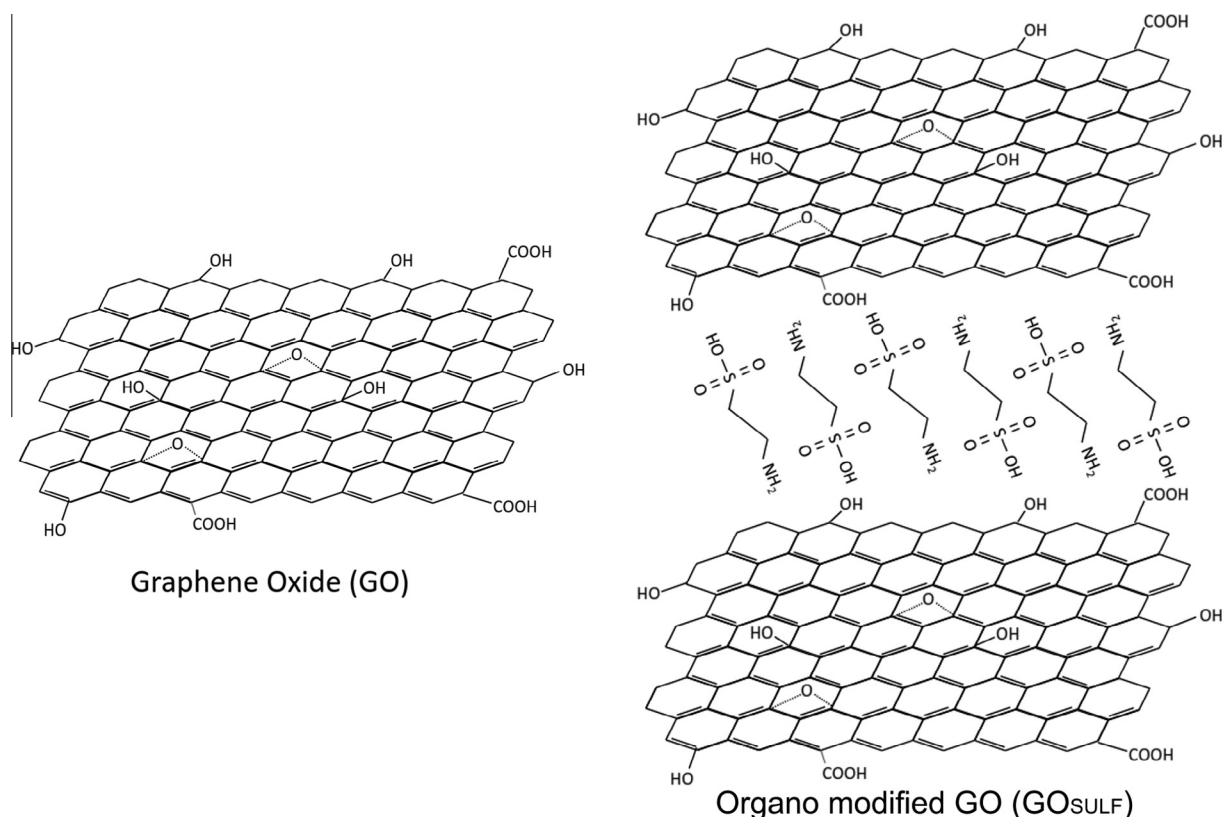


Fig. 2 – Schematic representation of the structures of GO and GO_{SULF} nanoplatelets.

ized H₂O for 40 min twice to remove excess acid. As far as it concerns pristine Nafion membranes, an appropriate amount of Nafion solution was dried at about 60 °C and then re-dissolved in the dimethylformamide (DMF) until a clear solution was obtained. Finally, the suspension was cast on a petri dish at 80 °C overnight.

Regeneration processes were performed, after adsorption/ photocatalysis experiments, by boiling the membrane in de-ionized water for 15 min, in order to release the adsorbed dye molecules. Then they were dried at 80 °C on a hot plate for 30 min before each use.

2.3. Characterization

Field emission scanning electron microscope (Zeiss Supra35 FE-SEM) equipped with EDX microanalysis system (Oxford Instruments, X-MAX, 80 mm²) was used to observe morphology, and to perform chemical mapping of the samples. Cross SEM analysis was carried out on the section of the membranes broken in two parts after freezing by immersion in liquid nitrogen.

The photocatalytic activity was evaluated by measuring the degradation of methyl orange (denoted as MO, with a concentration of $2 \cdot 10^{-5}$ M) in water solution under UV-Vis light irradiation carried out with a 18 W UVA/blue DULUX OSRAM lamp. During the photocatalytic experiment, one piece of membrane (about 1 cm²) was dipped into 2 ml of the above MO solution. The solutions were analysed by recording variations of the absorbance spectra of MO using an UV/Vis AGI-

LENT Cary 50 spectrophotometer in a wavelength range between 200 and 800 nm. The degradation of MO was evaluated by the Lambert–Beer law via the absorbance peak at 465 nm. MO dye adsorption (in dark conditions) for each membrane was also evaluated in order to discriminate between the contributions of the mere adsorption and the photocatalytic activity. MO solution pH was measured by a Mettler Toledo SevenGO duo SG23 pH-meter. The water content value of each membrane was determined using a micro-balance and recorded as: uptake% = $[(m_{\text{wet}} - m_{\text{dry}})/m_{\text{dry}}] \times 100$, where, m_{dry} is the mass of membrane dried in oven at 60 °C for 2 h and then put to equilibrate in a desiccator before being weighted; m_{wet} is the weight of the membrane after immersion in distilled water at room temperature for at least 48 h and quickly blotted dry with a paper tissue in order to eliminate most of the free surface liquid.

