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Effect of Fe₃O₄:RGO Ratios in Magnetic Nanocomposites Applied for Dye Discoloration

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Nanocomposites of magnetite anchored on reduced graphene oxide with different magnetite:reduced graphene oxide mass ratios were synthesized and evaluated in indigo carmine photo Fenton discoloration. All nanocomposites are magnetic and showed comparable amounts of magnetite and hematite with a higher level of hematite for low iron contents. The highest value of 63.6 emu g⁻¹ was obtained for the nanocomposite with the highest magnetite content. The nanocomposites presented high dispersion of iron oxide particles, at about 12 nm on reduced graphene oxide surface sheets. The samples also showed bandgap energies below that found for bulk magnetite, showing an important effect of reduced graphene oxide. The nanocomposite with an iron nitrate precursors mass ratio of 17:1 showed the best performance (99.7% of indigo carmine discoloration (2.1×10^{-5} mol L⁻¹) at 30 min of reaction, hydrogen peroxide (2.3×10^{-1} mol L⁻¹), and a catalyst dosage of 0.67 g L⁻¹). Reusability tests were performed, and this nanocomposite was shown to be active for at least three recycles. X-ray photoelectron spectrum of Fe2p_{3/2} showed that the Fe^{III}/Fe^{II} ratio was maintained even after three recycles (4 runs), meaning that reduced graphene oxide is responsible for stabilizing magnetite particles, thus maintaining its photocatalytic activity.

Keywords: iron oxides, reduced graphene oxide, heterogeneous photocatalysis, indigo carmine

Introduction

Water contamination is one of the major environmentrelated issues, and it is associated not only with health problems but with severe socioeconomic impacts.^{1.4} It is estimated that around 10,000 different synthetic dyes are used, with significant losses of these compounds to the environment after dyeing procedures.^{5.6} Indigo carmine (IC) is an artificial vibrant blue dye, spread worldwide due to its use in denim making. It is an indigoid organic dye and its molecule possesses two sulfonic groups. Besides, it is

*e-mail: cah@uerj.br; alexandre.gaspar@int.gov.br Editor handled this article: Célia M. Ronconi (Associate) well known that IC brings health risks because it is toxic, mutagenic, and very stable in nature.⁷ These characteristics are driving forces to develop new technologies to mitigate water pollution by synthetic organic dyes.

Different techniques are investigated to remediate dying wastewater pollution, such as ultrafiltration, electrochemical, and adsorption.⁸ However, heterogeneous photocatalysis of organic dyes emerges as a promising approach due to its advantages, such as catalyst recovery and reuse, use in mild conditions, pollutant chemical transformation, and others.^{9,10} These reactions are considered advanced oxidative processes (AOPs), where hydroxyl radicals (•OH) are generated from H_2O_2 decomposition, assisted by a light source and a semiconductor oxide.¹¹ These

structures are then responsible for attacking the organic pollutant molecules, breaking the molecule bonds until mineralization (transforming a pollutant organic molecule into CO_2 , H_2O , and mineral acids).

An attractive abundant semiconductor oxide studied in heterogeneous photocatalysis reactions is magnetite (Fe₃O₄).¹² This mixed oxide has a Fe^{III}/Fe^{II} ratio of 2:1 and narrow bandgap values.^{13,14} The first characteristic is responsible for the aforementioned •OH radical generation. The second, is related to the compound electronic activation, an important parameter to be considered in photocatalysts.¹⁵ However, if non-supported iron oxides are employed in aqueous medium, its particles tend to aggregate quickly.¹⁶ Also, the Fe^{II} oxidation to Fe^{III} results in a deactivated passive oxide layer.¹⁷ Both phenomena are bound to the •OH generation suppression, hindering the capability of decomposing the pollutant. Therefore, supporting iron nanoparticles in materials that stabilize them and improve their physical-chemical properties is a good alternative to mitigate these issues.¹⁸

Due to their remarkable optical,¹⁹ electronic,²⁰ and textural properties,²¹ graphene derived compounds, such as graphene oxide (GO), and reduced graphene oxide (RGO), have been used to immobilize semiconductor oxide particles, avoiding particle agglomeration, and to improve their photocatalytic activity in various organic dyes removal systems.^{18,22-25} For instance, Zarrabi et al.²⁵ produced a ZnO-GO-Fe₃O₄ nanocomposite, and achieved 97% of methylene blue (MB) discoloration. Yet for this dye, Umar et al.²⁶ obtained 91% of conversion within 30 min of reaction, with a Fe₃O₄-GO nanocomposite. For methyl orange dye (MO), Liu et al.²⁷ synthesized an organic-inorganic polyonic liquid-functionalized graphene oxide (PGO) PGO-TiO₂/Fe₃O₄, reaching 95% of MO removal. Using a monolithic 3D RGO-Fe₃O₄ aerogel, Sadegh *et al.*²⁸ observed 100% of acid red 1 (AR1) dye discoloration. Silva et al.²⁹ tested an amino-Fe₃O₄ functionalized graphene oxide, named AmGO, and observed 97% of reactive black 5 (RB5). Besides their remarkable dye removal results, another important highlight reported by these works is that these nanocomposites can be simply synthesized by diverse approaches. In addition, the magnetic character of these nanocomposites leads to simpler catalyst recovery methods and possibilities for further reuse. Thus, the combination of these features results in promising materials to be used for a wide range of wastewater pollutants removal.

