Nitrogen-doped graphene-based materials for advanced oxidation processes

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Abstract

Nitrogen-doped graphene-based materials were prepared by the modified Hummers method using natural graphite as primary precursor, followed by chemical and thermal reduction processes, and finally ball milled with urea or melamine. The graphene-based materials were characterized at different stages of their synthesis by different techniques (including temperature programmed desorption and X-ray photoelectron spectroscopy) and then tested as metal-free catalysts in the degradation of oxalic acid and phenol by two different oxidation processes: catalytic wet air oxidation (temperature between 413 and 433 K, and 7 bar of O₂) and catalytic ozonation (room temperature and atmospheric pressure). The melamine treated sample was always found to be more active due to the presence of nitrogen groups and adequate surface area available.

Keywords: Metal-free catalysts; graphene-based materials; nitrogen-doping; liquid-phase oxidation; water treatment.

1. Introduction

The abatement of environmental pollution and especially the availability of clean water are among the most significant concerns of society. Advanced oxidation processes

(AOPs), based on the production and use of strongly reactive radicals, can decisively contribute to water purification. In particular, wet air oxidation (WAO) and ozonation are well-established AOPs that have been applied worldwide to treat highly polluted industrial wastewaters and sludge [1-3]. In these processes, oxygen and ozone are respectively used to generate active species capable of oxidizing the organic compounds, preferentially into carbon dioxide and water, or alternatively into easily biodegradable by-products [4].

Although metal-based catalysts have been playing a major role to enhance the efficiency of AOPs [5, 6], they often suffer from some disadvantages, such as high cost and detrimental environmental effects due to the catalyst residues. Owing to their environmental compatibility and unique surface properties, carbon nanomaterials have recently demonstrated to be promising metal-free alternatives in catalytic wet air oxidation (CWAO) and catalytic ozonation. In addition, oxygen and nitrogen functionalities can play the role of active sites on carbon materials, the most effective for environmental catalysis being the basic sites [7]. In this sense, different types of carbon materials with nitrogen (including carbon xerogels, carbon nanotubes, and carbon foams and fibres) have been tested in CWAO [4, 8-11] and in ozonation process [4, 8, 12, 13].

Since its isolation and characterization in 2004 [14], graphene and derivatives have emerged as materials of great interest due to their remarkable mechanical, thermal, optical and electrical properties [15, 16]. In particular, graphene oxide (GO) has attracted huge interest as a graphene precursor because oxygen functional groups attached on the GO surface can be partly removed, resulting in the partial restoration of the conjugated structure [17, 18].

In the present work, to the best of our knowledge, nitrogen-doped graphene-based materials were tested as metal-free catalysts in AOPs for the first time, namely in CWAO and ozonation. The materials were characterized at different stages of their synthesis by several techniques, including temperature programmed desorption and X-ray photoelectron spectroscopy, and used as catalysts for the mineralization of oxalic acid and phenol in aqueous solutions. Oxalic acid is a refractory short chain carboxylic acid appearing as end-product in other advanced oxidation processes, while phenol is a more complex molecule extensively studied in the literature (usually used as probe species to evaluate the process efficiency) which is also an organic pollutant commonly found in industrial effluents.

2. Experimental

2.1. Materials

2.1.1. Synthesis of graphene oxide

GO was synthesized from natural graphite (20 μm , Sigma-Aldrich), by a modified Hummers method [19, 20]. Briefly, 50 mL of concentrated sulphuric acid was slowly added, under appropriate cooling and stirring conditions, to a flask containing 2 g of graphite. Then, 6 g of potassium permanganate were slowly added to the mixture and the suspension kept at 35 $^{\circ}\text{C}$ for 2 h under stirring. The solution was diluted in 350 mL of distilled water. Afterwards, H_2O_2 (30% w/v) was added in order to reduce residual permanganate to soluble manganese ions. The oxidized material was purified with an hydrochloric acid solution (10 wt.%) and the suspension was then filtered, washed several times with distilled water until the neutrality of the rinsing waters was reached, and dried at 60 $^{\circ}\text{C}$ for 24 h to obtain graphite oxide. The resulting material was

dispersed in a given volume of water and sonicated in an ultrasound bath (ultrasonic processor UP400S, 24 kHz) for 1 h, GO being obtained in this way