3. Results and discussion

Before testing the photocatalytic action of these hybrid polymeric systems we have analysed the samples by SEM in order to study the membrane morphology and to get qualitative information as far as it concerns surface and cross-sectional details.

Fig. 3 shows the cross-sections of all the nanocomposite membranes: Nafion (Fig. 3a), Nafion–TiO₂ (Fig. 3b–d), Nafion–GO (Fig. 3e and f), Nafion–GO_{SULF} (Fig. 3g and h). Fig. 3a reveals that Nafion pristine membrane is quite smooth and homogeneous; in Nafion–TiO₂ membranes, nanoparticles are well dis-

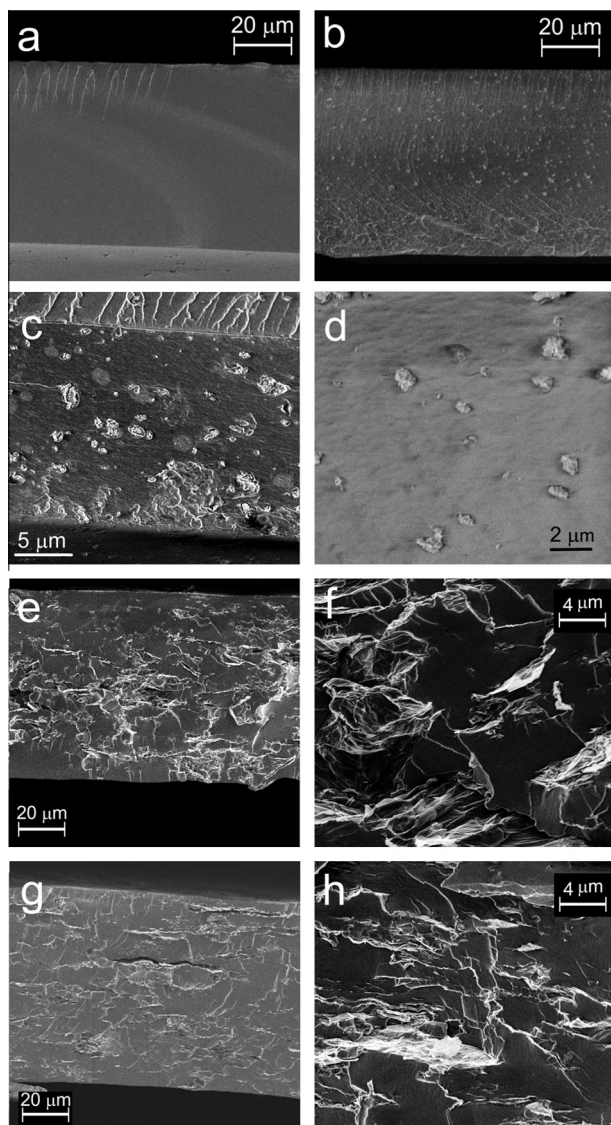
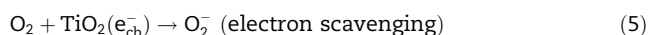
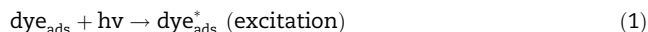


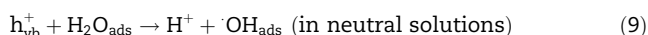
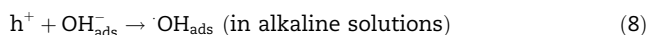
Fig. 3 – Cross-sectional SEM images of Nafion membrane (a) and hybrid nanocomposite Nafion membranes loaded with 3% of TiO₂ (b–d), GO (e, f) and GO_{SULF} (g, h). More details are visible in the images at higher magnification (b, f, h).

tributed throughout all the section (Fig. 3b–d). Additionally GO (Fig. 3e and f) and GO_{SULF} (Fig. 3g and h) nanocomposite membranes show a wrinkled and spongy structure, where graphitic planes are visible in the polymeric matrix. The presence and the chemical composition of the fillers in the membranes is confirmed by EDX analysis (see Supplementary data).

The photocatalytic activity of all the prepared membranes was investigated. In particular, it is known that np-TiO₂ can degrade dyes under UV-light illumination, according to the reactions 1–5 that are presented herein [36]. As one can see in the following reactions, excited dye molecules are generated upon absorption of visible photons (Eq. (1) and subsequently inject electrons into TiO₂ CB26 (e_{cb}[−]) (Eq. (2)). As a consequence, dye molecules degrade (Eq. (4)) and e_{cb}[−] reacts with oxygen (Eq. (5)) that acts as electron acceptor avoiding the recombination of dye⁺ and e_{cb}[−].



The overall rate of the dye degradation should be determined by the competition between the forward electron injection (Eq. (2)) and the backward recombination (Eq. (3)). The adsorption of dyes on the photocatalytic surface is needed in order to achieve dye degradation because in this way reaction of Eq. (2) is favoured. In the case of Nafion–TiO₂ membrane, the dye adsorption depends on the interactions of the dye with the membrane surface and on the water absorption equilibrium of the membranes. In addition, the absorption of water on polymer surface favours the interaction of electrons and holes with water molecules or hydroxyl ions forming reactive species (reactions in Eqs. (6–9)) [37]. These species are able to degrade organic compounds.



