Using a Surface-Response Approach to Optimize the Photocatalytic Activity of rGO/g-C₃N₄ for Bisphenol A Degradation

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Supplementary Material

1. Additional Information about the experimental procedures

1.1 Details regarding the GrO synthesis

Graphite powder (1.00 g) was mixed with 70 mL of concentrated sulfuric acid under vigorous magnetic stirring in a 2 L beaker. To this mixture, 9.00 g of potassium permanganate were added within 5 min. The system was heated to 40°C and magnetically stirred for 40 min. Then, 150 mL of ultrapure water was poured within 5 min with the aid of a separating funnel. The temperature was kept below 95°C during this operation, by the careful dropwise addition of water. Finally, 500 mL of ultrapure water were added to the flask. It was magnetically stirred for more than 15 min and 10.0 mL of concentrated hydrogen peroxide (10 mol L^{-1}) was slowly added over 3 min.

This mixture was magnetically stirred for 20 min and vacuum filtered using a quantitative filter paper to recover the material. The material was suspended in 250 mL of hydrochloric acid 1.0

mol L^{-1} and vacuum filtered on a quantitative paper filter. The collected material was then dried at room temperature and protected from direct exposure to light. The amount of synthesized GrO required for all experiments was prepared and homogenized. The solid was previously frozen with liquid nitrogen, grounded with a porcelain mortar/pestle, and dialyzed with a membrane capable of removing ions from 8,000 to 14,000 Da. The membranes (20 cm) were filled with 4.0 g of GrO and 60 mL of ultrapure water. The bags were kept in a 2 L beaker filled with ultrapure water (1.5 L) kept under magnetic stirring. That water was renovated every 2 h during the first day, every 4 h during the second one, and then every 12 h thereafter, until the spent water pH matched the one of ultrapure water (pHmeter Marconi PA 200). The purified material was air dried at room temperature for seven days, frozen with liquid nitrogen, and lyophilized for six days. This material was ground into an agate mortar/pestle and transferred to Falcon$^{®}$ tubes (50 mL) which were also kept away from light.

1.2 Optimization of the rGO/g-C$_3$N$_4$ synthesis

The experiments were randomly performed to minimize systematic errors. The experimental error was determined by Equation S1, in which s is the experimental error, and v_i and s_i^2 are the degrees of freedom and the variance of each duplicate, respectively.

$$s = \sqrt{\frac{v_1 s_1^2 + v_2 s_2^2 + \cdots + v_n s_n^2}{v_1 + v_2 + \cdots + v_n}} \tag{S1}$$

The factors were coded to prevent any biases due to their magnitude using Equation S2, in which x_c is a coded factor, x_r a factor in real units, L_{upper} is the upper level, and L_{lower} is the lower level [31].

$$x_c = \frac{x_r - \left(\frac{L_{upper} + L_{lower}}{2}\right)}{\frac{L_{upper} - L_{lower}}{2}} \quad\quad\quad (S2)$$

Second, based on the obtained results, a polynomial was adjusted to the data and a set of experiments was performed along the path of steepest ascent, i.e., towards increased BPA degradation.

1.3 Characterization

X-ray diffraction (XRD) – X-ray diffractograms were obtained in a Brucker D8 advance 6000 using a Cu Kα, with a nickel filter, and emission at 0.154 nm. Routine: angular step of 0.02° and integration time of 4 s, scan from 5 to 90°.

Fourier Transform Infrared Spectrophotometry (FTIR) – infrared spectra were obtained by a Bruker spectrophotometer, model Equinox 55, equipped with an Attenuated Total Reflectance accessory. Acquisition was in the range from 400 to 4000 cm^{-1}, with a resolution of 4 cm^{-1}.

N_2 physisorption using the Brunnauer–Emmett–Teller isotherm – specific surface area measurements were performed in a Micromeritics, model ASAP 2020, and in a Quantachrome NOVA 1000 version 10.02. The samples were previously degassed at 150°C and 6 μmHg for 3 h. The temperature during the analysis was that of liquid nitrogen and graphite was used as reference.