Recently, our group described dispersed Fe_3O_4 nanoparticles anchored on RGO sheets,³⁰ synthesized by a facile redox synthesis adapted from the Stöber method, where $Fe(NO_3)_3$.9H₂O oxidates to Fe_3O_4 and GO is reduced to RGO.³¹ In this way, a nanocomposite with approximately 90 wt.% of Fe₃O₄ and 10 wt.% of RGO was employed to treat an IC solution $(2.1 \times 10^{-5} \text{ mol L}^{-1})$ in a photo-Fenton system. Within 5 min after the light was turned on, a rapid and complete discoloration of the IC solution was observed. Its remarkable characteristics such as less negative zeta potential, narrow bandgap, and the persistent cycle conversion process of Fe^{III}/Fe^{II} promoted by RGO; explained its outstanding activity. Furthermore, due to its strong magnetic character, the nanocomposite could be easily recovered and reused. These observations supported that the Stöber-like method is a powerful synthesis to immobilize Fe₃O₄ nanoparticles on RGO, improving its photocatalytic properties.

In this sense, the present work aims to expand the study of IC photo-Fenton discoloration with Fe_3O_4/RGO nanocomposites produced by the adapted Stöber-like method. Nanocomposites with different ratios of Fe_3O_4 :RGO were synthesized, characterized, and evaluated in the IC photo-Fenton discoloration. The nanocomposite with the best performance was selected to perform a study varying the oxidant reactant (H₂O₂) and nanocomposite loads, providing kinetic data. Furthermore, reusability tests were conducted to highlight the photocatalyst stability.

Experimental

Synthesis of the materials

Graphite (Grafine 996100), provided by Nacional de Grafite (São Paulo, Brazil), was oxidized by the modified Hummers method.32 At 0 °C, assisted by an ice bath, 11.5 mL of H₂SO₄ (95 wt.%, Vetec, Rio de Janeiro, Brazil), and 270 mg of NaNO₃ (98 wt.%, Isofar, Rio de Janeiro, Brazil) were added to 220 mg of graphite under magnetic stirring. Then, the temperature was set to 35 ± 5 °C and six portions of 250 mg of KMnO₄ (99 wt.%, Isofar, Rio de Janeiro, Brazil) were slowly added into the mixture, which remained under stirring for 1 h. After that, distilled water was added, and the temperature was raised to 98 ± 5 °C and kept for 15 min. Next, 60 mL of H₂O₂ (10 wt.%, Isofar, Rio de Janeiro, Brazil) were added to the system, and the temperature was lowered to 20 °C and maintained for 1 h. After the oxidation procedure, the slurry was washed to remove impurities. Each washing cycle was performed as follows: the slurry was filtered and the solid obtained was washed with 20 mL of H_2O_2 (10 wt.%), then with 20 mL of H_2SO_4 (5 wt.%), centrifuged, and washed with distilled water until pH = 6.0.

The synthesis of the Fe_3O_4/RGO magnetic nanocomposites was performed by varying the iron precursor solution concentration in the adapted Stöberlike method.³¹ In a beaker, an ethanol/acetonitrile (3:1)

solution was used to disperse 200 mg of GO for 90 min in an ultrasonic bath. After that, the beaker was placed on a magnetic plate, 1.33 mL of ammonium hydroxide (28 wt.%, Sigma-Aldrich, São Paulo, Brazil) was added, and the suspension stirred for 30 min. The desired solutions of Fe(NO₃)₃.9H₂O (Sigma-Aldrich, São Paulo, Brazil) were added dropwise to the suspension and kept stirring for 30 min. Then, the mixture was transferred to a round bottom glass flask and a reflux system was assembled. The temperature was set to 60 °C, and the mixture was magnetically stirred for 40 h. At the end of this step, the iron oxide/GO solid was centrifuged from the solution, washed with ethanol to remove impurities, and dried in an oven. The iron oxide/GO solid was then heated to 500 °C (with a rate of 1.5 °C min⁻¹) and treated for 2 h with a pure nitrogen flow of 50 mL min⁻¹. Table 1 shows the precursor Fe(NO₃)₃.9H₂O quantities used in each synthesis, and the respective names of the prepared samples. Also, an appropriate mass of GO was separated and thermally treated as the iron oxide/GO likewise to yield pure RGO. A sample of bulk Fe₃O₄ obtained as described by da Costa et al.³³ was also used as a standard.

 Table 1. Nanocomposite nomenclatures, iron precursor contents, and mass ratio of the precursors

Sample	Fe(NO ₃) ₃ .9H ₂ O / g	Fe(NO ₃) ₃ .9H ₂ O:GO ^a
Nanocomposite 1	1.1260	6:1
Nanocomposite 2	2.2510	11:1
Nanocomposite 3	3.3760	17:1

^aApproximate mass ratio.

