

The Effect of the Chemical Structure of Graphene Oxide on the Fenton and Photo-Fenton Reaction.

Florencia Podetti
*Instituto de Investigaciones en
Tecnologías Energéticas y
Materiales Avanzados-
(CONICET)*
*Departamento de Química
(UNRC)*
Río Cuarto, Argentina
fpodetti@exa.unrc.edu.ar

Julieta L.Sacchetto
*Instituto para el Desarrollo
Agroindustrial y de la Salud
(IDAS)- (CONICET).*
*Departamento de Química
(UNRC)*
Río Cuarto, Argentina
jsacchetto@exa.unrc.edu.ar

Walter A.Massad
*Instituto para el Desarrollo
Agroindustrial y de la Salud
(IDAS)- (CONICET).*
*Departamento de Química
(UNRC)*
Río Cuarto, Argentina
wmassad@exa.unrc.edu.ar

Gustavo M. Morales
*Instituto de Investigaciones en
Tecnologías Energéticas. y
Materiales Avanzados –
(CONICET)*
*Departamento de Química
(UNRC)*
Río Cuarto, Argentina
gmorales@exa.unrc.edu.ar

Abstract—The efficiency of Fenton and photo-Fenton reaction for the degradation of methyl orange (MO) is strongly dependent on the structure of graphenic material used as heterogeneous catalyst. The photocatalytic activities of a graphene oxide (GO) prepared by a modified Hummer method and a base washed graphene oxide (bwGO) were compared through UV spectroscopy. GO showed the highest performance, degrading MO completely in only 30 minutes under an UV irradiation.

Keywords— *Graphene oxide, Photocatalysis, Heterogeneous Fenton reaction, Methyl orange degradation.*

I. INTRODUCTION

Graphene is a carbon material that has gained great attention in recent years due to its excellent electronic and mechanical properties. However, most of the possible applications of graphene are hampered by its low dispersibility in water and polar organic solvents. On possibility to overcome this limitation and produce massive amounts of materials required in energy storage, energy conversion and environmental applications is the use of graphene oxide (GO).

The GO is a graphene with defects on the sp^2 structure which contain various oxygenated functional groups. Those groups are mainly hydroxyl and epoxy groups in the plane basal and carboxyl, carbonyl, phenol, lactone, and quinone at the edges (leaf edges and basal holes). The GO can be synthesized in large quantities and presents important characteristics for applications. Those includes, excellent dispersibility in water, large surface area, and tune the physicochemical properties by chemical modification. The synthesis of GO in general involve the oxidation and further exfoliation of graphite. The methods used to the synthesis and purification determine the carbon to oxygen (C/O) relationship, which determine its final properties.

Rourke et al. showed that the as-made GO from Hummers' method is composed of low functionalized graphene sheets decorated by high functionalized oxidation debris [1]. According with this model, these physi-absorbed polyaromatic

compounds can be removed by a simple washing with an aqueous solution of NaOH to give the base-washed GO (bwGO). The oxygen content of bwGO is lower than its precursor GO, changing its hydrophilic nature to slightly hydrophobic, and increasing the electrical conductivity. The chemical structure of GO and its derivative bwGO are controversial, more recently has been claimed than the one component (dynamic structural model) seems to be more realistic than the Rourke's two component model. Dimiev and Polson assigned the final chemical structure of bwGO to chemical reactions of GO in basic media under heating, and the oxidation debris as products of this reactions [2]. Whatever the chemical structure of GO and bwGO, they clearly differ considerably from each other.

According to the broad properties of graphene derivative materials, they have been also used as supports in environmental photocatalysis [3]. The Advanced oxidation processes (AOPs) have emerged as promising alternative strategies for water treatment, especially for persistent and non-biodegradable pollutants. One of the most studied is the process based on the Fenton reaction and its variants, which present advantages such as high degradation efficiency, inexpensive materials and general applicability. To solve the disadvantages of the homogeneous Fenton process, more attention has been paid to the development of heterogeneous or semi-heterogeneous catalysts. In recent years, the application of heterogeneous or semi-heterogeneous catalysts for photo-Fenton degradation of aquatic pollutants based on GOs has been reported [4][5].

GO has been reported to exhibit photosensitizing activity and also participates efficiently in the catalytic decomposition of H_2O_2 . These capabilities could increase the production of $OH\cdot$ radicals in conjunction with the Fenton reaction. [6][7].