2.1.2. Incorporation of N-functionalities

The GO material was subjected to mechanical treatments in a ball milling Retsch M200 equipment. The conditions used were selected from a previous work, where the preparation of N-doped carbons by ball milling was proposed and optimized [21]. 0.6 g of GO was mixed with 0.26 g of N using urea or melamine as nitrogen precursor and the mixture was ball-milled during 4 h at a constant frequency of 15 vibrations/s. Then, the resulting materials were subjected to a thermal treatment under N₂ flow (100 cm³ min⁻¹) until 600 °C (at 2 °C min⁻¹) and kept at the maximum temperature during 1 h. Partial reduction of GO occurs during the thermal treatment. The reduced GO materials are denoted as rGO-U (prepared with urea) or rGO-M (prepared with melamine). Reduced GO was also prepared by using the same procedure (mechanical and thermal treatment), but without addition of a nitrogen source (rGO).

2.2. Catalyst characterization

The textural characterization of the materials was based on the N₂ adsorption isotherms determined at -196 °C with a Quantachrome Nova 4200e apparatus. The nature and amounts of the surface oxygenated groups were determined by temperature programmed desorption (TPD), carried out in an Altamira Instruments AMI-300 apparatus connected to a Dycor Dymaxion Mass Spectrometer. The pH at the point of zero-charge (pH_{PZC}) was determined by using a drift method described elsewhere [22, 23]. Elemental analysis was performed on a Carlo Erba instrument, model EA 1108 and X-ray photoelectron spectroscopy (XPS) performed in a Kratos AXIS Ultra HSA using

a monochromatic Al K α X-ray source (1486.7 eV), operating at 15 kV (90 W), in FAT mode (Fixed Analyser Transmission), with a pass energy of 40 eV for regions of interest and 80 eV for survey.

2.3 Experimental procedure

Catalytic wet air oxidation (CWAO) experiments with phenol and oxalic acid aqueous solutions were performed in a 160 mL 316-SS high pressure batch reactor housing a glass liner (Parr Instruments, USA Mod. 4564). 100 mg of the catalyst were added to 75 mL of the organic pollutant solution and placed into the reactor. The reactor was flushed with pure nitrogen until complete removal of oxygen, pressurized with 5 bar of nitrogen and then pre-heated up to the desired temperature under continuous stirring at 500 rpm in order to ensure proper mass transfer of oxygen in the liquid phase [24, 25]. When the desired temperature was reached, pure air was injected to obtain a total pressure of 40 bar inside the reactor (corresponding to 7 bar of oxygen partial pressure), this being considered time zero for the reaction. CWAO of oxalic acid was performed at 413 K (1000 mg L⁻¹ of oxalic acid as starting solution) and phenol experiments at 433 K (75 mg L⁻¹ of phenol as starting solution) [26]. In addition, non-catalytic wet air oxidation (WAO) runs were carried out with air in the absence of catalyst and adsorption experiments were also performed in the autoclave under similar experimental conditions but replacing air by pure nitrogen (40 bar of total pressure). The carbon materials were recovered at the end of each run for further characterization.

Ozonation experiments with the same pollutants (oxalic acid and phenol) were performed at room temperature and pressure in a stirred semi-batch tank reactor. Ozone generated from pure oxygen, using a BMT 802X ozone generator, was bubbled into the bulk of the solution using a diffuser (total flow rate = 150 cm³ min⁻¹; ozone

concentration = 50 g m^{-3}). Ozone in the gas phase was monitored using a BMT 964 ozone analyser. In each ozonation experiment the reactor was filled with 700 mL of a solution containing 90 mg L^{-1} of oxalic acid or 75 mg L^{-1} of phenol, at natural pH. 100 mg of catalysts were introduced into the reactor before starting gas flow admission and kept in suspension by stirring at 200 rpm. Single ozonation experiments (without catalyst) were also performed.