Characterization

Microscopic studies of the iron oxide nanoparticles of the Fe₃O₄/RGO nanocomposites were performed using scanning transmission electron mode on a SEM microscope (STEM-in-SEM) operated at 30 kV, with a specific sample holder for conventional copper transmission electron microscopy (TEM) grids and a high angular STEM detector (HAADF-STEM) in a Helios Nanolab Dual Beam G3 CX equipment. Field emission gun scanning electron microscopy (FE-SEM) analysis was carried out in a Quanta FEG 450 equipment. Both microscopes are from FEI/Thermo Fischer (Waltham, USA). C, O, and Fe distribution and composition in the Fe₃O₄/RGO nanocomposites were determined by electron dispersive X-ray (FE-SEM-EDX). Particle size measurements were performed using ImageJ (1.52a) software.³⁴ The crystallinity of all materials was observed by X-ray diffraction (XRD). The diffractograms were obtained in a Rigaku Miniflex II (Tokyo, Japan), with Cu Ka radiation of 1.540562 Å, 30 kV voltage, and 15 mA current. The acquisition parameters were: 2θ (from 5 to 70°), a step of 0.05, and 2 degree min⁻¹ per step. Textural analysis of RGO and the nanocomposites was performed in an ASAP 2020 from Micromeritics (Norcross, USA). Specific areas and pore volumes were estimated by N₂ adsorption at -196 °C, using Brunauer-Emmett-Teller (BET) method for the estimation of the specific area, and Barrett-Joyner-Halenda (BJH) method for the estimation of the average pore diameter. The thermal stability of the materials was investigated using thermo gravimetric analysis (TGA), in which the measurements were performed in a STA 409 Pc Luxx (NETZSCH) equipment (Selb, Germany), from room temperature to 1000 °C with a 20 °C min⁻¹ heating rate and 20 mL min⁻¹ of airflow.

Diffuse reflectance spectroscopy (DRS) was performed to estimate the bandgap of the nanocomposites and the bulk Fe_3O_4 . The materials were mixed with $BaSO_4$ (1:25) and analyzed in a Varian Cary 5000 UV-Vis-NIR spectrometer from 200 to 1500 nm (Palo Alto, USA).

The magnetic properties of the Fe_3O_4/RGO nanocomposites were studied combining electronic paramagnetic resonance (EPR) and vibrating-sample magnetometer (VSM) techniques. EPR analysis was performed in an ESP 300e (Bruker, Billerica, USA) with band cavity-X of 9 GHz at room temperature. VSM measurements were obtained in a Physical Property Measurements System (PPMS) DynaCool, from Quantum Design (San Diego, USA).

⁵⁷Fe Mössbauer absorption spectra were taken at room temperature in transmission mode using a standard spectrometer with sinusoidal velocity sweep of the ⁵⁷Co/Rh source (about 5 mCi). The hyperfine parameters derived from the spectra allow to distinguish different iron oxide phases.

X-ray photoelectron spectroscopy was employed to evaluate the surface chemical environment of iron before and after reuse cycles. The spectra were recorded in a PHOIBOS 150 (SPECS, Berlin, Germany), without a monochromator, and Al K α X-ray source. Adventitious carbon (C1s at 284.6 eV) was used to calibrate the whole spectra, whilst all mathematical treatment was performed with Casa XPS software (2.3.17).³⁵ The pressure inside the analysis chamber during all measurements was in the range of 10⁻¹⁰ to 10⁻⁹ mbar.

Indigo carmine (IC) photocatalysis

The IC photo-Fenton discoloration was evaluated in a system set up into a box that prevents external light interference, with a 50 mL glass reactor surrounded by a

cooling jacket, already described in previous works.^{30,36,37} Nanocomposite dosages of 0.67, 0.33, 0.17, and 0.07 g L⁻¹, were dispersed in distilled water using an ultrasonic bath for 30 min. Then, 15 mL of IC solution $(4.2 \times 10^{-5} \text{ mol } \text{L}^{-1})$ was aggregated to the dispersion to reach a final IC concentration of $(2.1 \times 10^{-5} \text{ mol } \text{L}^{-1})$. This IC concentration was selected because it is reported to be within the typical textile wastewater range.³⁸ Finally, the appropriate amounts of 30% H₂O₂ were transferred to the reactor, to complete a final volume of 30 mL and reach H₂O₂ concentrations of 2.3×10^{-1} , 1.2×10^{-1} , and 0.6×10^{-1} mol L⁻¹. At first, the magnetic stirring started, the chamber door was closed, and the mixture remained stirring for 30 min in the dark to reach the dye-catalyst adsorption equilibrium. Then, the lamp Master HPI-T (400 W), from PHILIPS, which emits predominantly visible light in the range of 380-740 nm,³⁷ was activated, and aliquots were extracted in periodic time intervals. The time when the lamp was turned on was denominated as 0 min. A magnet was used to separate the magnetic materials from the reaction medium. After that, the liquid was filtered with a Millipore filter (MILEX-GV PVDF-0.22 µm) and taken to a Varian Cary 500 UV-Vis spectrometer. Before each analysis, a calibration curve (Figure S1, Supplementary Information (SI) section) was performed by measuring the absorbance in the specific concentration at 611 nm, and this wavelength was used to monitor IC discoloration. Equation 1 was employed to calculate the IC discoloration.

Discoloration (%) =
$$\frac{\left(C_0 - C_A\right)}{C_0} \times 100$$
 (1)

where, C_A is the calculated concentration of the specific aliquot and C_0 is the initial concentration of indigo carmine dye.