We have chosen methyl orange (MO) as a model compound for the photocatalytic study. The UV–visible absorbance spectrum of MO dissolved in water shows two maxima: the first one at 270 nm and the second one at 465 nm. The absorbance at 270 nm is assigned to the benzene ring in MO, whereas the absorbance at 465 nm is due to the azo linkage of MO [38].

The latter absorbance was used to quantify the MO concentration reduction or degradation due to adsorption and photocatalysis; any variation of the 270 nm peak position is correlated to the formation of by-products as a consequence of the photodegradation of the azo dye. We have not observed any degradation of MO under UVA/blue irradiation for 1 h as one can see in Fig. 4; degradation of MO is only observed when the membranes are dipped in the solution and MO is incorporated in the polymeric matrix.

Changing the pH by adding HNO₃ or NaOH did not result in a variation of MO absorbance spectra after irradiation, as one can see in Fig. 5; moreover, UV–Vis spectra at pH 10.5 and at pH 6.0 are almost the same. On the other hand, at acidic pH (value of 3.7) the absorbance bands shift towards larger wavelengths, and an additional feature (a hump) appears at larger wavelength on both peaks, due to the protonation of MO.

The pH value 3.7 is within the transition pH range of this indicator (value of about 3.1–4.4), but the observed shift and the hump appearance in MO spectra have already been shown in the literature even for lower pH values [39]. MO solution is orange in basic medium and red in acidic medium, as highlighted in the photo of Fig. 5 where the coloured MO solutions at pH 3.7, 6.0 and 10.5 are in beakers numbered 5,

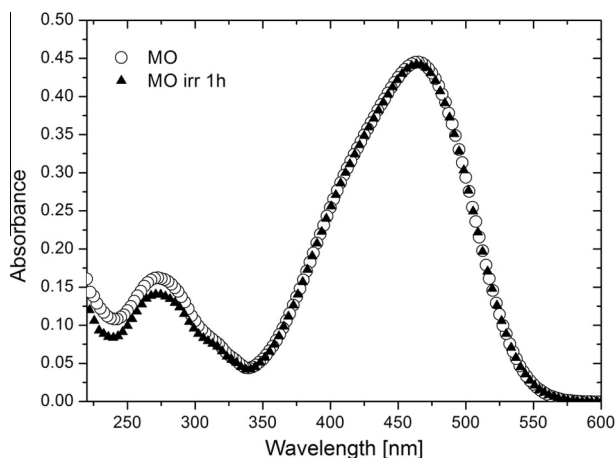


Fig. 4 – UV-Vis absorbance spectra of MO ($C = 2 \cdot 10^{-5}$ M) before (open circles) and after irradiation for 1 h (closed triangles).

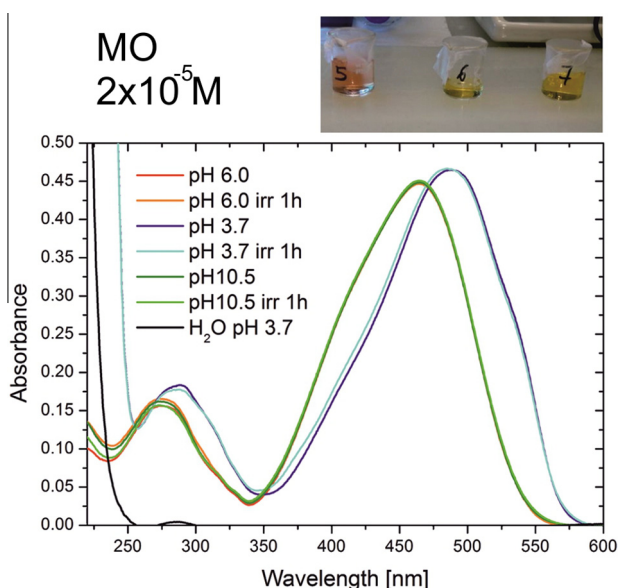


Fig. 5 – UV-Vis absorbance spectra of MO solution at different pH values in dark condition (red line for pH 6.0, blue line for pH 3.7, green line for pH 10.5) and after one hour irradiation (orange line for pH 6.0, cyan line for pH 3.7, light-green line for pH 10.5). The UV-Vis absorbance of H_2O with pH 3.7 is reported as a reference (black line). The photo above the graph shows the beakers containing the MO solution at pH 3.7, pH 6.0 and pH 10.5 (from left to the right). (A colour version of this figure can be viewed online.)

6 and 7, respectively. The equilibrium between acid and basic form of the used dye is shown in Fig. 6a, while the equilibrium of protonation and deprotonation of sulfonic group in the polymer is shown in Fig. 6b.

MO is an anionic dye molecule, and its adsorption on Nafion based composite membranes should be hindered because of the electrostatic repulsions between the negative molecular charge of the dye and the negative sulfonic group in Nafion. After one hour of immersion (Fig. 7a), all the Nafion

membranes adsorb similar amounts of dye independently of the used filler with the exception of Nafion- GO_{SULF} that shows a slight decrease of the peak at 465 nm. After two and three hours (Fig. 7b and c, respectively), the membranes continue to adsorb the dye and the absorbance band shifts to larger wavelength due to the decrease of the pH value of the solution as discussed above. Fig. 7d shows the time dependence of the pH value of the MO solution.

In the first hour the pH value decreases more for Nafion- TiO_2 , while in the second and third hour a larger pH decreasing is observed for the other membranes, especially for Nafion- GO_{SULF} . A reduction of the pH value is related to an increase of proton concentration due to the fact that when the dye is adsorbed on the polymeric surface, protons are released from the polymer and protonate dye molecules in solution, as described in Fig. 6.

