Cationic and anionic azo-dye removal from water by sulfonated graphene oxide nanosheets in Nafion membranes

Silvia Scalese,*a Isabella Nicotera,*b Daniele D’Angelo,a Simona Filice,a,b,c Sebania Libertino,a Cataldo Simari,c Konstantinos Dimosd and Vittorio Privitera*a

Graphene oxide flakes functionalized with 3-amino-1-propanesulfonic acid (denoted as GO_{SULF}) as a powder or incorporated into an ionomer membrane such as Nafion (DuPont) were studied for water purification applications. The adsorption and the photocatalytic activity of the GO_{SULF} powder itself or confined as a nano-additive in the membrane (Nafion–GO_{SULF}) were investigated by measuring the degradation of a cationic dye, methylene blue (MB), in the dark and under UV/Visible light illumination. The results were compared with the ability of these systems to degrade an anionic dye, methyl orange (MO), in order to evaluate the role of the polymer–dye interaction. The degradation of the azo dyes depends on the mutual interaction between GO_{SULF} flakes, the polymeric matrix and the dye: Nafion–GO_{SULF} strongly reduces MB both under dark and illumination conditions in the same way as the GO_{SULF} powder, while, for MO degradation, the composite membrane is more efficient than GO_{SULF} alone. Finally, the possibility of reusing the same photocatalytic material several times, which is the main advantage of embedding active nanomaterials in a polymer matrix, is demonstrated by the effective regeneration of the nanocomposite membranes.

Introduction

The use of nanotechnology for water purification applications has attracted increasing interest in the last decade. The development of new, efficient, eco-friendly and specific methods to treat contaminated waters is of fundamental importance due to the increase of pollution mainly coming from industrial sites.1–5

Among a huge variety of chemical pollutants, the effluent streams coming from textile plants must be treated in order to remove the toxic or carcinogenic dye residues and their by-products, which otherwise could be released into the environment.3,6 In particular, azo dyes constitute about 50% of dyes normally used in textile industries. Many technologies have been developed for dye removal from aquatic environments, including physical, chemical, and even biological approaches.7,8 Among these approaches, absorption is regarded as an easy and economic process.9,10 Various materials such as commercial activated carbon, natural materials, bio-adsorbents and wastes from agriculture have been used for such processes.9,10

Carbon-based nanomaterials have been used as high capacity and selective sorbents for organic solutes in aqueous solutions,11 or in combination with other nanomaterials to increase the photocatalytic activity of these nanomaterials in water purification, energy conversion, etc.12–15 In particular, graphene oxide (GO), composed of graphene flakes with oxygen functional groups on the basal planes and at the edges,16 can be used as a precursor of graphene for the synthesis of graphene-based semiconductors17 or it can be directly used as an effective absorbent for methylene blue (MB), which is widely applied to dye cotton, wood and silk. The huge and fast MB absorption capacity18 of GO flakes makes this material very competitive compared with other high performance absorbents.

Recently, photocatalytic properties have been reported for GO19 due to the creation of highly reactive species in water (hydroxyl radicals or oxygen ions) induced by light absorption capable of removing organic contaminants. GO is also used as a starting material for the preparation of graphene-based composite photocatalysts used in many reactions, such as nitroaromatic reduction, alcohol oxidation, CO₂ reduction, in water splitting applications, disinfection and elimination of water pollutants.20,21 In particular, reduced GO (rGO) and rGO–TiO₂ composites have been tested to
remove cationic dyes such as MB from water by simple adsorption phenomena.\textsuperscript{22} In addition, recently sulfonated graphene has been mostly used as a catalyst for esterifications, Friedel Crafts reactions and biomass transformation.\textsuperscript{23} Recent studies also suggested that sulfonated graphene (GR-SO$_3$H) can enter in the production of electrodes for the next generation high performance electrochemical capacitors and can be crosslinked with hierarchical mesoporous TiO$_2$ for the fabrication of membranes used for water purification.\textsuperscript{23} The versatile properties of these sulfonated materials can be attributed, at least in part, to the peculiar structure of graphene, consisting of a honeycomb-structured two-dimensional sheet of sp$^2$-hybridized carbon having one-atomic thickness, and to the fact that GR-SO$_3$H displays Brønsted acid properties.\textsuperscript{23}