2.4 Analytical techniques

Samples periodically withdrawn from the reactors were analysed by high performance liquid chromatography (HPLC) with a Hitachi Elite LaChrom system equipped with a Diode Array Detector (L - 2450). A Bio-Rad Aminex HPX-87H column ($300 \text{ mm} \times 7.8 \text{ mm}$) and a H_2SO_4 solution (4 mM) at a flow rate of 0.6 mL min^{-1} (as mobile phase) were used for the determination of oxalic acid concentration in the CWAO experiments. The quantification of oxalic acid was performed at $\lambda = 210 \text{ nm}$. In the ozonation experiments, the concentration of oxalic acid in solution was determined with an Alltech OA-1000 chromatography column using an isocratic 5 mM H_2SO_4 mobile phase at 0.5 mL min^{-1} . Quantification of the organic acid was made at 200 nm. In phenol oxidation experiments, the samples were analysed in a Purospher Star RP-18 endcapped column ($250 \text{ mm} \times 4.6 \text{ mm}$, $5 \mu\text{m}$ particles) working at room temperature at a fixed flow rate of 1 mL min^{-1} and phenol concentration determined at $\lambda = 270 \text{ nm}$. In the CWAO experiments, the mobile phase was a mixture of water and methanol 40/60 (v/v). Samples withdrawn from ozonation experiments were analysed using a different method: at first, the column was equilibrated with an A:B (70:30) mixture of ultra-pure water (A) and methanol (B), followed by a linear gradient run to A:B (30:70) in 30 min,

and finally with isocratic elution during 2 min. The total organic carbon (TOC) was also determined using a Shimadzu TOC-5000A analyser.

3. Results and discussion

3.1. Characterization of graphene-based materials

The ball milling and thermal (600 °C) treatments applied to the GO material promoted several modifications in its textural and chemical properties, as can be seen in Table 1. Regarding the textural properties, the apparent surface area (S_{BET}) increased when GO was subjected to the mechanical and thermal treatments without addition of a nitrogen source, i.e. from 23 m² g⁻¹ (GO) to 263 m² g⁻¹ (rGO). This effect could be due to the thermal treatment until 600 °C since an increase of GO exfoliation with partial reduction to rGO occurs during this step, in addition to the mechanical treatment that can also exfoliate GO and cut the graphene sheets during milling. Nevertheless, this value was significantly lower than the theoretical surface area of 2600 m² g⁻¹ for individual isolated graphene sheets [27] mostly due to the partial exfoliation of the graphene sheets, the defective graphene structure formed during the synthesis of GO, and the O-functional groups remaining on rGO.

The N-doping of GO using melamine and urea resulted in a decrease of the surface area in comparison with the rGO material (102, 47 and 263 m² g⁻¹, for rGO-M, rGO-U and rGO, respectively, Table 1), which suggests that the addition of the N-precursor contributes to a larger aggregation of the graphene sheets, more pronounced when urea is used. Nevertheless, these surface areas are higher than that obtained for the original GO sample (23 m² g⁻¹). This effect could be due to the cutting of the graphene sheets that increase the surface area during the ball milling treatment and also due to nitrogen incorporation into the graphene layers. In addition, some agglomeration of the graphene

173 sheets can occur due to the vibration frequency and duration of the milling used in this
174 work, which are higher than the values normally reported for graphene exfoliation [28].

175 **TABLE 1**

176 The N₂ adsorption-desorption isotherms for rGO, rGO-U and rGO-M materials
177 (Figure 1) can be classified as type II, accordingly to IUPAC [29]. In spite of the similar
178 shape of the isotherms, the amounts of N₂ adsorbed at the relative pressure $p/p_0 = 0.95$
179 are much lower in the case of N-doped samples (rGO-U and rGO-M); these differences
180 may reflect different degrees of agglomeration of the graphene sheets, a result of the
181 different nitrogen precursors used.