Under UVA/Vis light irradiation (Fig. 8), we observe a different photocatalytic activity for each membrane. In particular, when irradiation is performed in the presence of recast Nafion, the intensity at 465 nm of the MO absorbance gradually decreases and the peak position shifts towards higher wavelengths (up to 470 nm) with irradiation time. This shift can be attributed to the variation of pH towards more acidic values according to previous studies [36]. At the same time, the maximum of this band decreases strongly for Nafion- TiO_2 and even more for Nafion- GO_{SULF} . Nafion- GO membrane has a lower photocatalytic activity compared to the other composites, as we can conclude observing the degradation path of MO solutions reported in Fig. 8. The difference between the degradation capability of Nafion- GO and Nafion- GO_{SULF} is likely due to the sulfonic functionality of the filler. The presence of SO_3^- groups increases the acidity of the GO_{SULF} material, with respect to the pristine graphene oxide, consequently its incorporation in the polymer matrix produces a more acid hybrid composite. This results in an increment of the water absorption of the membrane (about 27 wt% Nafion- GO against about 50 wt% Nafion- GO_{SULF}), and a likely acid-photocatalytic mechanism, as will be explained later on. As concerns the characteristic MO absorption peak at 270 nm, we have observed that after 1 h of irradiation, it decreases independently of the membrane used. In the case of Nafion- TiO_2 we also observe a change of the peak shape and a shift towards shorter wavelengths, in particular a new peak at 250 nm appears. In the description of Fig. 9 this peak will be explained in more detail. All the observed changes become more evident as the irradiation time is increased (Fig. 8c).

Table 1 reports the amount (%) of MO removed by each membrane after three hours irradiation and the rate constant k , calculated by fitting the experimental C/C_0 data of Fig. 10b, considering $C = C_0 \exp(-kt)$.

Our results clearly show as the use of GO_{SULF} as nanoadditive in Nafion matrix is very efficient for the photocatalytic degradation of MO dye, even more than $np-TiO_2$, that is one of the most used photocatalysts for water purification. Fig. 9 reports in detail how MO UV-Vis absorbance spectra change during three hours under irradiation, for the solutions where Nafion- TiO_2 (Fig. 9a) and Nafion- GO_{SULF} (Fig. 9b) are immersed. The lowest MO absorbance, that is the lowest residual MO concentration (according to Lambert-Beer law),

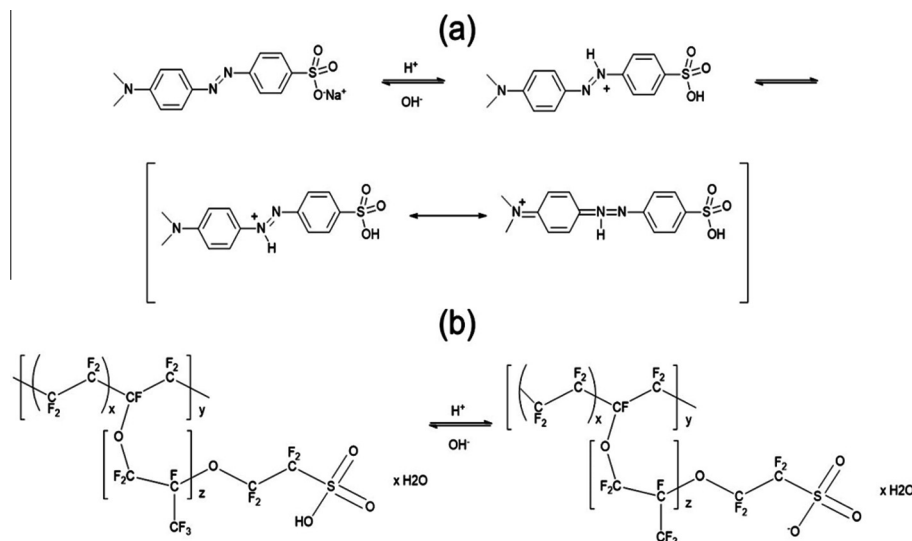


Fig. 6 – Acid–base equilibria of MO (a) and Nafion (b).

is observed for the solution where Nafion- GO_{SULF} was dipped. However, for the solution containing Nafion- TiO_2 , the 465 nm peak intensity decreases with time and a new peak at 250 nm appears after one hour irradiation. In the next two hours, this new band becomes more defined, indicating the formation of by-products due to photocatalysis. This phenomenon was also observed in previous studies and it was assigned to the formation of aromatic intermediate compounds [40]. These species, probably as harmful as the original MO species [41], are not forming in the case of Nafion- GO_{SULF} (the peak at 250 nm is not present) indicating that the decrease of MO concentration for Nafion- GO_{SULF} is due to adsorption of the MO molecules and/or possible by-products generated by the dye degradation, and this process is favoured by irradiation. Therefore, the use of Nafion- GO_{SULF} membrane for MO dye removal from water seems to be a more safe method than the use of Nafion- TiO_2 membrane.