Dynamic light scattering – zeta potentials were measured within the 2 to 12 pH range, adjusted with HCl 0.25 mol L^{-1} and NaOH 0.25 mol L^{-1}, in a Malvern Zeta-Sizer, model nano-ZS. The measurements were performed in DTS1070 cells using the Smoluchowski model.

Scanning Electron Microscopy with Field Emission Gun – the particles' morphology was observed in a Jeol microscope, model JSM-6701F, and in a Hitachi TM 3000 one, for precursors and composite, respectively.

Energy Dispersive Spectroscopy (EDS) – the relative elemental composition was obtained in a Hitachi TM 3000 coupled to a Quanta EDS Bruker, Karlsruhe X-ray dispersive system.

Diffuse Reflectance Spectroscopy (DRS) – the reflectance spectra were obtained in a Varian Cary 5G and in a Shimadzu (ISR-603 Integrating Sphere Attachment) for precursors and composite, respectively. The scan range was from 190 to 800 nm. The data were submitted to the Kubelka–Munk transformation and then used for a Tauc plot aiming at estimating the band gap, according to the Khan et al. [51] approach.
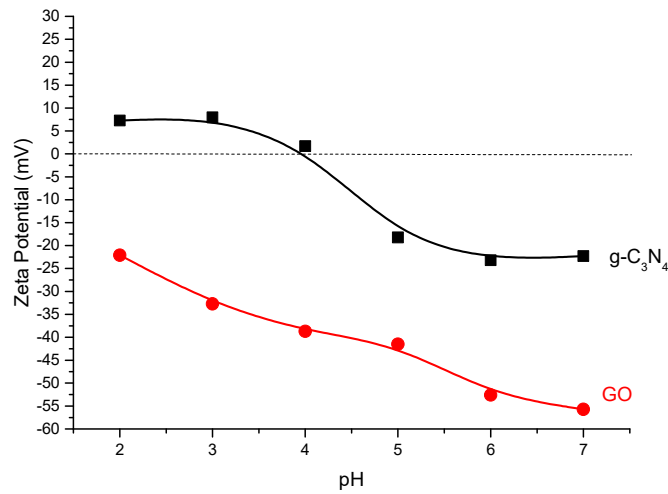
Elemental Analysis (CHNSO) – the elemental analysis was performed in duplicate in a Thermo Fisher Scientific flash smart model analyzer. The sample was kept at 950 °C for 720 s for C, H, N, and S determination and at 1060 °C for 400 s to determine O.

2. Additional Information about the Results and Discussion

2.1 About the pre-optimization experiments

At pH 3.0, the surface charge of g-C_3N_4 and the exfoliated GrO (called graphene oxide, GO) are approximately +7.96 and −32.7 mV (Figure S1).

Figure S1 – Zeta potential versus pH curve of g-C$_3$N$_4$ and GO.

2.2 Optimization of the formation of rGO/g-C$_3$N$_4$

Table S1 shows the results of the 2^3 initial full factorial experimental design.

Table S1 – Factors, levels, experimental matrix, and results of the initial 2^3 full factorial design.

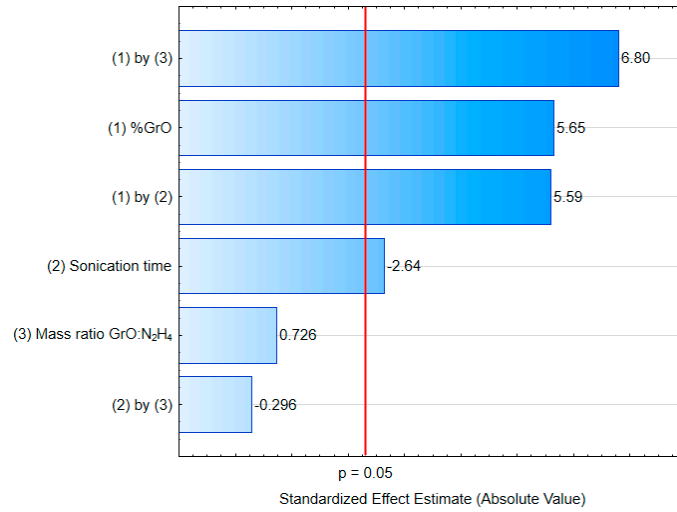| Factors				Levels	
				Low (−1)	High (+1)
%GrO				4	10
Sonication time (min)				10	20
Mass ratio N$_2$H$_4$:GrO				1:4	1:1
Run #	x_1 %GrO	x_2 sonication time (min)	x_3 weight ratio N$_2$H$_4$:GrO	Degradation (%)	
				Replicate 1	Replicate 2
1	−1	−1	−1	28.5	24.3
2	+1	−1	−1	21.1	23.1
3	−1	+1	−1	19.8	22.2
4	+1	+1	−1	23.6	22.7
5	−1	−1	+1	22.2	23.8
6	+1	−1	+1	25.8	29.0
7	−1	+1	+1	11.6	14.6
8	+1	+1	+1	30.7	33.0