In general, the main disadvantage of using nanomaterials for water purification is that they are dispersed as powders in water and the powder itself could be a contaminant for the environment and, furthermore, cannot be easily reused. The combined use of membrane technology and nanomaterials is expected to overcome these problems. In particular, carbon nanomaterials provide novel opportunities to develop more efficient reactive membranes for the removal of water pollutants. In previous studies\textsuperscript{24,25} we have already shown the promising use of a Nafion\textsuperscript{R} (DuPont) polymer for producing a nanocomposite membrane (containing GO or TiO$_2$) for water purification applications. In particular these nanocomposites were tested for the removal of methyl orange and methylene blue from aqueous solution.

In this work, we prepared organo-modified GO containing sulfonilic functional groups (GO$_{SULF}$) by reaction with an acidic amine derivative covalently bonded to the graphite surfaces via nucleophilic substitution reactions on the epoxy groups of GO (see Fig. 1).\textsuperscript{26}

GO$_{SULF}$ was then dispersed into an ionomer, such as Nafion, in order to create nanocomposite membranes. Nafion\textsuperscript{R} (DuPont) is a perfluorosulfonic polymer that shows significant properties such as high ionic conductivity, ion-exchange capacity and stable structure, and therefore it is used for various applications such as fuel cells, sensors, and electrochemical devices.\textsuperscript{27,28}

The choice of this ionomer for the creation of hybrid films to be tested in water purification applications is substantially linked to two reasons: (1) the acidic properties promote the separation of ionic compounds present in the water and (2) the Nafion membranes have a high capacity to absorb water favouring the effective interaction between contaminants and the active material.\textsuperscript{24} The organo-functionalization of the GO surfaces with hydrophilic groups, such as –SO$_3$H, improves both the acidity and the water uptake of the resulting nanocomposite membranes, but also their mechanical, chemical, and thermal strength.\textsuperscript{26}

Recent results show that GO$_{SULF}$ nanosheets exhibit a better absorption capability in the removal of MB with respect to the GO powder.\textsuperscript{29} In this work, the degradation ability of GO and GO$_{SULF}$ flakes for removing methylene blue (MB) molecules from water in the dark and under UVA/blue illumination was investigated and compared. Our study was focused on the Nafion–GO$_{SULF}$ composite membrane in the removal of both MB and methyl orange (MO) (the structural formulae of these two molecules are reported in Fig. 2), which differ by their superficial charge.

The degradation mechanism involves both adsorption and photocatalytic processes, and the results point out that such hybrid nanocomposites are effective for the selective removal of different azo dyes. In this mechanism the polymer matrix seems to play a crucial role and synergic with the nano-additive. Finally, the possibility of regeneration and reuse of the Nafion–GO$_{SULF}$ composite was also tested in order to demonstrate that the incorporation of nanomaterials inside a polymeric film is a more efficient and ecologically friendly method with respect to the direct dispersion of powders in aqueous solution.

\section*{Experimental}

Methylene blue (0.1 M in H$_2$O) and methyl orange (0.1 wt\% in H$_2$O) were acquired from Sigma-Aldrich. Nafion as a 20 wt\% dispersion in water and lower aliphatic alcohols were supplied by Aldrich. GO$_{SULF}$ was obtained by treating GO prepared using Staudenmaier’s method\textsuperscript{30} with 3-amino-1-propanesulfonic acid, as described in a previous work.\textsuperscript{26} With respect to the synthesis of sulfonated graphene reported in the literature\textsuperscript{23} in which the sulfonlic group is linked to the graphene layer by a phenyl ring, in our work the modification of graphene oxide occurs by the
replacement of epoxy functionalities by amine derivatives ending with a sulfonic group. The result is schematically reported in Fig. 1. This reaction occurs without the formation of intermediate products that should be isolated and purified by filtration and centrifugation, as in the case of the synthesis reported in the literature. In a previous work, Fourier Transform infra-red (FT-IR) spectroscopy performed on GO-SULF showed the reduction of the epoxy groups along with the appearance of the signals related to CH\textsubscript{2} on amine groups; TGA/DTA analysis confirmed a 22% functionalization of graphene oxide epoxy functionalization with the amine derivative.