The GOs has been used as active or support material in various photocatalytic reaction [9]. So far, however, little or no attention at all was paid to the effects of the chemical structure to the reaction itself, stability of the carbonaceous material,

degradation products, among other aspects. Here is analyzed the effect of the addition of two graphene oxides, GO and bwGO with different structural characteristics, for the degradation of the methyl orange (MO) model compound by Fenton and photo-Fenton reaction.

II. EXPERIMENTAL

A. Synthesis of GO and bwGO

Graphite oxide was prepared by a modified Hummer method [10]. The graphite oxide was then exfoliated in water by successive centrifugation steps at 1500 rpm to obtain GO. The GO was purified using water by consecutive centrifugation steps until the pH of the supernatant liquid was constant. The aqueous dispersion of GO was stored at 5 °C, and protected from the light until used.

The bwGO was synthesized by a hydrothermal reaction at atmospheric pressure. 20 mg of GO were dispersed in 45 mL of a NaOH 0.1 M and the mixture heated under reflux for 24 h. The resulting product was purified by successive steps of centrifugation and resuspension using fresh water and stored at 5°C as an aqueous dispersion.

B. Adsorption studies

The adsorption study was performed following the degradation of MO by absorption spectroscopy at different times of reaction. Then, the system consisting of dye and catalyst was subjected to centrifugation (12000 rpm) for one minute to remove GOs sheets from the medium. Changes in the pH of the MO solution (initial pH=2.85) were measured over the time of adsorption process, before and after the addition of the catalysts.

C. Heterogeneous Fenton and photo-Fenton degradation of Methyl Orange (MO)

The photocatalytic activities of GO and bwGO were evaluated by photodegradation of MO in the presence of the Fenton's reagent in aqueous solution. The photo-Fenton experiences were performed using an ultraviolet (UV) lamp (λ :364 nm, 151 $\mu\text{W}/\text{cm}^2$) located 3.5 cm above the solution as the UV irradiation source. Before illumination, all reagents except ferrous solution was magnetically stirred in the dark for 20 min to disperse the carbonaceous material and allow to reach the possible adsorption/desorption equilibrium. The ferrous sulfate in acid aqueous solution was added to the reaction mixture just before the start of the irradiation process. The variation of the pH generated by the Fenton and photo-Fenton reaction was monitored over the time.

For Fenton and photo-Fenton reaction the concentration used was for H_2O_2 1×10^{-3} M, FeSO_4 1×10^{-5} M and HClO_4 1×10^{-3} M. The dye solution presented an absorbance 0.52. The stock solutions of GO and bwGO were made from the respective lyophilized oxides, dispersed in water. The concentrations of the oxides used were 2.5 $\mu\text{g}/\text{ml}$ for GO and 1 $\mu\text{g}/\text{ml}$ for bwGO, at this concentration both oxides have the same absorbance.

The photocatalytic experiments were carried out at room temperature in a quartz cell (3ml), with continuous stirring. The samples were collected at 30 min of irradiation and the absorbance of the MO solution was analyzed using a UV-Vis spectrophotometer at 503 nm.

D. Surface analysis of GO and bwGO after Fenton and photo-Fenton reaction

The morphology and surface characterization of the samples were analyzed using an atomic force microscope (AFM, Agilent Technologies, SPM model 5500) operated in acoustic AC mode. Imaging was carried out in air at room temperature using AFM probes (Micromasch, HQ:XSC11/A1 BS) with a resonance frequency of 155 KHz and a force constant for the cantilever of 7 N/m. The images were recorded as 512×512 pixel using the software PicoView and the analysis performed using the Gwyddion v2.39.

The samples were deposited from dispersions in water on a fresh cleaved surface of V4 muscovite mica (Structure Probe, Inc. West Chester, West Chester, Pennsylvania, USA). They were dried at room temperature in a desiccator containing silica as desiccant material.