The generated model for Table S1 experimental design, by linear regression, is shown in equation S3. The statistical significance of the main and interaction effects (95% confidence interval) is presented in the Figure S2. The standardized effects estimates are plotted as bars whose sizes are

proportional to those effects (absolute values). Bars crossing the red line ($p = 0.05$) mean statistically significant effects (95% confidence interval).

$$Removal\ (\%) = 23.5 + 5.25x_1 - 2.45x_2 + 5.20x_1x_2 + 6.32x_1x_3 \qquad \text{(S3)}$$
$$\pm 0.465 \quad \pm 0.930 \qquad \pm 0.930 \qquad \pm 0.930 \qquad \pm 0.930$$

Figure S2 – Pareto's chart for the 2^3 full factorial design.

The conditions for the experiments along the path of steepest ascent were defined by taking the greatest factor coefficient (absolute value) as a reference, which was the one for %GrO (5.25). Therefore, for each increase in %GrO ($\Delta x_{\%GrO}$), a correspondent decrease in the sonication time was calculated ($\Delta x_{sonication\ time}$), taking into consideration the other factor coefficient (2.45), as shown in Equation S4 (coded factors). The experiments performed in real units and their respective responses are shown in Table S2.

$$\Delta x_{sonication\ time} = \frac{5.25}{2.45} \Delta x_{\%GrO} \qquad \text{(S4)}$$

Table S2 – Path of steepest ascent.

Run #	%GrO	Sonication time (min:s)	Removal (%)
9	7	15:00	24.1
10	10	12:40	37.7
11	13	10:20	57.5
12	16	8:00	64.9
13	19	5:40	42.3
14	22	3:20	43.9

As the best BPA, removal was achieved in run 12, the respective experimental conditions were used as the central point of a CCD. Table S3 presents factors, levels, experimental matrix, and results of that design. One adjusted a polynomial (Equation S5) to the obtained results.

Table S3 – Factors, levels, experimental matrix, and results of the CCD.

Factors	Levels	
	Low (−1)	High (+1)
%GrO	13	19
Sonication time (min)	5	11

Run #	x_1 %GrO	x_2 sonication time (min)	Removal (%)
15	+1.414	0	48.7
16	0	0	60.0
17	0	0	60.1
18	−1	−1	50.9
19	+1	−1	35.7
20	0	0	62.8
21	−1.414	0	40.5
22	0	+1.414	53.0
23	+1	+1	43.7
24	−1	+1	40.0
25	0	+1.414	40.8

$$Removal\ (\%) = 61.0 - 8.65x_1 - 2.52x_2 + 4.73x_1x_2 - 8.98x_1^2 - 7.83x_2^2 + 5.78x_1^3 \qquad (S5)$$
$$\pm 0.917 \quad \pm 1.78 \quad \pm 0.562 \quad \pm 0.794 \quad \pm 0.669 \quad \pm 0.669 \quad \pm 1.12$$