X-Ray photoelectron spectroscopy (XPS) measurements were performed under ultrahigh vacuum conditions with a base pressure of 5 x 10\textsuperscript{-10} mbar using a SPECS GmbH instrument equipped with a monochromatic MgKa source (h\nu = 1253.6 eV) and a Phoibos-100 hemispherical analyzer. All binding energies were referenced to the C1s core level at 284.6 eV. Spectral analysis included a Shirley background subtraction and peak deconvolution employing mixed Gaussian–Lorentzian functions in a least squares curve-fitting program (WinSpec) developed at the Laboratoire Interdisciplinaire de Spectroscopie Electronique, University of Namur, Belgium.

A field emission scanning electron microscope (Zeiss Supra35 FE-SEM) was used to observe the morphology of the samples. Cross SEM analysis was carried out on the section of the membranes broken into two parts after freezing by immersion in liquid nitrogen.

Nafion and Nafion–GO\textsubscript{SULF} composite membranes were prepared using a solvent casting method as described in previous studies. The composite was prepared with 3 wt% filler-to-polymer loading. All the membranes produced were subsequently acid-activated by rinsing in: (i) boiling H\textsubscript{2}O\textsubscript{3} solution (1 M) for 1 h to oxidize the organic impurities, (ii) boiling H\textsubscript{2}O\textsubscript{2} (3 vol%) for 1 h in order to remove all the organic impurities, (iii) boiling deionized H\textsubscript{2}O for 40 min three times, (iv) boiling H\textsubscript{2}SO\textsubscript{4} (0.5 M) for 1 h to remove any metallic impurities, and again (v) in boiling deionized H\textsubscript{2}O for 40 min twice to remove excess acid.

The regeneration process of the membranes after the adsorption experiments was performed by boiling them in acid water (1% of nitric acid in deionised water) for about 30 min, until the membranes return to their initial colour as a consequence of the release of the adsorbed dye molecules. Then, the membranes were rinsed again in boiling acid water for 15 minutes and, finally, twice in boiling water for 15 min, respectively. Membranes were dried at 100 °C on a hot plate for 180 min and weighted before each adsorption test.

The surface charge of sulfonated graphene oxide and graphene oxide solutions was measured using a Horiba Scientific Nano-Particle Analyzer SZ-100-Z. The results show that at pH = 6.3 both materials are negatively charged, confirming the literature data. In particular, the zeta potential of GO is higher (−46 mV) than the zeta potential of GO\textsubscript{SULF} (−42.8 mV).

The adsorption ability of the GO\textsubscript{SULF} powder directly dispersed in MB solutions at different concentrations (10, 70 and 100 mg l\textsuperscript{−1}) was evaluated by measuring the decrease of MB concentration.

The photocatalytic activity of the GO\textsubscript{SULF} powder and membranes was evaluated by measuring the degradation of MO and MB in water solution with an initial concentration of 1.5 x 10\textsuperscript{−6} M under UV-Vis light irradiation carried out using an 18 W UVA/blue DULUX OSRAM lamp. In the case of membranes, the photocatalytic experiment was performed by dipping one piece of about 1 cm\textsuperscript{2} into 2 ml of dye solutions. The solutions were analysed by recording variations of the absorbance spectra of dyes using an UV/Vis AGILENT Cary 50 spectrophotometer in a wavelength range between 200 and 800 nm and wide optical window cuvettes (200–2500 nm). The degradation of dyes was evaluated using the Lambert–Beer law via the absorbance peak at 465 nm and 664 nm for MO and MB, respectively. Dye adsorption (under dark conditions) for each membrane was also evaluated in order to discriminate between the contributions of the mere adsorption and photocatalytic activity. The absorption of the MB dye was also tested by varying the size of the membrane piece.