182 **FIGURE 1**

183 Figures 2a and 2b represent the TPD profiles corresponding to the groups evolved as
184 CO₂ and CO, respectively, from the surface of GO, rGO, rGO-U and rGO-M. The total
185 amounts of CO₂ and CO released, the oxygen contents, as well as the pH_{PZC} for GO,
186 rGO and N-doped materials are presented in Table 1. The TPD analysis of the graphene-
187 based materials after the thermal treatment reveals a decrease of the oxygen content in
188 the case of rGO (5.6 wt.%) compared to GO (23.6 wt.%), which is related to the release
189 of the oxygen-surface groups during the heating until 600 °C, mainly epoxy and
190 hydroxyl groups. After N-doping (both with melamine or urea), a decrease of the
191 oxygen content was also observed, indicating the loss of some oxygenated groups by
192 the incorporation of nitrogen functional groups on the GO material (3.5 and 3.4 wt.%
193 for rGO-M and rGO-U, respectively).

194 For the rGO and N-doped graphene samples (Figure 2), there is not a different
195 contribution of the type of groups released as CO and/or CO₂ during TPD. In fact most
196 of the surface groups of the samples decomposed as CO (the amount of CO released
197 was always significantly higher than that of CO₂, Table 1), namely as phenol and

carbonyl/quinone groups. The presence of these particular groups is linked with the thermal treatment applied; i.e. carbonyl/quinone groups were not removed from the surface since their release occurs at temperatures above 873 K [30]. On the other hand, the thermal treatments should have removed the most labile oxygen functional groups, namely epoxy and hydroxyl groups located on the basal planes of GO [18], and carboxylic acid and anhydride groups, since they are released at temperatures below 873 K. Phenols and lactones were partially removed since they are decomposed in the range of 773 to 973 K.

FIGURE 2

The absence (or low content) of acidic surface groups (carboxylic acids, phenol, anhydrides) contributes to the neutral/basic nature of the surface of the graphene-based materials with the samples presenting pH_{PZC} values higher than 6. The incorporation of the surface nitrogen groups (rGO-M and rGO-U samples) contributes with additional electrons, increasing the surface basicity [31] (higher values of pH_{pzc}). Significant amounts of N (Table 1) were introduced on the surface of the graphene-based materials after the milling treatments (determined by XPS analysis).

The sample milled with melamine presents the largest amount of N (9.3% and 7.5% for rGO-M and rGO-U, respectively). The XPS N1s spectra of the rGO-M and rGO-U samples were decomposed into three peaks (Figures 3a and 3b, respectively). The first peak identified at around 398 eV, designated as N6, is attributed to pyridinic-N. The second peak, situated ca. 400.0 eV, is ascribed to pyrrolic-N, and will be referred as N5. The next peak identified at around 400.9 eV is attributed to quaternary nitrogen (NQ) [32, 33]. However, similar proportions of the different types of nitrogen species were observed in these samples. For instance, the ratio between pyrrolic and pyridinic groups

(N5/N6 ratio) is 0.6 in rGO-M and 0.5 rGO-U. N-quaternary species are also present with similar proportions, corresponding to 17 % in rGO-M and 25 % in rGO-U.

FIGURE 3

3.2. Catalytic tests

The graphene-based materials doped and undoped with nitrogen groups were tested as catalysts in the oxidation of oxalic acid and phenol (used as model pollutants) by CWAO and catalytic ozonation. The catalytic activity of the GO sample was not evaluated in the processes due to its strong acidic character ($\text{pH}_{\text{pzc}} < 3$, see Table 1), which is well known to have a negative effect on the catalytic performance of carbon materials in the oxidation processes in study [10, 22, 26].

3.2.1 Catalytic wet air oxidation

Figure 4 shows the normalized concentrations of both compounds during the reaction time. Under the operating conditions, both compounds are quite stable and poorly oxidized in the absence of catalysts (WAO curves). However, the conversion of both model pollutants significantly increased by using the graphene-based materials.