Fig. 10 shows the maximum value of the MO absorbance as a function of the dipping time for all the membranes in dark condition (Fig. 10a) or after irradiation (Fig. 10b). Without irradiation, in the first hour the adsorption does not increase significantly for all membranes, in particular Nafion, Nafion-GO and Nafion- TiO_2 membranes adsorb the same MO quantity. In the second and third hour a different behaviour can be observed: Nafion, Nafion-GO and Nafion- GO_{SULF} adsorb more than Nafion- TiO_2 and after three hours Nafion and Nafion- GO_{SULF} have adsorbed the same amount of dye. It is well known that Nafion is a very strong Bronsted acid and has been widely investigated as an acidic catalyst for organic reactions [42]. When the membranes are immersed in the solution, the acid-base equilibrium of SO_3H groups, of both polymer and GO_{SULF} filler shifts to the deprotonated form (SO_3^-), while the equilibrium of MO shifts towards protonated forms (MO^+). In this way, the electrostatic interaction between SO_3^- and MO^+ is favoured and the adsorption increases, accompanied by an increase of the solution pH value, as already evidenced in Fig. 7d. It seems there is a correlation

between the adsorption and the decreasing of pH versus dipping time. In fact, both show a great change during the second hour, likely due to an initial slow kinetic caused by the electrostatic repulsion between the negative charges of the dye and of the sulfonic groups. The effect of UVA/Vis irradiation on the reduction of dye concentration (Fig. 10b) is larger than that of adsorption, in particular for Nafion- GO_{SULF} and Nafion- TiO_2 . The membranes immersed in solution absorb both dye molecules and water, but the dye adsorption does not necessarily follow the same trend of the water uptake. Indeed the dye adsorption depend on its chemical interaction with the membrane and the filler. The water uptake measured for these membranes is 24% for Nafion, 27% for Nafion-GO, 35% for Nafion- TiO_2 and 50% for Nafion- GO_{SULF} . Therefore, the water uptake of Nafion-GO is lower than Nafion- TiO_2 , whereas the adsorption of MO by Nafion-GO is higher than that of Nafion- TiO_2 for each dipping time.

To better highlight the differences between mere immersion in dark conditions or under irradiation, we report in Fig. 11 the UV-Vis absorbance spectra of the MO solutions where the Nafion- GO_{SULF} and Nafion- TiO_2 membranes were dipped for 3 h. The spectra are different: in the case of dipping in dark conditions the peaks are shifted towards larger wavelengths and also the shape changes, showing a hump on the right of the peaks; on the contrary, in the case of three hours irradiation, the spectra of the solution show a larger decrease of dye concentration, but the shape of the peak at 465 nm remains the same of pristine MO. Vice versa in the peak at lower wavelength a strong difference is observed between Nafion- TiO_2 and Nafion- GO_{SULF} .

From these results we can draw two main conclusions: (1) the reduction of MO concentration is due to different processes occurring in dark condition or under irradiation; (2) both membranes are able to reduce the amount of MO under irradiation, but different photocatalytic mechanisms take place. The adsorption mechanism in dark was explained considering the acid-base equilibria of dye and polymer. Under

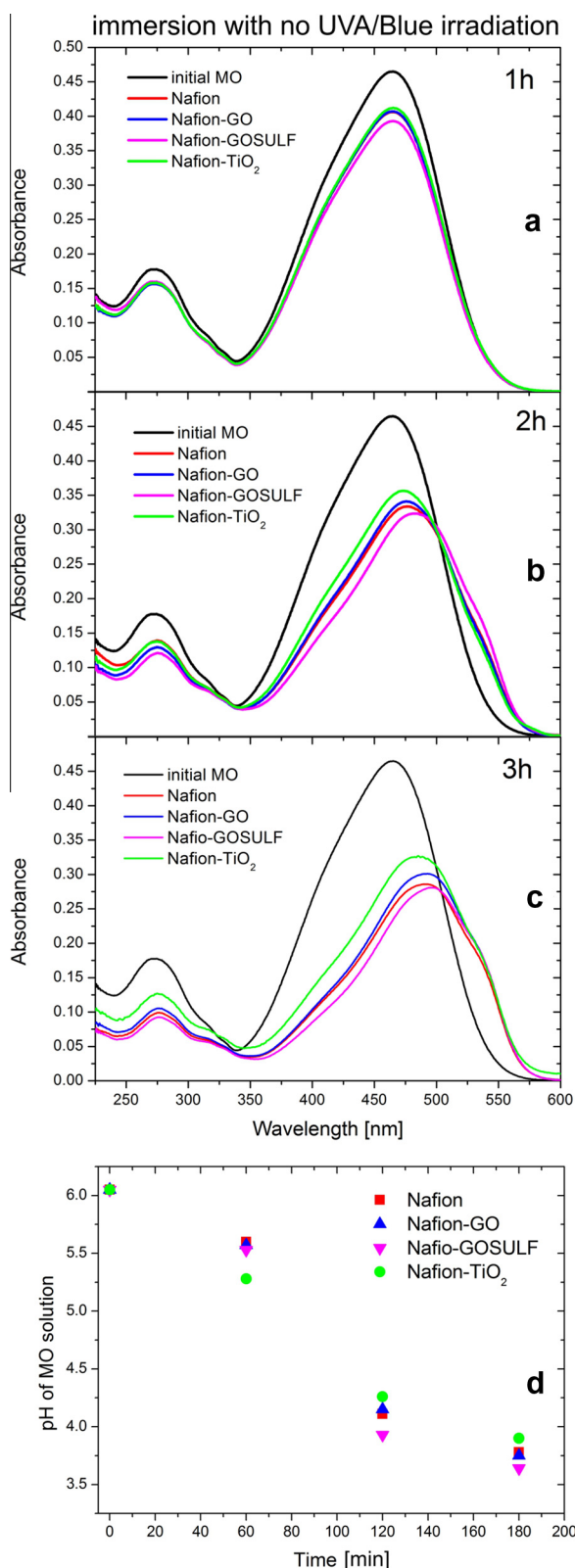


Fig. 7 – UV-Vis absorbance spectra of methyl orange after immersing Nafion composite membranes in MO solution for one hour (a), two hours (b) and three hours (c). The Figure (d) shows how pH changes during the adsorption time. (A colour version of this figure can be viewed online.)