Dye solution pH was measured using a Mettler Toledo SevenGO duo SG23 pH-meter. The water content value of each membrane was determined using a microbalance and recorded as: uptake\% = [(m\textsubscript{wet} − m\textsubscript{dry})/m\textsubscript{dry}] x 100, where m\textsubscript{dry} is the mass of the membrane dried in an oven at 60 °C for 2 h and then put to equilibrate in a desiccator before being weighted; m\textsubscript{wet} is the weight of the membrane after immersion in distilled water at room temperature for at least 48 h and quickly blotted dry using a paper tissue in order to eliminate most of the free surface liquid.

Results and discussion

XPS and SEM characterization

The C1s core level X-ray photoemission spectra of starting GO and sulfonated GO are shown in Fig. 3a and b. After deconvolution with mixed Gaussian–Lorentzian functions both spectra consist of five components. The first peak at 284.6 eV is attributed to C–C/C–H bonds, while the second at ~285.6–285.9 eV is assigned either to C–O bonds in the case of starting GO or to C–O and C–N/C–S bonds for the sulfonated GO. The following bands at higher binding energies (i.e. ~286.6–286.9 eV, ~287.9–288.1 eV and ~289.2–289.3 eV) are ascribed to C–O–C, C=O bonds and C(O)O groups in that order.

Comparison of the two C1s XPS spectra suggests that the successful sulfonation of GO as the contribution to the total C1s integrated intensity of the first two peaks is significantly enhanced upon sulfonation. Specifically and as expected, the incorporation of 3-amino-1-propanesulfonate leads to the insertion of additional C–C, C–H, C–N and C–S bonds and thus we observe a 26.4% contribution for C–C/H and 42.8% for C–O/C–N/C–S, in contrast to the relevant percentages, 14.3% and 24.4%, of the starting GO.

These findings are verified by the detection of nitrogen and sulphur in the case of sulfonated GO (Fig. 3c and d). Three dominant signals are revealed in the N1s binding energy window upon fitting with an admixture of Gaussian–Lorentzian functions. All three originate from 3-amino-1-propanesulfonate.
and are correlated with C–N and N–H bonds of protonated/deprotonated amines. Furthermore, a sulphur species is exposed at a high binding energy in the S2p region. The latter is associated with highly oxidized sulphur groups, i.e. sulfonates. The aforementioned data along with the fact that no nitrogen and sulphur were detected in the starting GO sample conclude that the XPS results clearly demonstrate successful GO sulfonation.

Fig. 4a and b show the cross-sectional SEM images of Nafion and Nafion–GO\textsubscript{SULF} membranes, respectively. GO\textsubscript{SULF} sheets appear to be homogeneously distributed throughout the membrane thickness. In our previous work, EDX analyses of the cross section of Nafion–GO\textsubscript{SULF} were added as supplementary information to confirm the homogeneous dispersion of nanomaterials inside the polymeric matrix. The GO\textsubscript{SULF} powder has been dispersed on a silicon substrate by drop-casting and SEM images at two different magnifications show both well dispersed GO sheets (dark regions) and GO aggregates on the Si substrate, as reported in Fig. 4c.

Removal of methylene blue
The degradation of MO and MB dye-molecules arising from contact with the GO\textsubscript{SULF} powder and the Nafion–GO\textsubscript{SULF} membrane has been investigated. The membrane sheets used in this experiment have an area of 1 cm\textsuperscript{2} and a thickness of about 60 μm. In order to compare the degradation results both through the powder and through the membrane, the mass...
weight of the GO\textsubscript{SULF} powder dispersed in 2 ml of dye solutions is exactly the same amount loaded into a 1 cm\textsuperscript{2} membrane, i.e. 70 \textmu g ml\textsuperscript{-1}. We have chosen MO and MB as model compounds for the photocatalytic study, since azo-dyes constitute one of the most diffuse water contaminants. In particular, these two dyes differ in the sign of their superficial charge (Fig. 2) allowing us to investigate the charge effect on their adsorption and degradation by the polymeric matrix.