FIGURE 4

Figure 4.a shows that total removal of oxalic acid can be achieved in less than 60 min using the graphene-based materials with no by-products being detected by HPLC analysis. Oxalic acid was faster removed from the solution using samples rGO and rGO-M than using the rGO-U sample. However, adsorption contributes to the decay of oxalic acid concentration. Although the adsorption of oxalic acid over the N-doped samples (rGO-M and rGO-U) was lower than 15 % after 60 min, about 30 % of oxalic acid was adsorbed in the case of the rGO sample (reaching about 45 % after 120 min). Therefore, the fast removal of the compound under catalytic conditions using the rGO

sample has a significant contribution from adsorption, which cannot be negligible. Besides that, rGO leads to total oxalic acid removal, exhibiting a good catalytic activity for the reaction, probably due to the presence of the π electron system of the reduced graphene oxide [17], which contributes to the basicity of the carbon surface [7]. Regarding the rGO-M sample, where the adsorption contribution is minor, it seems that the introduction of the nitrogen surface groups leads to an increase of the catalytic performance of the graphene-based material. The worst performance was obtained with the rGO-U sample, more time being required to oxidize oxalic acid completely. This can be due to the lower amount of nitrogen and to the low surface area of the material. In fact, this sample only has $47 \text{ m}^2 \text{ g}^{-1}$ of specific surface area due to the compaction of the layers during the ball milling treatment with urea, which can decrease the outer surface accessible to oxalic acid. The good catalytic activity of the graphene-based materials for oxalic acid oxidation by CWAO is related to their surface properties (essentially basic/neutral nature and absence of strong acidic groups), which is in agreement with previous reports using different carbon materials [4, 8, 10, 26, 34, 35]. Regarding phenol oxidation experiments (Figure 4.b), once again, the use of the graphene-based materials increases the removal of the pollutant from the solution (that is not converted in the absence of catalyst). In this case, the rGO-M sample clearly exhibits the best catalytic performance (50 % of phenol removal after 120 min) followed by the rGO and rGO-U samples, with a small contribution of adsorption using samples rGO-M and rGO-U (less than 8 %). The adsorption experiment using the rGO sample was not performed but it is expected to be higher than this value, as in the oxalic acid case, due to the high surface area of the sample. It is important to note that the CWAO experiments do not lead to total oxidation of phenol; several compounds are involved in the possible reaction pathways of phenol oxidation by CWAO [26, 36], such

as hydroquinone and benzoquinone, which have been identified as the most representative intermediates in the present work. Furthermore, TOC conversions in the oxidation of phenol were low with the rGO-M and rGO-U samples (only 22 and 11 %, respectively).

The good catalytic performance obtained in the degradation of oxalic acid and phenol by CWAQ with the rGO-M sample highlights the positive effect of the nitrogen groups, as already reported in our previous works using different carbon materials (carbon nanotubes [8, 10], carbon xerogels [4] and carbon fibres and foams [9]). In some of the cited works [4, 9], linear correlations were found between the model pollutant removal and the amount of N surface groups.

Those dependences may be related with the interaction of oxygen with the carbon surface in the presence of the N surface groups [37] and the active oxygen species that can be generated [11], which can react with adsorbed organic compounds leading to the oxidation of the organic pollutants. This explanation is also corroborated by some works [4, 10] where it was reported that, in the presence of N functionalities on the carbon surface, hydroxyl radicals in the liquid phase may not be required, suggesting that the oxidation reaction can occur by an alternative surface reaction mechanism, possibly as described above.

An advantage of the use of N-doped carbon materials is the stability of the N groups. In the oxidation of oxalic acid by CWAQ only a slight decrease of the catalytic activity of the materials (carbon nanotubes and carbon xerogels) was observed after the third use [4, 10]. Post-reaction analysis of the rGO-M (CWAQ) and rGO-U (CWAQ) samples by XPS (Figures 3.c and 3.d, respectively) showed that nitrogen functionalities were stable and there are not significant changes of the N groups after oxalic acid oxidation by CWAQ, as also observed with carbon xerogels [4].