The photocatalyst with the best performance was selected to perform reuse experiments. In this case, the

nanocomposites magnetically separated from the reaction were washed with distilled water and dried in an oven at 100 °C overnight. Then, the dried catalyst was used in the following reuse cycle, with a fixed IC/nanocomposite mass ratio of 0.015.

Results and Discussion

Materials characterization

Figure 1 shows the microscopic analysis for bare RGO (FE-SEM), bulk Fe₃O₄ (SEM), and all nanocomposites (STEM-in-SEM). RGO (Figure 1a) has a compact sheet morphology, while bulk Fe₃O₄ (Figure 1b) is a powder characteristic with different sizes of agglomerates. Meanwhile, nearly spherical iron oxide nanoparticles were successfully anchored on RGO sheets for the three nanocomposites (Figures 1c-1e). The nanoparticle counts by STEM-in-SEM (Figures 1c-1e and Table 2) indicate that the anchored iron oxide particles mean sizes are 12 nm for nanocomposites 1 and 2, and 15 nm for nanocomposite 3. It is worth mentioning that even with higher Fe_3O_4 loads, all nanocomposites showed well dispersed Fe₃O₄ nanoparticles on RGO sheets. The high dispersion of the small particles of iron oxide was favored by the synthesis method used, as shown by Qiu et al.³¹

FE-SEM-EDX (Table 2) iron semiquantitative analysis obtained from different regions, for nanocomposites 3 and 2 showed iron contents (wt.%) of 55.4 ± 2.8 , and 41.6 ± 2.5 , respectively. The observed deviation between each region is accepted due to the semiquantitative characteristic of this analysis and the heterogeneous nature of these nanocomposites. However, the FE-SEM-EDX iron content (wt.%) for nanocomposite 1 was found to be 29.1 ± 18.3 , with a very pronounced discrepancy among the regions.

EDX mapping (Figure S2, SI section) was performed to investigate the Fe distribution in the photocatalysts.



Figure 1. SEM images of bare reduced graphene oxide (a) and Fe_3O_4 (b). STEM-in-SEM micrographs for the nanocomposites with their histogram of particle size distribution: nanocomposite 3 (c), nanocomposite 2 (d) and nanocomposite 1 (e).

Sample	Iron oxide mean particle size ^a / nm	EDX Fe content ^b / %	Crystallite size ^c / nm	BET specific surface a rea / (m ² g ⁻¹)	V _{meso} / (cm ³ g ⁻¹)	V_{micro} / (cm ³ g ⁻¹)	Pore diameter / nm
Nanocomposite 1	12	29.1 ± 18.3	15	25	0.046	0.0013	8.51
Nanocomposite 2	12	41.6 ± 2.5	16	81	0.079	0.0044	3.62
Nanocomposite 3	15	55.4 ± 2.8	22	74	0.087	0.0043	4.25

Table 2. STEM-in-SEM particle counting, EDX iron content, crystallite size (by XRD), and textural data for all nanocomposites

^aSTEM-in-SEM particle counting; ^bcalculation for 5 different regions; ^cestimation by Scherrer equation with peak at $2\theta = 35.4^{\circ}$ of Fe₃O₄. EDX: electron dispersive X-ray; BET: Brunauer-Emmett-Teller; V_{meso} and V_{micro}: mesopore and micropore volume, respectively, by Barret-Joyner-Halenda (BJH).

RGO sheets of nanocomposites 3 and 2 showed to be fully covered by Fe (not shown). However, due to a high discrepancy in the different points of EDX semiquantitative analysis for nanocomposite 1, two different Fe₃O₄/RGO aliquots were selected to perform the EDX mapping. As a result, site 1 map (Figure S2a) shows an iron oxide-rich sheet, where the circle clearly reveals a RGO sheet prolongation with no detectable iron oxide. On the contrary, site 2 map (Figure S2b) indicates an iron oxide poor RGO folded sheet. Therefore, although some heterogeneity in these materials is expected, nanocomposite 1 showed to contain manifold regions with very different characteristics, suggesting the insufficient filling of iron oxides on RGO sheets, probably due to the lower iron precursor content in this synthesis, which is 3 times lower than nanocomposite 3.

XRD patterns for all Fe₃O₄/RGO nanocomposites, and RGO are shown in Figure 2a. For nanocomposites 2 and 3, it can be seen the crystalline Fe₃O₄ diffraction peaks and their respective Miller indexes, which are: 29.9° (220), 35.4° (311), 43.1° (400), 56.9° (511), and 62.5° (440). The JCPDS 76-1849 diffraction peaks, highlighted by pink bars, confirm that Fe₃O₄ particles were successfully formed on RGO sheets. For nanocomposite 1, however, a considerable displacement of ca. 0.5° of these peaks to higher 2 theta values are observed. Also, the intensity of the peaks indicated by the asterisks at $2\theta = 24.3$, 33.3, 40.8, and 64.2° becomes higher with the decreasing of Fe₃O₄ contents, suggesting that hematite (α -Fe₂O₃) might be formed in lower Fe(NO₃)₃.9H₂O loads (JCPDS 24-0072).³⁹