MB is a cationic, thiazine dye, which absorbs light in a band centred at 664 nm (\(\pi-\pi^*\)) (monomer) with a shoulder at 610 nm corresponding to the MB dimer.\textsuperscript{16} The first absorbance peak was used to quantify the MB concentration reduction or degradation due to adsorption and photocatalysis. Fig. 5 shows the absorbance spectra of MB solution containing different concentrations of the GO\textsubscript{SULF} powder (10, 70 and 100 mg l\textsuperscript{-1}).

The presence of the GO\textsubscript{SULF} powder significantly reduces the MB concentration in the dark. This is likely related to the dye positive superficial charge that favours its adsorption on the GO\textsubscript{SULF} surface through electrostatic interactions with the negative charge of sulfonilic groups. The removal of MB increases with powder concentration and occurs immediately in the first few minutes, causing the formation of MB–GO\textsubscript{SULF} precipitates at the bottom of the beaker (see the inset photos of Fig. 5). The addition of a larger amount of GO\textsubscript{SULF} allows the removal of MB from water more effectively and rapidly. A 35% decrease of MB due to adsorption is observed for a GO\textsubscript{SULF} content of 10 mg l\textsuperscript{-1}. By increasing the GO\textsubscript{SULF} concentration in solution of one order of magnitude (100 mg l\textsuperscript{-1}), the residual MB reduces down to \(~1\%\) of the initial value. An important factor affecting the adsorption is the ratio between dye and GO\textsubscript{SULF} concentrations. In our case the MB concentration is 4.8 mg l\textsuperscript{-1} and is comparable with the lower GO\textsubscript{SULF} concentration considered here (10 mg l\textsuperscript{-1}). In Fig. 5b and c we report the removed amount (\%) of the dye as a function of GO\textsubscript{SULF} concentration or as a function of the MB/GO\textsubscript{SULF} concentration ratio. The trend in the graph in Fig. 5b is linear only in a limited region, where the two concentrations are comparable, then it seems to reach a plateau value; the plot reported in Fig. 5c suggests that the range \([\text{MB}]/[\text{GO\textsubscript{SULF}}]\) between 0.1 and 0.5 should be further studied in order to investigate the linearity of the trend.

The GO\textsubscript{SULF} powder was also tested as a photocatalyst under UV-blue light irradiation. We have tested the photostability of GO and GO\textsubscript{SULF} in water, without the presence of the dye, under the experimental irradiation conditions used in this work, and we observed no evident variation in the UV-Vis absorbance spectra. As explained in the Introduction, recently a photocatalytic activity has been observed for GO and this was shown to depend on the oxygen quantity bound on graphene layers.\textsuperscript{19} Clearly, it is expected that the functionalization of the graphene oxide surface by, for example, the grafting of amine derivatives (as in this case) can change its photocatalytic activity. In Fig. 6 we compare the residual concentration of MB as a function of dipping time with GO\textsubscript{SULF} and GO powders (70 mg l\textsuperscript{-1}).

After 30 minutes of adsorption in the dark, the solution is exposed to UV-blue light irradiation up to three hours. The time zero indicates the starting of UV-blue irradiation. The adsorption takes place immediately for both the powders and is more efficient for GO\textsubscript{SULF} than for GO, even though the loss of O groups due to sulfonilic functionalization (confirmed by XPS measurements) makes GO\textsubscript{SULF} less negative than GO, as shown by zeta-potential measurements. This can be explained by considering also the structural differences between the two kinds of GO observed by XRD analysis:\textsuperscript{26} the sulfonilic functionalization induces a larger distance between GO planes and, therefore, the accessibility of the active sites to the dye molecules in the two GO materials is different. The adsorption on GO layers occurs immediately with the formation of aggregates depending on the oxygen moieties on the graphene layers and MB–GO flocculates appear in the solution, as explained in ref. 22.