III. RESULTS AND DISCUSSION

A. Spectroscopy Characterization of GO and bwGO

The extinction spectra of graphene derivate materials are determined by electronic transitions in the UV with its tail extending into the visible. The spectrum of the pristine GO suspension in Fig. 1 shows a broad extinction band with a maximum at 228 nm and a shoulder at 300 attributed to the π - π^* plasmon and n - π^* plasmon respectively [11]. After chemical treatment in basic medium, the spectrum of aqueous dispersions formed by the purified carbonaceous product (called bwGO) shows a bathochromic band shift to approximately 264 nm and an increase in extinction for the full range of wavelengths. Both effects have been associated in the literature with the partial restoration of the electronic conjugation within the carbon lattice combined with removal of oxygen-containing groups [12]. From a structural point of view, has been suggested that the chemical treatment with base removes part of the oxygenated functional groups of GO. [1][13]

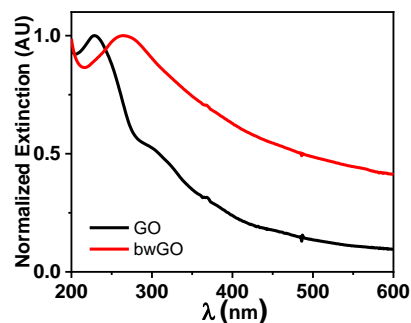


Fig. 1. Normalized extinction spectra of the aqueous dispersion of GO and bwGO.

The Fig. 2 shows typical FT-IR spectra of GO before and after treatment in basic media. The FT-IR features of bwGO changes significantly, the bands assigned to O-H and C=O stretching almost disappear. The band at 1630 cm^{-1} is shifted to 1590 cm^{-1} . The presence of a peak in the 1570 - 1580 cm^{-1} region is attributed mainly to the aromatic C=C vibrations of graphitic domain (aromatic regions). The low intensity of absorptions associated to hydroxyl and others groups is consistent with the increase in

the hydrophobicity observed in bwGO. It seems that the treatment in base change the chemical structure of GO, becoming in a material with lower content of oxygenated functional groups and a more graphitic character. Those observations are in agreement with the UV-vis absorption behavior previously discussed.

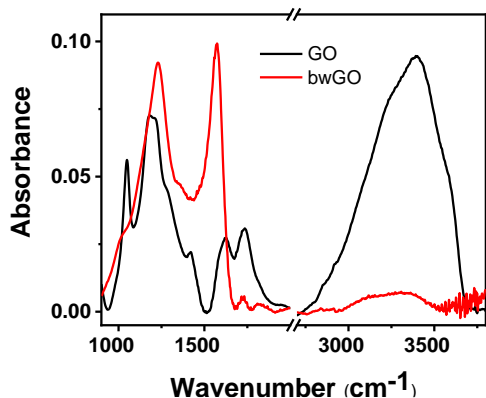


Fig. 2. Infrared spectra of aqueous GO and bwGO suspensions.

B. Study of the interaction between MO and oxides

The possible interaction between GOs and MO was studied by UV-vis spectroscopy in acid medium (pH 3 for bwGO and 2.85 for GO) of the colloidal suspension with MO. As observed in Fig. 3, the spectrum shows a bathochromic shift in the characteristic MO absorption band when bwGO is present in the dispersion. The dye interactions or adsorption on the surface of the bwGO could explain this behavior. In contrast, no spectroscopic changes were observed when GO was added to the MO solution.

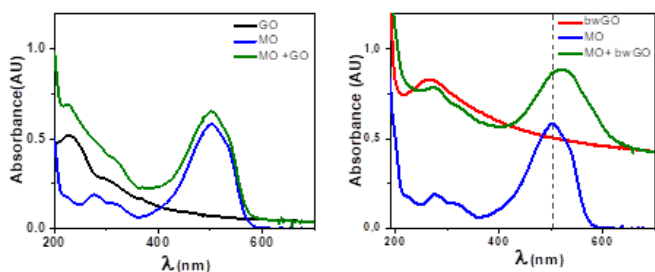


Fig. 3. UV-Vis absorption spectrum of MO, bwGO, GO, aqueous solutions of MO + GO and MO + bwGO. pH = 3 for bwGO and 2.85 for GO

When comparing the initial spectrum of MO with that of the addition of catalysts, an appreciable change in the absorption spectrum of the dye solution with bwGO is observed. A decrease in the intensity of the absorption peaks is observed at ~ 275 nm and ~ 500 nm with the addition of the oxide bwGO, suggesting that the dye is highly adsorbed by the surface. However, no significant changes in the spectrum of MO were detected when GO is used as the catalyst, which indicates that the dye does not interact superficially with this oxide. Moreover, there were no significant changes in the pH of the MO solution after the addition of both oxides.