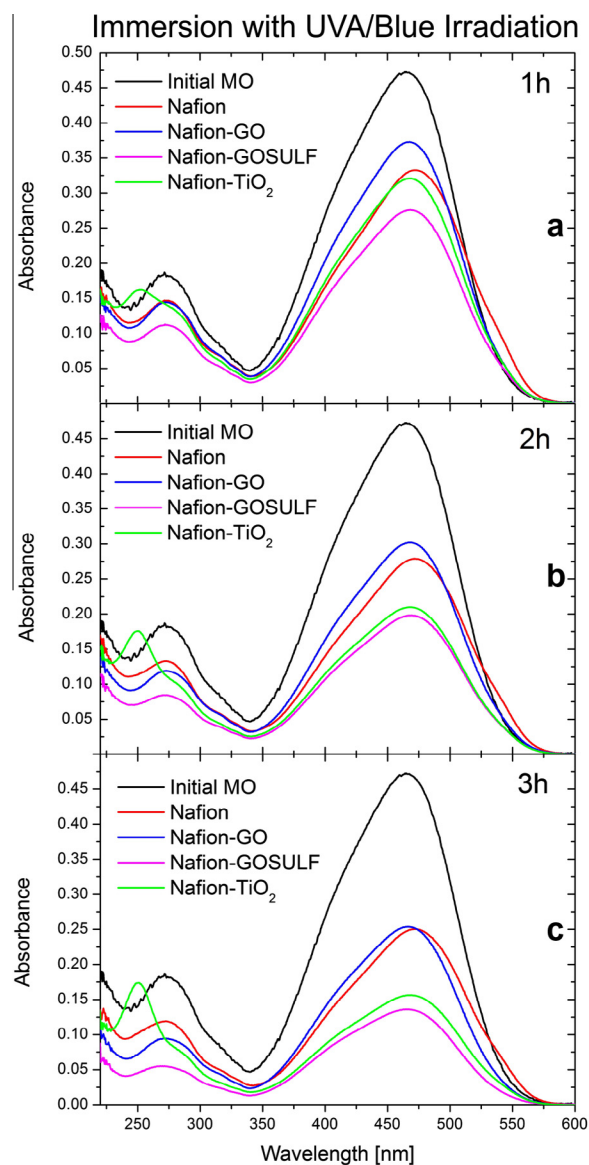


Fig. 8 – UV-Vis absorbance spectra of methyl orange after immersing Nafion composite membranes in MO solution and irradiated with UVA-Vis light for one hour (a), two hours (b) and three hours (c). (A colour version of this figure can be viewed online.)

irradiation Nafion-TiO₂ degrades MO following the same pathway of TiO₂ powder [37], hence Nafion membrane can be used as a support to incorporate the catalyst.

Previous studies on the characterization of methyl orange photocatalytic degradation compound in the presence of TiO₂ powder, individuate mono- and di-hydroxylated species as byproducts of MO degradation, the which absorbance spectra show the same profile of MO spectrum, but with the maximum shifted to 470 nm [36–37,41,43]. Additionally it was confirmed that under UV irradiation hydroxylation of benzene can occur in the presence of a photocatalyst and acid catalysis. Fig. 8 has shown the shift of the absorbance peak for

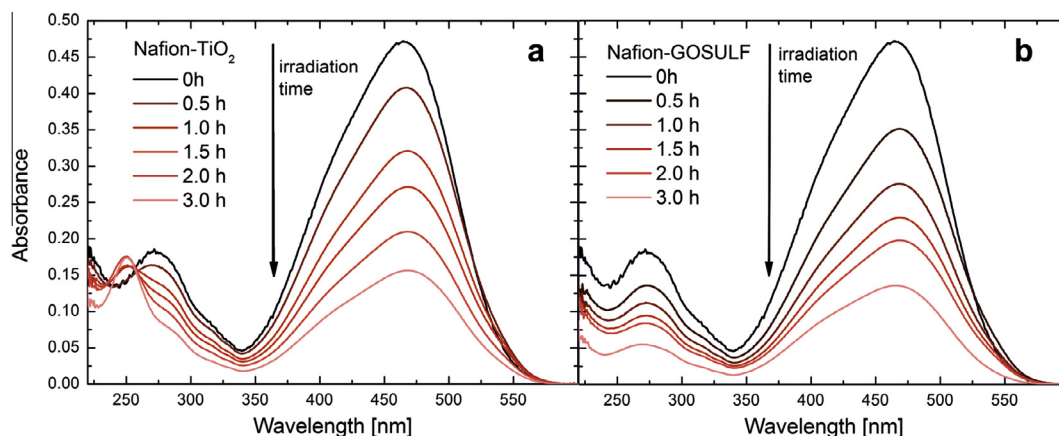


Fig. 9 – UV-Vis absorbance spectra of MO solution after irradiation for three hours in the presence of Nafion TiO₂ (a) and Nafion GO_{SULF} (b). (A colour version of this figure can be viewed online.)

Table 1 – Amount (%) of MO dye removed after 3 h irradiation (initial concentration $C_0 = 2 \times 10^{-5}$ M); the rate constant k is calculated by fitting the experimental C/C_0 data of Fig. 10b, considering $C = C_0 \exp(-kt)$.