![Fig. 5](image-url) (a) UV-Vis absorbance spectra of MB solution after adding the GO\textsubscript{SULF} powder with different concentrations: 10 mg l\textsuperscript{-1} (green curve), 70 mg l\textsuperscript{-1} (blue curve) and 100 mg l\textsuperscript{-1} (red curve). The initial absorbance of the MB is also reported (black curve). The photo in the inset shows the beakers containing the MB solutions with GO\textsubscript{SULF} with increasing concentration (from left to the right). In (b) and (c) the removed MB (%) as a function of GO\textsubscript{SULF} concentration or as a function of the [MB]/[GO\textsubscript{SULF}] concentration ratio are reported, respectively. The lines in the plots are just a guide to the eye.
In contrast, when the epoxy functionalities on the graphene layers are substituted by organo-amines ending with acid groups, MB aggregation does not occur, but MB-GO\textsc{sulf} precipitates immediately at the bottom of the beaker.

MB–GO aggregation is clearly evidenced by the appearance of a peak at 577 nm,\textsuperscript{22} which instead is not observed for GO\textsc{sulf} (see Fig. 5). In addition, GO\textsc{sulf} shows a slightly further MB decrease when irradiation starts, after 30 minutes of absorption in the dark, while in GO the MB concentration reaches the minimum value after 10 min in the dark and then there is no further reduction either with time or during irradiation. In the absence of photocatalysts we have not observed any degradation of MB under UVA/blue irradiation for the same irradiation time. Since the main removal effect is due to adsorption that reduces drastically the initial MB concentration, the photocatalytic activity of the powders has not been further investigated under these experimental conditions in this paper.

However, the use of photocatalytic powders directly dispersed in solution for contaminant removal is not advisable for two main issues: (i) the removal of these powders from the water at the end of the process and (ii) the possibility to reuse them.

In this study, we tested the activity of the photocatalytic material incorporated inside a polymeric membrane, through the creation of a nanocomposite, which prevents its release. A comparison among the activities of the materials directly dispersed in water or embedded in a polymeric membrane is reported in the following discussion. In order to understand the role of the polymeric matrix in dye degradation, the results obtained for MB were compared with those obtained for the removal of an anionic dye, methyl orange (MO), as explained later on.

Fig. 7 compares the residual MB concentration of aqueous solutions in contact with Nafion and Nafion–GO\textsc{sulf} membranes, both in the dark and under UV-blue irradiation. Nafion itself can easily adsorb MB.\textsuperscript{24}

The ability of these membranes in the degradation of azo dyes depends mainly on the mutual interaction between the dye and the Nafion polymer.\textsuperscript{37} Nafion is a proton exchange membrane, thanks to the sulfonilic groups (SO\textsubscript{3}H) on the side chains, and responsible for its high proton conductivity. Cationic molecules, such as the MB dye, are strongly affected by electrostatic attraction from the SO\textsubscript{3}− groups in Nafion, and ion exchange in the hydrophilic sites of the membrane can be achieved. Consequently, the Nafion–GO\textsc{sulf} composite shows better performance than the filler-free Nafion membrane, both in the dark and under illumination, since the nano-dispersion of the filler inside the polymeric matrix increases the number of acid sites in the electrolyte (SO\textsubscript{3}−) for adsorption and also its water uptake and proton conductivity.\textsuperscript{26}

Fig. 8 reports the MB residual concentration after Nafion–GO\textsc{sulf} membranes of different sizes (0.25, 0.50 and 1.00 cm\textsuperscript{2}) were immersed in the solution in the dark as a function of time (until 5 hours).

The adsorption increases proportionally to the membrane area as a consequence of the variation in the number of active sites. The figure also reports the pictures of the cuvettes filled with MB solutions (from left to right: MB initial concentration and after immersing a 0.25 cm\textsuperscript{2}, a 0.5 cm\textsuperscript{2} and a 1 cm\textsuperscript{2} membrane respectively) and the corresponding membranes after the experiment. Clearly, for the same volume and MB concentration, a membrane with a larger area induces a more significant decolourisation effect.