It is worth mentioning that nanocomposite 1, besides the characteristic magnetite black color, also presented portions with reddish color, which could be associated with the α -Fe₂O₃ formation. These observations agree with the study performed by Dong et al.,40 who detected higher Fe₂O₃ amounts for the nanocomposites with higher RGO contents. In parallel, no diffraction peak at $2\theta < 10^{\circ}$ was detected for the three nanocomposites, indicating that GO in the three samples was reduced to RGO. Furthermore, for nanocomposites 2 and 1, the appearance of a halo with a maximum around $2\theta = 25^{\circ}$ is related to RGO. The crescent intensity of this halo was expected once the amount of RGO in these samples increased (Figure 2b).⁴¹ The Scherrer equation was used to estimate the average crystallite size, using the most intense Fe_3O_4 peak ($2\theta = 35.4^\circ$) of the synthesized nanocomposites. The results are shown in Table 2, evidencing average crystallite sizes close to the particle size counting by STEM-in-SEM. These results suggest that no significant particle agglomeration occurs in this synthesis. It is noteworthy that nanocomposite 3



Figure 2. XRD patterns of RGO and all nanocomposites (a) and XRD patterns of all nanocomposites to highlight RGO halo (b). Pink bars and the asterisk are related to Fe₃O₄ and α -Fe₂O₃, respectively.

showed a slightly larger average crystallite size, as well as particle size (by STEM-in-SEM).

Figure 3 shows the TGA for RGO and the three Fe₃O₄/RGO nanocomposites. It was observed a mass gain up to 350 °C for nanocomposite 3. This phenomenon was already discussed elsewhere for nanocomposites of Fe_3O_4/RGO_4 and it is related to the oxidation of Fe_3O_4 particles.⁴² Considering the increasing XRD α-Fe₂O₃ diffraction peak intensities from nanocomposite 3 to nanocomposite 1, it can be argued that the samples with lower iron contents could possess more iron particles in higher oxidation states. These results could explain that the nanocomposites 2 and 1 did not present a mass gain. The maximum mass losses up to 1000 °C for nanocomposites 3, 2, and 1 were about 7, 18, and 26%, respectively. Once bare RGO has a total mass loss of about 95%, the iron oxide contents estimations for nanocomposites 3, 2, and 1 are 88, 77, and 69%, respectively.



Figure 3. TGA analysis with the nanocomposites and RGO mass losses in function of temperature.

The main aspects of the textural analysis of the nanocomposites are shown in Table 2. Isotherm plots Figure S3 (SI section) suggest that all nanocomposites are mesoporous (type IV isotherms). As shown in Table 2, the BET specific surface area of nanocomposite 3 is slightly lower than that of nanocomposite 2, 74 and 81 m² g⁻¹,

respectively. Interestingly, nanocomposite 1 presented a much lower BET specific surface area (25 m² g⁻¹) than nanocomposites 3 and 2. XRD results showed the peaks related to the formation of α -Fe₂O₃, yet much larger for nanocomposite 1. A study performed by Jozwiak *et al.*⁴³ reported a BET specific surface area for an α -Fe₂O₃, heat-treated at 600 °C, equal to 24 m² g⁻¹. Therefore, a plausible hypothesis is that the pronounced formation of α -Fe₂O₃ in nanocomposite 1 reduces its BET specific surface area.

DRS analysis was used to obtain the UV-Vis spectra of the nanocomposites and Fe₃O₄, aiming to use the Kulbelka-Munk and Tauc methods to extrapolate the indirect bandgap of the materials studied in this work.^{44,45} Figure 4 shows the curves of the indirect bandgap function $(F(R)hv)^{1/2}$ versus energy for each synthesized nanocomposites and Fe₃O₄, while the UV-Vis spectra are shown inset. The estimated bandgap values (Table 3) for nanocomposites 3, 2, and 1 were 1.30, 1.41, and 1.50 eV, respectively. All bandgap values of the nanocomposites showed to be lower than the bulk Fe₃O₄ (1.66 eV), suggesting that RGO is responsible for reducing the gap between the valence and conduction bands.^{18,46,47} Furthermore, the bandgap energies of nanocomposites 2 and 1 are, respectively, 0.11 and 0.20 eV higher than for nanocomposite 3.

Wang *et al.*⁴⁸ studied hematite photoanodes for water splitting, where a bandgap energy of 2 eV was observed for bulk α -Fe₂O₃. Therefore, these results might be linked to the more pronounced α -Fe₂O₃ formation in nanocomposites 2 and 1, already discussed in XRD results.

Electron paramagnetic resonance (EPR) and vibratingsample magnetometry (VSM) were performed to investigate the magnetic properties of the nanocomposites. EPR parameters were obtained by analyzing Figure 5, considering the effective gyromagnetic factor (g_{eff}) and the asymmetry ratio (A), according to equations 2 and 3, respectively:

$$g_{\rm eff} = \frac{h\nu}{\mu_{\rm B} H_{\rm eff}}$$
(2)

where, h, v, μ_B , and H_{eff} are the Planck constant, microwave

Table 3. Parameters obtained by DRS, EPR spectra and VSM curves for all nanocomposites

Sample	Bandgap / eV —	EPR		VSM			
		g _{eff}	А	$\frac{1}{Mr / (emu g^{-1})}$	H _c / Oe	M _s / (emu g ⁻¹)	M _r /M _s
Nanocomposite 1	1.50	3.10	1.34	8.7	136.4	31.7	0.27
Nanocomposite 2	1.57	3.25	1.09	9.1	136.4	51.6	0.18
Nanocomposite 3	1.30	3.74	1.20	28.0	327.5	63.6	0.44
Fe ₃ O ₄	1.66	_	_	_	_	_	_

EPR: electron paramagnetic resonance; VSM: vibrating-sample magnetometry; g_{eff} : effective gyromagnetic factor; A: asymmetry ratio; M_r : remanence magnetization; H_c : coercive fields; M_r : saturation magnetization; M_s/M_s : squareness ratio.