Equation S5 generates the surface in Figure S3 (in real units). The model was considered adjusted by an ANOVA (Table S4) and the Fisher statistics. However, as MS_R/MS_r was not ten times higher than the critical value of $F_{6,4}$, the model cannot be used as a predictive one [31].
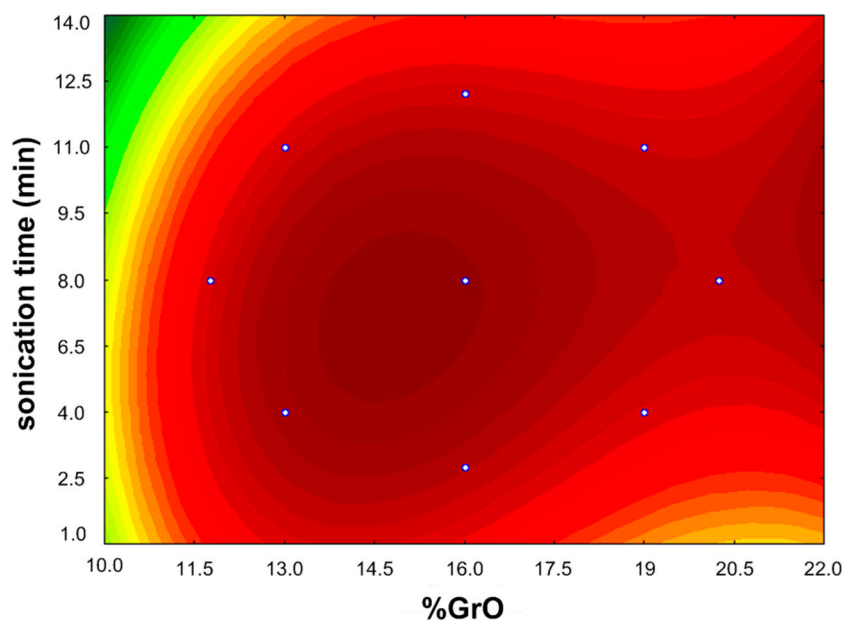
Figure S3 – CCD response surface.

Table S4 – ANOVA analysis.

Variation source	SS	DF	MS
Regression (R)	828.2	6	138
Residues (r)	50.9	4	
Lack of fit (lof)	48.85	2	12.73
Pure error (pe)	5.047	2	
Total	879.1	10	

% maximum explained variation (R^2):	0.942
% maximum explanable variation:	0.994
MS_R/MS_r	10.85
$F_{6,4}$ (critical)	6.163
MS_{lof}/MS_{pe}	9.086
$F_{2,2}$ (critical)	19.00

Note: SS – sum of squares; DF – degrees of freedom; MS – mean square.

As the model was well adjusted, its maximum (optimum synthetic conditions) can be estimated: $x_1 = -0.039$ and $x_2 = -0.26$, i.e., %GrO = 15% and sonication time = 7 min e 20 s, respectively.

2.3 About the characterizations

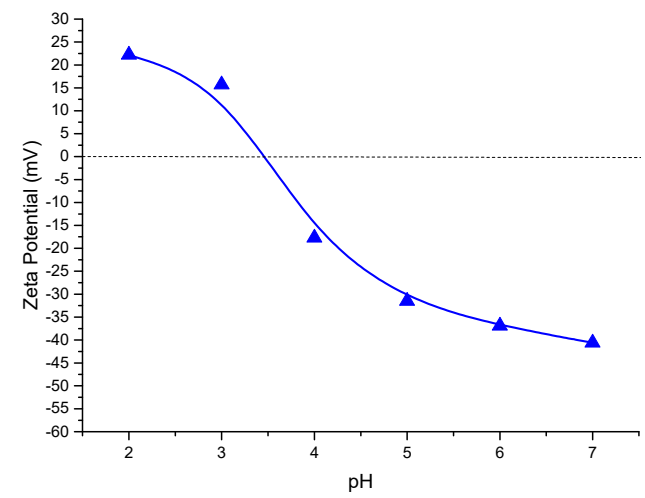Figure S4 – ZP versus pH curve for the optimized composite.