Another aspect to be considered in this analysis is related to the capacity of a membrane to absorb water. In fact, water absorption on the polymer surface favours the interaction of electrons and holes with water molecules or hydroxyl ions, forming reactive species that are able to degrade organic compounds.\textsuperscript{38} As reported elsewhere,\textsuperscript{26,39} the Nafion–GO\textsc{sulf} composite membrane is much more hydrophilic with respect to filler-free Nafion, showing a doubled water uptake value, i.e. about 50 wt% and about 24 wt%, respectively. This so high
hydrophilicity of the composite can be addressed as the main cause of its better dye removal ability both as an adsorbent and under irradiation.

Comparing the results of Fig. 6 and 7, the degradation of MB is larger when GO_SULF is directly dispersed in dye solution with respect to the case of GO_SULF embedded in the polymeric matrix. MB adsorption by GO_SULF occurs immediately and it is larger in comparison with the adsorption capacity of Nafion–GO_SULF; it is also known that the adsorption of dyes on the surface of photocatalytic materials is needed in order to achieve dye degradation. Adsorption on GO_SULF nanoparticles is favoured with respect to the adsorption on Nafion nanocomposites since in the former case the active sites are immediately accessible to MB molecules while in the latter case the MB molecules have to diffuse inside the polymeric matrix. Nevertheless, the powder incorporation inside a polymeric matrix gives the advantage to overcome the problems related to the recovery of materials at the end of the process and nanocomposite Nafion membranes can be reused for several purification processes.

Removal of methyl orange
The role of the polymeric matrix in the degradation ability of organo-modified graphene oxide is discussed below comparing the results obtained for MB with the ones obtained for MO. As discussed before, in the latter case the interaction between the dye and the composite (both Nafion polymers and nano-additives) is not favoured due to electrostatic repulsion.

Fig. 9a and b report the absorbance spectra of MO solution obtained after dipping the Nafion membrane, the Nafion–GO_SULF membrane and the GO_SULF powder for one hour in the dark and under UVA/blue irradiation, respectively.

The UV/Vis absorbance spectrum of MO dissolved in water shows two maxima: the first at 270 nm and the second 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. The latter absorbance peak was used to quantify MO concentration reduction or degradation due to adsorption and photocatalysis; any variation of the 270 nm peak position is correlated with the formation of by-products as a consequence of azo-dye photodegradation. No degradation of MO under UVA/blue irradiation for 1 h has been observed in the absence of photocatalysts (membranes or powder).

MO adsorption, clearly, is quite small for all the materials, whereas irradiation induces a significant decrease of the dye, in particular in the case of Nafion–GO_SULF. As explained in our previous work, MO is an anionic dye molecule, so its adsorption on Nafion based composite membranes is hindered because of electrostatic repulsions between the negative molecular charge of the dye and the negative charge of sulfonilic groups in Nafion. The effect of MO adsorption on the GO_SULF powder under dark conditions consists of a small reduction of the initial dye concentration (6.5%) and this reduction rises to 15.6% in the presence of the polymer.

GO can work as a photocatalyst for water decomposition, and that different oxygen functionalities (in our case an amine-derivative functionality replaces oxygen atoms) can modify the valence band and conduction band positions.
Under UV/Vis light irradiation, the decrease of MO is larger with respect to the absorption in the dark (Fig. 9b). In the case of the Nafion membrane a small shift towards a larger wavelength is observed, due to the protonation of MO. In fact, a reduction of the pH of the solution is recorded due to the release of protons from the acid membrane to the solution when the dye is adsorbed. As we have seen, the best performance is achieved by using the Nafion–GO SULF composite membrane because with respect to the filler free Nafion membrane, the nano-additive increases the acidity and the water uptake capacity of the polymer film.