The UV-Vis absorption spectrum of MO azo dye has two characteristic peaks. The peaks at ~ 275 nm and ~ 500 nm are

assigned to the π - π^* aromatic transition and the substituted azo group ($\text{N}=\text{N}$) respectively. The bwGO oxide could be considered as a non-polar and hydrophobic surface, providing a delocalized π electron system, with a high affinity for aromatic structures. Therefore, the adsorption of methyl orange on the bwGO is possible to be achieved through π - π interactions between graphitic domains and the two benzene rings connected to each other by an azo-bridge in methyl orange [14].

In comparison, GO has a large number of oxygen-containing functional groups on the surface, some of them with capacity to form hydrogen bonds. However, UV-Vis data shows that MO is not adsorbed on the GO surface and may be due to a repulsion between the charges of methyl orange and the surface of the graphene oxide [15].

C. MO degradation by Fenton and photo-Fenton reaction

In order to study the effect of the chemical structure of the GOs on the Fenton and photo-Fenton reaction, the MO degradation kinetics was studied and analyzed by absorption spectroscopy, with and without the addition of GOs.

After the addition of the Fenton reagent at a pH close to 3, a decrease in the intensity of the absorption band at 504 nm is observed after approximately 100 min, suggesting a degradation of the MO in the solution. Furthermore, it is noted that in presence of GO, the discoloration is faster and was completed in about 60 min.

The MO discoloration by the Fenton reaction determined that the addition of GO to the reaction mixture catalyzed the degradation of the dye with respect to the reaction without oxide. On the other hand, a protective effect of the dye is observed with the addition of bwGO to the solution, since the registered absorbance change was less than that of the MO reaction without GO (Fig. 4.). According to these results, it could be inferred that bwGO reacts with the radical $\text{OH}\cdot$ faster than MO, results obtained by AFM support this hypothesis. The percentage of MO degradation obtained with the classic Fenton reaction at 40 minutes, without the addition of oxides, was 48.6%, while with the addition of GO at the same time was 88.5%. It is clear that the reaction was catalyzed by GO, exhibiting an increase in the percentage of degradation. However, in the case of the addition of bwGO, the degradation rate and its percentage decreased, obtaining only 14.8% after 40 min of reaction. The Fig. 5. shows that the degradation of MO by the photo-Fenton reaction. As expected, the results showed a higher efficiency for the dye degradation. These results are due to the larger reaction speed in the photo-Fenton process as a result of the application of ultraviolet irradiation. In photo-Fenton processes, Fe^{2+} in presence of an excess of H_2O_2 is rapidly converted to Fe^{3+} producing $\text{OH}\cdot$ radicals. The Fe^{3+} ion is reduced to Fe^{2+} , mainly by UV-Vis irradiation (light up to 380 nm). Consequently, the generation of reactive $\text{OH}\cdot$ during the photo-Fenton reaction increase the OM degradation efficiency under all conditions studied. For the photo-Fenton reaction, the determined degradation percentage was 81.5% after 30 minutes of reaction. Using the same conditions, the addition of GO to the reaction mixture, rise the degradation rate to 98.3% at the same time. Following the same tendency observed for the Fenton reaction, the percentage of MO degradation observed in presence of

bwGO was 28.8%. It should be pointed out that, the GO in the presence of light acts as a sensitizer, and ROS generator [6]. The