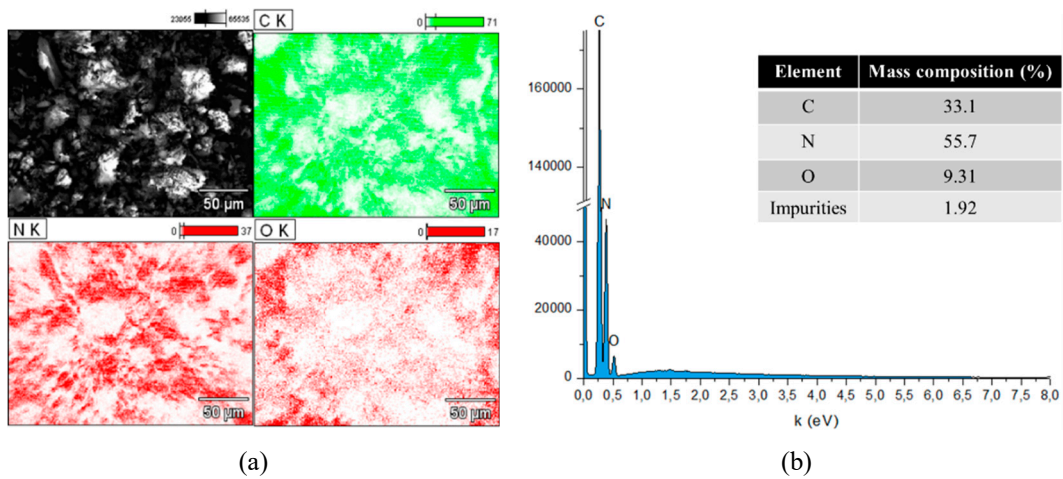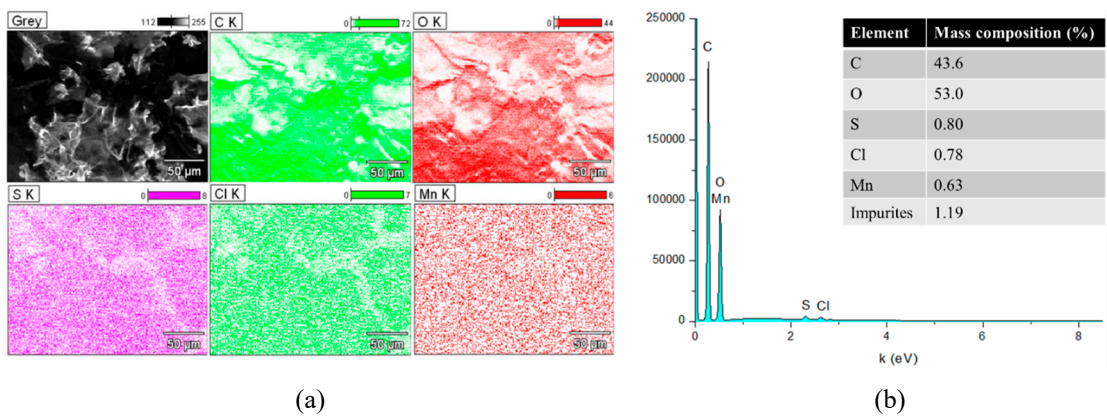

Figure S5 – EDS (a) distribution and (b) spectrum for g-C$_3$N$_4$.

Element	Mass composition (%)
C	33.1
N	55.7
O	9.31
Impurities	1.92

(a)   (b)

Figure S6 – EDS (a) distribution and (b) spectrum for GrO.

Element	Mass composition (%)
C	43.6
O	53.0
S	0.80
Cl	0.78
Mn	0.63
Impurities	1.19

(a)   (b)

The VB and CB potentials for g-C₃N₄ were estimated by the empirical Equations S6-8 [39], in which χ is the electronegativity of the material, $x(I)$ is the electronegativity of element I, i is the number of atoms of element I, n is the total number of atoms, and N is the number of different atoms, all of them in the composite empirical formula, E_{VB} and E_{CB} are the potentials of VB and CB bands, respectively, E^e is the (constant) energy of the free electrons measured against the Normal Hydrogen Electrode, whose value is 4.5 eV, and E_g is the (measured) energy of the band gap.

$$\chi = \sqrt[\Sigma_{i=1}^{n} i]{\prod_{j=1}^{N} x(I_j)^{i_{I_j}}} \tag{S6}$$

$$E_{CB} = \chi - E^e - 0.5E_g \tag{S7}$$

$$E_{VB} = E_{CB} + E_g \tag{S8}$$

2.4 Regarding the degradation products identification and ecotoxicity

Figure S7 – Mass Spectra for BPA, DP1, and DP2.