3.2.2 Catalytic ozonation

In the present study, the ozonation of oxalic acid at the natural pH (approximately 3) in the presence of the prepared graphene-based materials was investigated. The results are depicted in Figure 5.

FIGURE 5

It was observed that single ozonation only removes about 32% of the oxalic acid in solution after 2 h, while the addition of the prepared graphene samples significantly enhanced its mineralization. Almost complete degradation of oxalic acid can be achieved in 2 h using rGO-M, while oxalic acid conversions of 83% and 75% were obtained using the rGO and rGO-U samples, respectively.

The two different precursors (melamine or urea) used during the preparation of N-doped samples originated two materials with different textural properties and surface chemistry, which led to the different performances when used as ozonation catalysts.

Concerning the rGO-M sample, although it presents lower specific surface area than rGO (where oxalic acid and molecular ozone can adsorb and react), this catalyst presents a better performance in the oxalic acid degradation, which may be related to the introduction of the N-surface groups. On the other hand, the worse performance of rGO-U can be due to the very low specific surface area (only $47 \text{ m}^2 \text{ g}^{-1}$) compared to the rGO and rGO-U samples (263 and $102 \text{ m}^2 \text{ g}^{-1}$, respectively), and the lower amount of nitrogen on the surface when compared to the rGO-M sample.

The ozonation of phenol was carried out at the natural solution pH (approximately 6). Both phenol and TOC decay were followed during 300 min, and the corresponding experimental data are depicted in Figure 6.

FIGURE 6

It can be observed that ozonation by itself enables a fast decay of the phenol concentration and, under the selected experimental conditions, total conversion of this compound from aqueous solution is achieved in about 60 min. This is because ozone preferentially attacks activated aromatic rings present in compounds, which is the case of phenol. In fact, the –OH group present in the phenol molecule is electron donating, activating the aromatic ring by increasing its electron density. Furthermore, aromatic compounds such as phenol have a high delocalization of electrons and exhibit improved reactivity towards ozone. There are no significant differences between single ozonation and catalytic ozonation. However, when TOC results are compared (see Figure 6b), the presence of graphene-based materials leads to higher mineralization degrees than single ozonation. Their catalytic performance in ozonation of phenol is similar to those obtained with oxalic acid. Thus, with the simultaneous use of ozone and the rGO-M sample, a mineralization degree of 85 % was achieved after 180 min, whereas a worse mineralization degree was obtained using the rGO-U sample (65 % after 180 min). The oxidation of phenol originated several intermediates and by-products [38]. Hydroquinone and p-benzoquinone were identified, representing the main intermediates produced during single and catalytic ozonation of phenol. They are produced in higher amount at the beginning of the reaction (between 15-20 min). Besides these compounds, some other organic compounds, such as, oxalic, maleic and pyruvic acids were found as oxidation by-products of phenol, which are resultant not only from phenol degradation but also from their intermediates. These acids are accumulated in solution, their degradation starting later. After 180 min of ozonation catalysed by rGO-M, oxalic acid is the only acid present in solution. However, in the case of rGO-U and rGO, traces of other non-identified acids persist in solution at the end of the reaction period.

The performance of the graphene-based materials in catalytic ozonation is influenced by their surface chemical properties, similarly to what occurs with activated carbon [35] and carbon nanotubes [22]: in general, this process is favoured by carbon materials with basic/ neutral character [22, 35]. However, the pH of the medium plays an important role on the reaction mechanism. In fact, the decomposition of ozone catalysed by graphene-based materials will depend on the solution pH, because of their amphoteric nature, the surface being positively or negatively charged, according to what occurs with other carbon materials [34, 39]. In case of the oxalic acid solution, the pH is about 3, between the pK_{a1} (1.23) and pK_{a2} (4.19) values and, consequently, a fraction of the acid is deprotonated. Therefore, the surfaces of the materials investigated in this work (rGO, rGO-U and r-GO-M), which have a pH_{PZC} higher than the pH of the solution, become positively charged, enhancing the attraction of hydroxide ions and thus, the degradation of oxalic acid. On the other hand, in the case of phenol, the solution pH (approximately 6) is lower than the pK_a (9.89), the protonated form being the predominant species. Since the surfaces of the graphene-based materials are positively charged at this pH, there are repulsive electrostatic interactions between the carbon surface and phenol species, disavouring the mineralization.