Figure 4. DRS spectra showing the indirect bandgap energy $(F(R)hv)^{1/2}$ for all nanocomposites and bulk Fe₃O₄.

frequency, Bohr magneton and microwave absorption maximum, respectively.

$$A = \frac{\Delta H_{high}}{\Delta H_{low}}$$
(3)

where, ΔH_{high} and ΔH_{low} are the half values of the full width at half maximum on the right and left of H_{eff} as represented in Figure 5, respectively. Table 3 shows that the g_{eff} values are 3.74 (nanocomposite 3), 3.25 (nanocomposite 2), and 3.10 (nanocomposite 1). These results suggest the presence of larger Fe₃O₄ particles and/or aggregates in the nanocomposites with higher Fe₃O₄ contents, as discussed in XRD and STEM-in-SEM results. Also, A values for all nanocomposites are higher than 1, indicating cubic magnetocrystalline anisotropy for all nanocomposites.⁴⁹ It is important to note that the Fe₃O₄/RGO nanocomposites were synthesized by an *in situ* one-step synthesis to anchor iron oxide on GO sheets, before obtaining Fe₃O₄ particles



Figure 5. EPR spectra for all nanocomposites, and the visual indication of ΔH_{hieh} , ΔH_{low} , and H_{eff} values.

on RGO sheets. This process might lead to a non-uniform material, due to the heterogeneous nucleation, as discussed in a study performed by Bertran *et al.*⁵⁰

VSM curves of the magnetic nanocomposites are shown in Figure 6, and Table 3 shows the parameters obtained. The descending order of saturation magnetization (M_s) is: 63.6 emu g⁻¹ (nanocomposite 3), 51.6 emu g⁻¹ (nanocomposite 2), and 31.7 emu g^{-1} (nanocomposite 1). The coercive fields (H_c) are 327.5 Oe (nanocomposite 3), and 136.4 (nanocomposites 2 and 1). These results, combined with the squareness ratio (M_R/M_S) indicate the better response of nanocomposite 3 to the applied magnetic field, probably due to the higher iron oxide content that results in larger Fe₃O₄ particles and/or aggregates.⁵¹ Even though it is clear that the magnetization saturation values decrease with lower Fe₃O₄ contents in the nanocomposites, the EPR and VSM results combination shows that all nanocomposites still maintain their pronounced ferromagnetic character.



Figure 6. VSM curves for all nanocomposites. The inset shows an amplification from –370 Oe to 370 Oe used to define Mr and Hc parameters.

Figure 7 shows the Mössbauer spectra of the nanocomposites taken at room temperature. It is well resolved magnetic hyperfine patterns with no indications for superparamagnetism on the time scale of nuclear Larmor precession (i.e., magnetic fluctuations must be slower than $10^{-8} \cdot 10^{-9} \text{ s}^{-1}$) as expected for the here investigated crystallite sizes (see Table 2). Under these conditions ⁵⁷Fe Mössbauer spectra allow to discriminate various iron oxide phases by their different hyperfine parameters, i.e., primarily the isomer shift S (its value indicates the iron valency in various lattice sites), the nuclear electric quadrupole splitting QS (reflecting the deviations from cubic site symmetry), and the magnetic hyperfine field B. In addition to these for the different iron oxides specific parameters one can determine the population of lattice sites (e.g., the tetrahedral A and octahedral B sites in Fe₃O₄). Data analysis was performed

using MossWinn 4.0i software.⁵² For the fit of the spectra we used a superposition of 4 magnetic sextet patterns: one for the trivalent A site of Fe₃O₄, one for its intermediate valent B site, a further pattern of minor intensity attributed to distorted and less magnetic sites B', and one sextet for α -Fe₂O₃. The line shapes were assumed as Lorentzians with full width W. The magnetic hyperfine fields show a distribution (as typically found for nanoparticles) that is assumed to have Gaussian shape of width σ .

All magnetic patterns reveal indications for a nonrandom orientation of magnetic moments with respect to the gamma ray direction. This can be taken as an indication for a texture effect induced by the graphene sheet morphology.

For nanocomposites 1 and 2 (not 3) a further contribution is visible in the center of spectra that can be reproduced by a doublet pattern, i.e., a non-magnetic contribution, yet with a spectral weight of only a few percent, of a not well defined FeO_x .