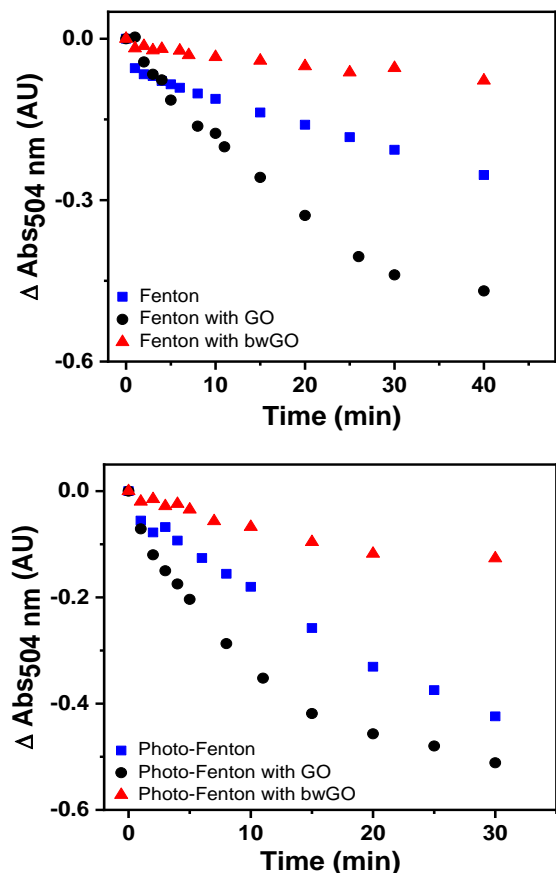


Fig. 4. Change in absorbance at 504 nm vs reaction time. Abs_{t0} MO= 0.528, Fe²⁺ = 1x10⁻⁵ M, H₂O₂ = 1x10⁻³ M, HClO₄ = 1x10⁻³ M, [bwGO]= 80 μl / 3ml solution, [GO]= 29ul / 3ml solution, pH= 3. Irradiation with lamp at 364 nm, light flux (290-390 nm) = 151 μW/cm²

additional reactive species generated by GO can explain the increased efficiency in MO degradation observed for this material.

The Table I compares the percentages of MO degradation by the Fenton and photo-Fenton reaction in the presence and absence of the oxides studied.

TABLE I.

| | Without Oxide | GO | bwGO |
|--------------------------|------------------|-------|-------|
| Fenton (40 min) | 48.6% | 88.5% | 14.8% |
| Photo-Fenton (30 min) | 81.5% | 98.3% | 28.8% |

A. Atomic force microscopy

The surface of GOs materials after reaction was monitored by atomic force microscopy (AFM) imaging. Fig. 5 shows the topography AFM images of GO sheets in contact with Fenton reagent before reaction (a), after Fenton reaction (b) and after photo-Fenton reaction under UV irradiation for 30 minutes (c). The images were acquired through deposition of the reaction dispersions on freshly cleaved mica substrates by a drop-casting method. The presence of irregular edges over GO sheet before reaction can be attributed to salt form the Fenton reagents deposited on the surface. After Fenton reaction the integrity of the GO sheets is preserved, but pores are observed on the basal plane. However, the images of GO after photo-Fenton reaction shows the damage of the sheets. These changes are associated to the production of OH• radical which is higher in photo-Fenton reaction. Fig. 5d and 5e show AFM images of bwGO sheets before and after photo-Fenton reaction. In both images, can be appreciated the presence of holes and irregular edges, which has been associated to reactions with the hydroxyl ion during the base treatment. Whereas a complete rupture of structure, visualized as a diminution of the sheet size, is observed after reaction as depicted in Fig. 5e. It seems that the bwGO is more easily attacked by reactive species than the surface of GO. This might explain in part the apparent protection of bwGO against oxidative reactions of OM under Fenton and photo-Fenton conditions.

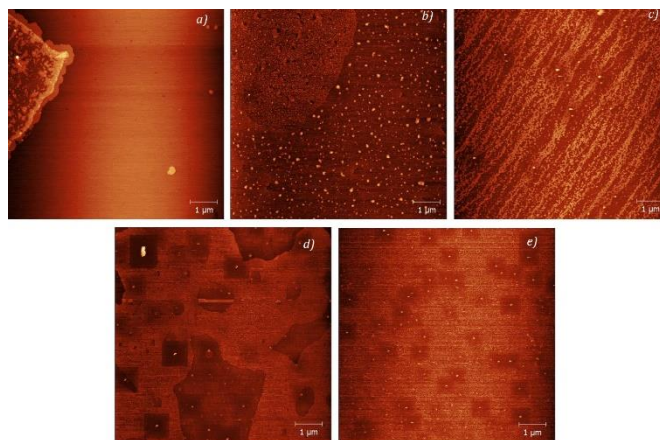


Fig. 5. Topography AFM images. (a) GO sheets in contact with Fenton reagent before reaction. (b) GO sheets after Fenton reaction. (c) GO sheets after photo-Fenton reaction under UV irradiation for 30 minutes. (d) bwGO sheets before photo-Fenton reaction. (e) bwGO sheets after photo-Fenton reaction under UV irradiation for 30 minutes.

I. CONCLUSIONS

In summary, two graphene materials with different oxidation degree were synthesized and characterized. We have demonstrated that GO enhance the photocatalytic performance with a 98.3% of methyl orange degradation in 30 min. The lowest decolorizing efficiency with bwGO can be attributed to the highest C/O ratio on the surface. It allows π-π interactions with the colorant allowing a protect effect.

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