For the degradation of oxalic acid and phenol, the rGO-M sample led to the best catalytic performance, which evidences a positive effect of the nitrogen groups on the surface of graphene-based materials in the ozonation process. After a first run, the surface of the graphene-based material may present acidic oxygenated groups due to the interaction with ozone, which impairs the catalytic performance; however, no major changes are expected after a second utilization, similarly to what was observed with other carbon materials, such as carbon nanotubes [8], xerogels [4] and activated carbon [12, 13].

4. Conclusions

The addition of N-groups to the graphene structure markedly affected the catalytic performance of the synthesized materials in the degradation of oxalic acid and phenol, either by CWAO or by catalytic ozonation. Oxalic acid remains refractory to oxidation in the absence of a catalyst, under wet air oxidation conditions, but is efficiently oxidized by CWAO using the N-modified graphene-based materials. Phenol can be converted by single ozonation, but the N-modified graphene-based materials significantly improve its mineralization. For the ozonation process, both oxalic acid and phenol are not completely mineralized without the introduction of graphene-based materials.

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TABLES

Table 1. Chemical and textural characterization of the graphene-based materials.

Sample	S_{BET} ($\text{m}^2 \text{g}^{-1}$)	CO_2 ($\mu\text{mol g}^{-1}$)	CO ($\mu\text{mol g}^{-1}$)	$\text{O}^{(a)}$ (%)	CO/CO_2	$\text{N}_{\text{XPS}}^{(b)}$		pH_{PZC}
						(%)	N5/N6	
GO	23	5305	4156	23.6	0.8	n.a.	n.a.	2.8
rGO	263	494	2481	5.6	5.0	n.a.	n.a.	6.2
rGO-M	102	405	1378	3.5	3.4	9.3	0.6	7.3
rGO-U	47	262	1626	3.4	6.2	7.5	0.5	8.1

(a) determined from the amount of CO and CO_2 released by TPD

(b) Nitrogen content obtained from XPS analysis

N5 – pyrrolic N groups; N6 – Pyridinic N groups

n.a. – not applicable

FIGURE CAPTIONS

Figure 1. N₂ adsorption–desorption isotherms at 77 K for graphene-based materials.

Figure 2. CO₂ (a) and CO (b) evolutions in TPD profiles of graphene oxide (GO) and thermally treated graphene-based samples (rGO, rGO-M and rGO-U).

Figure 3. N1s XPS spectra for the fresh rGO-M (a) and rGO-U (b) samples and after being used in CWAQ of oxalic acid (c and d).

Figure 4. Evolution of the normalized oxalic acid (a) and phenol (b) concentrations under non-catalytic conditions (WAO), adsorption experiments (Ads) and using graphene-based materials as catalysts in CWAQ.

Figure 5. Evolution of normalized concentration of oxalic acid at natural pH during single and catalytic ozonation ($C_{0,\text{oxalic acid}} = 90 \text{ mg L}^{-1}$, catalysts = 0.14 g L^{-1} , $Q_{\text{gas}} = 150 \text{ cm}^3 \text{ min}^{-1}$, $C_{\text{O}_3, \text{feeding}} = 50 \text{ g m}^{-3}$).

Figure 6. Evolution of normalized phenol (a) and TOC (b) concentrations at natural pH during single and catalytic ozonation ($C_{0,\text{phenol}} = 75 \text{ mg L}^{-1}$, catalysts = 0.14 g L^{-1} , $Q_{\text{gas}} = 150 \text{ cm}^3 \text{ min}^{-1}$, $C_{\text{O}_3, \text{feeding}} = 50 \text{ g m}^{-3}$).

500 **FIGURE 1**

501

FIGURE 2

a.

b.

FIGURE 3

519

520