The hyperfine parameters are summarized in Table 4. The central result from these Mössbauer data is the quantitative separation of the contributions by Fe_3O_4 and α -Fe₂O₃. The hyperfine parameters of both phases are in good agreement with literature values.^{53,54} The additional

octahedral B' site in Fe_3O_4 can be possibly associated with grain surface sites. The overall population of octahedral *versus* tetrahedral sites is about 1.7(2):1 and thus reduced against the ideal value of 2:1 for stoichiometric magnetite. A possible reason is that in our analysis we used the spectral areas as identical with site occupation without correction for differing Debye-Waller factors. While the nanocomposites 2 and 3 reveal comparable amounts of hematite, the amount in nanocomposite 1 is clearly enhanced which agrees with our XRD results.

IC photo-Fenton discoloration

IC discoloration in the absence of a heterogeneous catalyst

IC $(2.1 \times 10^{-5} \text{ mol L}^{-1})$ discoloration results by varying the H₂O₂ inputs without any nanocomposites, named photolysis, are shown in Figure 8a. These tests were conducted prior to the heterogeneous photo-Fenton IC discoloration aiming to set the H₂O₂ starting concentration. It is important to highlight that, in the absence of a heterogeneous catalyst, the IC discoloration already occurs with H₂O₂, due to its decomposition, as reported elsewhere.^{30,38} Table S1 (SI section) shows the apparent



Figure 7. ⁵⁷Fe Mössbauer absorption spectra at 300 K for nanocomposites 1 (a), 2 (b), and 3 (c).

Nanocomposite 1	Area / %	S (rel. a Fe)	B / T	QS / (mm s ⁻¹)	σ/Τ	W / (mm s ⁻¹)
Sextet magnetite site A	16(1)	0.26(1)	48.4(1)	O^a	1.2(1)	0.30ª
Sextet magnetite site B	22(1)	0.64 ^b	46.5(2)	O^a	5.9(1)	0.30 ^a
Sextet magnetite site B'	5(1)	0.64 ^a	18.3(5)	0.0(3)	3.0ª	0.30 ^a
Sextet hematite	55(2)	0.39(1)	51.3(1)	-0.15(2)	1.2(1)	0.30 ^a
Doublet	3(1)	0.50(5)		0.79(10)		0.4(1)
Nanocomposite 2						
Sextet magnetite site A	22(1)	0.26(1)	48.0(1)	O^a	2.5(1)	0.30ª
Sextet magnetite site B	30(1)	0.64 ^b	45.3(2)	O^a	6.3(1)	0.30 ^a
Sextet magnetite site B'	6(1)	0.67^{a}	17.5(5)	0.23(5)	3.0(1)	0.30 ^a
Sextet hematite	40(2)	0.33(1)	50.7(1)	-0.01(3)	1.3(1)	0.30 ^a
Doublet	3(1)	0.51(3)		1.1(1)		0.6(1)
Nanocomposite 3						
Sextet magnetite site A	21(1)	0.26(1)	49.2(1)	0^{a}	1.2(1)	0.30ª
Sextet magnetite site B	30(1)	0.64 ^b	46.0(2)	O^a	3.3(1)	0.30 ^a
Sextet magnetite site B'	5(1)	0.64ª	19.0(5)	0.0(1)	2.6(1)	0.30 ^a
Sextet hematite	44(2)	0.38(1)	50.4(1)	-0.03(2)	1.2(1)	0.30ª

Table 4. Hyperfine parameters from Mössbauer spectra of nanocomposites

^aValue fixed during fit; ^bdifference of isomer shift between sites A and B fixed during fit. S: isomer shift; QS: quadrupole splitting; σ : width; W: full width.

rate constant (k_{app}) obtained by applying the pseudofirst-order kinetics fitting,⁵⁵⁻⁵⁸ from the data displayed in Figure S4, for each test and their corresponding goodness of fit (R^2) values. The descending order of k_{app} values with their respective H_2O_2 concentrations was: $1.65 \times 10^{-2} \text{ min}^{-1}$ ($2.3 \times 10^{-1} \text{ mol } \text{L}^{-1}$) > $0.55 \times 10^{-2} \text{ min}^{-1}$ ($1.2 \times 10^{-1} \text{ mol } \text{L}^{-1}$) > $0.31 \times 10^{-2} \text{ min}^{-1}$ ($0.6 \times 10^{-1} \text{ mol } \text{L}^{-1}$). These results clearly indicate a significant contribution of the H_2O_2 as the oxidizing agent. However, UV-Vis spectra of the test with the highest IC discoloration ($2.3 \times 10^{-1} \text{ mol } \text{L}^{-1}$ of H_2O_2) shows that, even in the highest [H_2O_2], the peak 611 nm does not decrease in a satisfactory magnitude, reflecting in a maximum IC discoloration below 50%. IC discoloration in function of $[H_2O_2]$ can be explained by the more available H_2O_2 molecules to be photodecomposed, leading to higher •OH radical generation (equation 4).³⁸

$$H_2O_2 + h\nu \to 2 \bullet OH \tag{4}$$

It is worth mentioning that no decrease was observed in IC discoloration with the increasing of H_2O_2 loading, as discussed elsewhere.³⁸ If an excess of H_2O_2 is added to the photo-Fenton system, it may lead to the formation of hydroperoxyl radicals (•O₂H) and water, described in equations 5 and 6.