Under irradiation, the initial MO concentration (Fig. 9b) decreases and reaches the final value of 55% in the presence of Nafion–GO SULF and 82% for GO SULF. No toxic by-products, as for the known photocatalyst like TiO$_2$, are formed: the decrease of MO concentration by NafionGO SULF is due to the adsorption of MO molecules favoured by irradiation. Therefore, the use of the Nafion–GO SULF membrane for MO dye removal from water seems to be a more safe method than the use of photocatalyst powders directly dispersed in water.

As a consequence of the good result obtained after one hour under a UV-Vis lamp, the irradiation effect has been followed in time and the results are reported in the histogram of Fig. 10.

Nafion–GO SULF is able to remove about 70% of the initial MO concentration, after three hours. Comparing the degradation activity of the GO SULF powder with the relative nanocomposite, the reduction of MO concentration is much larger either in the dark or under irradiation when the filler is embedded in the Nafion matrix. As just said, the irradiation favours MO degradation and in both cases the polymer increases this degradation ability since it provides a larger number of active sites for MO absorption and this is also crucial for the photocatalytic process. In our previous work, a hypothesis of the possible photocatalytic mechanism for MO degradation by Nafion–GO SULF was presented.

In contrast, in the case of the cationic MB-dye, the powder itself works better than the composite membrane. This depends on the mutual interaction between the groups responsible for adsorption (SO$_3$H) and the dye. Nevertheless, the dispersion of the material in the polymeric matrix has many advantages as mentioned above, in particular it is possible to reuse the same material for successive purification processes. In our previous studies, we showed the possibility of reusing Nafion nanocomposites (with GO or TiO$_2$) after washing in water: after the first use, the membrane activity reduces but, then, it remains stable for the following cycles. The decreased efficiency after the first use could be due to the passivation of sulfonilic groups in the initial membrane preparation activated by rinsing in acidic media. Therefore, another regeneration process of the membranes was tested, by using 1% nitric acid in DI-water as described in the Experimental section. In Fig. 11 we report MO and MB concentration for two consecutive use of the same Nafion–GO SULF membranes as an adsorbent material in the dark (a) or as a photocatalytic material (b): a fresh membrane in the first process and the regenerated membrane in the second one.

In the two cycles the performance of the membrane remains exactly the same, confirming the possibility of regeneration and the reuse of these membranes without efficiency loss.

![Fig. 10](image1.png) 
*Fig. 10* Residual concentration of MO versus time of contact with Nafion (red bar), Nafion–GO SULF (blue bar) and GO SULF (green bar) under UV/blue light irradiation.

![Fig. 11](image2.png) 
*Fig. 11* MO and MB residual concentration versus two consecutive (a) adsorption processes for 3 hours in the dark or (b) photocatalytic processes for 3 hours, using the same pieces of Nafion–GO SULF membrane. Between the first and the second process (adsorption or photocatalysis) the membranes were regenerated, as described in the text.
Conclusion

Graphene oxide functionalized by the introduction of sulfonilic groups shows very good ability for the removal of dyes from water. In particular the material was tested directly dispersed in water or embedded in a polymeric matrix for the degradation of anionic and cationic dyes.

The presence of acid sulfonic groups on graphene oxide results in an increase of cationic methylene blue-dye adsorption due to electrostatic interactions and with the appearance of methylene blue-organo modified graphene oxide (GO-NULP) precipitates. A slight increase of degradation is observed after successive irradiation, while in graphene oxide, irradiation after adsorption does not induce any extra methylene blue decrease.

The idea to incorporate such nanomaterials into a polymeric matrix is attractive to avoid the dispersion of the powder in water and, in this work, the Nafion polymer was tested as a support matrix for photocatalysts. The results demonstrate that there is not any release of the powders in solution and that the nanocomposite membranes can be regenerated and reused.

In the case of a cationic dye, such as methylene blue, the role of the polymeric matrix is that of physical support for the nanomaterial avoiding its dispersion in the environment and allowing the reuse of the same amount of powder for successive purification processes. In contrast, in the case of an anionic dye, such as methyl orange, the role of Nafion is crucial for its purification processes. In contrast, in the case of an anionic water or embedded in a polymeric matrix for the degradation of anionic and cationic dyes.

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References