Membrane	MO removed after 3 h of irradiation %	$k [\times 10^{-3} \text{ min}^{-1}]$	
		Value	Error
Nafion	47	4.6	0.4
Nafion-GO	46	4.1	0.2
Nafion-GO _{SULF}	71	7.7	0.4
Nafion-TiO ₂	67	6.7	0.2

Nafion-GO_{SULF} from 465 nm shifts to 470 nm after irradiation, therefore we hypothesize a mechanism similar to that proposed for titania as reported in Fig. 12 [43]. Hydroxyl radicals are likely formed by Nafion-GO_{SULF} under irradiation, and added directly to MO phenyl ring, forming an intermediate radical; subsequently the removal of H-atom by oxidants (e.g. O₂) could lead to the hydroxylated species.

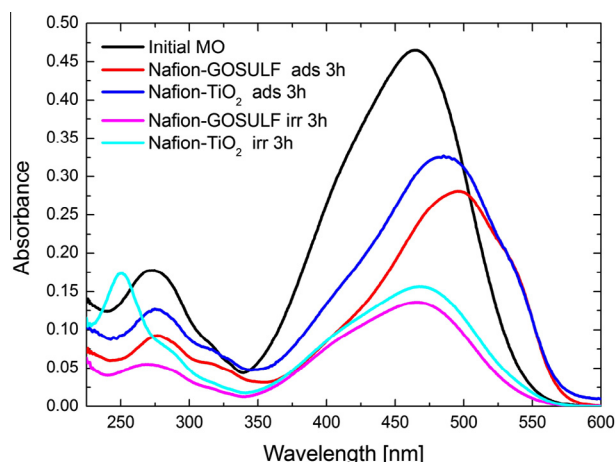


Fig. 11 – UV-Vis MO absorbance spectra for Nafion-TiO₂ and Nafion-GO_{SULF} after 3 h of immersion in dark and after 3 h of UVA-Vis irradiation. The initial absorbance spectrum of MO is reported as a reference. (A colour version of this figure can be viewed online.)

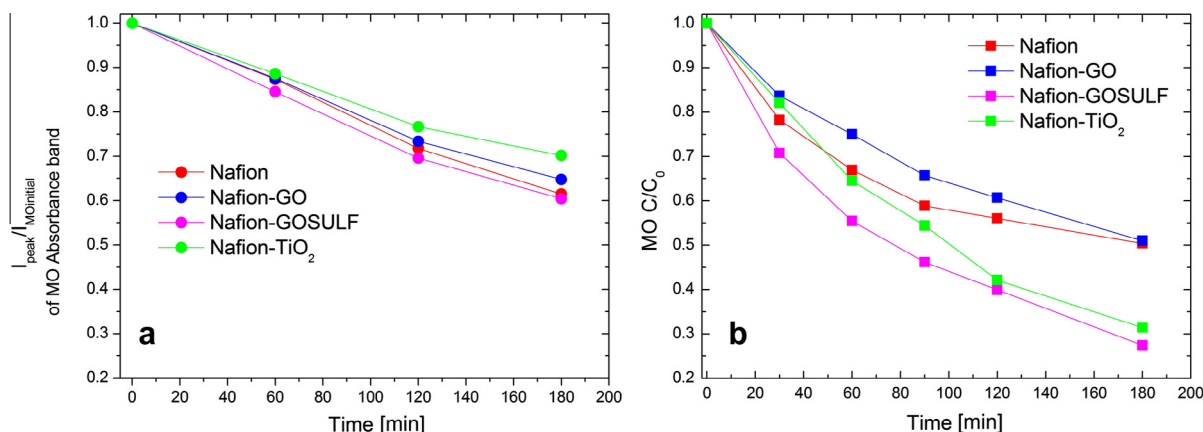


Fig. 10 – The maximum value of MO absorbance during time due to the adsorption of the membranes (a) and the residual MO concentration during the UVA/Vis irradiation time (b). (A colour version of this figure can be viewed online.)

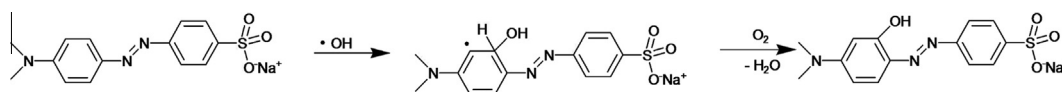


Fig. 12 – Proposed mechanism for MO degradation by GO_{SULF} .

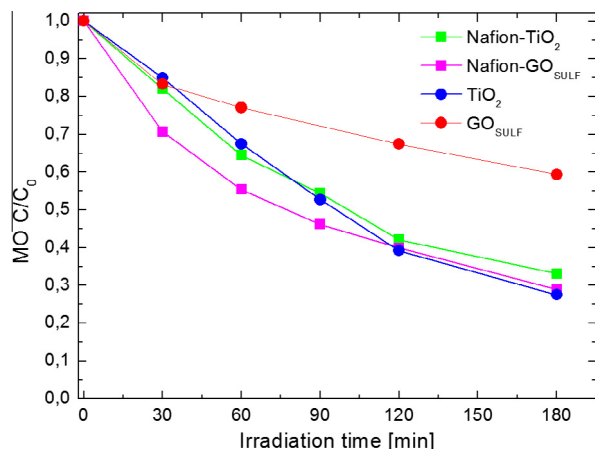


Fig. 13 – Residual MO concentration as a function of the irradiation time for TiO_2 and GO_{SULF} directly dispersed in the MO solution or incorporated as fillers in the hybrid membranes. (A colour version of this figure can be viewed online.)

The polymeric matrix incorporating the photocatalytic filler could reduce the photocatalytic activity of the filler itself. In order to verify this point, we have repeated the irradiation experiment using 70 mg/l of anatase TiO_2 nanoparticles or GO_{SULF} dispersed directly in MO solution (without Nafion). This concentration just corresponds to the filler weight contained in a membrane of 1 cm^2 dipped in 2 ml of MO solution, as the ones used in this work.

A comparison between the MO degradation for the fillers alone or embedded in Nafion is reported in Fig. 13. The photocatalytic efficiency of TiO_2 and Nafion- TiO_2 is almost the same up to three hours of irradiation and in both cases the formation of the same aromatic by-product is observed (MO absorbance peak at 250 nm). In the case of GO_{SULF} , embedding the filler in the Nafion matrix the reduction of MO concentration is much larger.

The effect of MO adsorption on GO_{SULF} powder in dark conditions consists of a small reduction of the initial dye concentration. Indeed after three hours the residual concentration reduces to about 90% (not reported here), whereas under irradiation the initial concentration is reduced down to 60%, as shown in Fig. 13. It was shown that GO can work as a photocatalyst for water decomposition [17], and that different oxygen functionalities can modify the valence band and conduction band positions. The photocatalytic activity of either GO_{SULF} , where an ammine-derivative functionality replaces oxygen atoms, or Nafion- GO_{SULF} has not been reported in the literature yet, but our results confirm the photoactivity of GO_{SULF} . The better photocatalytic performance shown by the hybrid Nafion- GO_{SULF} system depends on the following factors: (1) both (filler and polymer) under

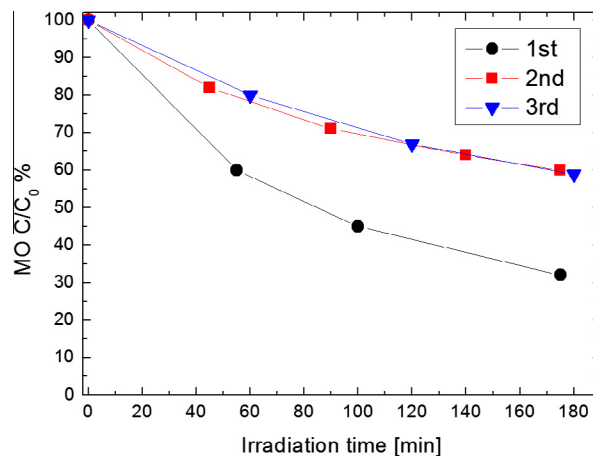


Fig. 14 – MO concentration versus irradiation time for three consecutive photocatalytic processes using the Nafion- GO_{SULF} membrane. Second and third process took place after membrane regeneration step. (A colour version of this figure can be viewed online.)

irradiation reduce the MO concentration; (2) GO_{SULF} enhances the water uptake and the proton conductivity of Nafion, favouring the dye degradation processes.

The results shown in Fig. 13 indicate that hybrid Nafion composites have a photocatalytic activity comparable (or even better in the case of GO_{SULF}) with respect to the filler itself. The possibility to re-use nanocomposite Nafion membranes for several purification processes has been investigated: the Nafion- GO_{SULF} and Nafion- TiO_2 membranes were dipped in MO solution under irradiation for three times. After each use the membranes were boiled in DI-water for 15 min for regeneration. In Fig. 14 we report MO concentration versus irradiation time for three consecutive uses of Nafion- GO_{SULF} composite under irradiation, alternated with regeneration processes. After the first use and regeneration the performance reduces [44] but, then, remains stable for the following cycles. The efficiency reduction after first use could be due to a passivation of sulfonic groups, that in the initial membrane preparation are activated by rinsing in acid media. As explained before, to have a stable activity it is mandatory to have sulfonic groups in their acid form. Most likely, a rinsing in acid solution could help to eliminate all the residual dye adsorbed in the membrane.

4. Conclusions

Hybrid Nafion nanocomposite membranes were synthesized in order to study their possible use for degradation of water pollutants. The systems we have developed aim to engineer the membrane properties for water purification applications, by using suitable fillers such as GO, GO_{SULF} and TiO_2

nanoparticles, joining the advantages of membrane technology and photocatalysis.

In order to investigate the adsorption and photocatalytic properties of these membranes, MO was chosen as model compound, since it is a common pollutant present in waste water coming out from textile industries. MO concentration is reduced by dipping the membranes in solution both in dark conditions and under irradiation, but a stronger effect is observed under irradiation. In particular, the best results are achieved for Nafion–TiO₂ and Nafion–GO_{SULF} and they are compared with photocatalytic activity shown by the fillers directly dispersed in MO solution. Nafion–TiO₂ under irradiation shows photocatalytic activity for degradation of MO with the formation of by-products, as already reported for TiO₂ powder dispersed in MO aqueous solution. The photoactivity of GO_{SULF} has been shown for the first time, but Nafion GO_{SULF} is more efficient in the dye removal, showing very promising results: after 3 h UVA/blue lamp irradiation a residual MO concentration of less than 30% of the initial value is found, without leaving any other harmful by-products in solution.

This indicates that Nafion can be used as a matrix in which TiO₂ and GO_{SULF} can be incorporated, with no photocatalytic efficiency reduction with respect to the same fillers dispersed directly in solution. The membranes may be regenerated and used for several MO removal processes.

Further work is ongoing in order to investigate the photocatalytic activity of these hybrid membranes relatively to other water pollutants. Furthermore, the use of other commercial low-cost polymers combined with GO fillers is worth being considered for future industrial development of such nanocomposite filtration membranes.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.carbon.2014.10.093>.

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