Figure 8. IC discoloration with different H_2O_2 inputs, and without a photocatalyst (a), and UV-Vis spectra for photolysis test with the following concentrations: [IC] = 2.1×10^{-5} mol L⁻¹, and [H_2O_2] = 2.3×10^{-1} mol L⁻¹ (b).

$$H_2O_2 + \bullet OH \to \bullet O_2H + H_2O$$
(5)

$$H_2O_2 + \bullet O_2H \rightarrow \bullet OH + H_2O + O_2H$$
(6)

Furthermore, if the system is saturated with •OH radicals, they may immediately combine to form hydrogen peroxide (equation 7).

$$\bullet OH + \bullet OH \to H_2O_2 \tag{7}$$

With respect to photo-Fenton dye discoloration, products formed in equations 5, 6, and 7 are not desirable, since they are much less reactive than •OH radicals.^{59,60} For instance, •O₂H and H₂O₂ have oxidation potentials of 1.4 and 1.8 V, respectively, while •OH radicals have a much higher oxidation potential of 2.8 V. According to Figures 8 and S4 (SI section), the highest H₂O₂ concentration tested in this work (2.3×10^{-1} mol L⁻¹) seems to be below the H₂O₂ limit, this concentration being therefore selected to perform the heterogeneous photo-Fenton tests with the three synthesized nanocomposites and bulk Fe₃O₄.

Heterogeneous IC photo-Fenton discoloration

At first, the heterogeneous photocatalytic tests were carried out with a catalyst load of 0.67 g L⁻¹, 30 mL of IC solution (2.1 \times 10⁻⁵ mol L⁻¹), and 30% H₂O₂ $(2.3 \times 10^{-1} \text{ mol } \text{L}^{-1})$ (Figure S5, SI section). The choice of using this catalyst dosage was based on our previous study,³⁰ which described a Fe₃O₄/RGO nanocomposite that discolored an IC solution $(2.1 \times 10^{-5} \text{ mol } \text{L}^{-1})$ within 5 min. All nanocomposites showed to be very active in the IC photo-Fenton discoloration and presented superior IC discoloration performance than the photolysis with 2.3×10^{-1} mol L⁻¹ of H₂O₂. However, with a catalyst dosage of 0.67 g L⁻¹, it was impossible to note a significant difference among the three nanocomposites. Furthermore, due to the fast discoloration observed with all nanocomposites, a reliable acquisition of enough points to perform the kinetics calculations was prevented, thus no kinetic plots for 0.67 g L⁻¹ are presented in this work. Aiming to investigate the IC photo-Fenton discoloration kinetics with the synthesized nanocomposites, the catalyst dosage was reduced by half. Figure 9 shows the IC discoloration with a catalyst dosage of 0.33 g L^{-1} and H_2O_2 (2.3 × 10⁻⁵ mol L⁻¹), as well as the kinetic plots for each nanocomposite.

In Figure 9, a noticeable difference can be observed among the three nanocomposites. IC discoloration at 5 min for nanocomposite 3 was 93.9%, followed by nanocomposite 2 (90.8%) and nanocomposite 1 (60.7%).



Figure 9. IC photo-Fenton discoloration for the different nanocomposites with a catalyst dosage of 0.33 g L⁻¹.

It is also important to note that nanocomposite 3 reached a maximum IC discoloration of 99.7% at 30 min. Once again, even lowering the catalyst dosage by half, all nanocomposites showed to be far more active than photolysis with 2.3×10^{-1} mol L⁻¹ of H₂O₂. Furthermore, nanocomposites 3 and 2 discoloration curves showed to be higher than for bulk Fe_3O_4 . The data for the heterogeneous photo-Fenton tests (Figure S6, SI section) were also best fitted with the pseudo-first order model, as described for the tests without the heterogeneous photocatalysts. The k_{app} and R^2 values for each nanocomposite and bulk Fe₃O₄ are presented in Table S1 (SI section). The k_{app}-descending ranking was as follows: nanocomposite $3(8.99 \times 10^{-2} \text{ min}^{-1}) >$ nanocomposite 2 (8.51 × 10^{-2} min⁻¹) > Fe₃O₄ $(6.13 \times 10^{-2} \text{ min}^{-1}) > \text{nanocomposite } 1 (3.69 \times 10^{-2} \text{ min}^{-1}).$ These results indicate that RGO improves the photocatalytic character of the Fe₃O₄ nanoparticles, except for nanocomposite 1.

This assumption can be supported by STEM-in-SEM particle counting and XRD crystallite size, which showed that Fe₃O₄ nanoparticles of 12-15 nm size (STEM-in-SEM) were successfully anchored on RGO sheets, resulting in more available particles to transform H₂O₂ molecule into •OH radicals. Furthermore, the narrower bandgap, estimated by DRS analysis, after Fe₃O₄ nanoparticles immobilization on RGO, leads to a more active photocatalyst. In addition, the slight difference in photocatalysis activity between nanocomposite 3 and 2 may be linked to their slightly different formation of α -Fe₂O₃, observed by XRD and Mössbauer analysis. Yet for these two nanocomposites, the appearance of a non-magnetic FeO_x oxide in composite 2, confirmed by Mössbauer analysis, also supports its lower activity. According to Liu et al.,61 hematite presents lower activity than other iron oxide phases in the Fenton reaction because it exhibits a high electron-hole recombination rate.

In addition, the bandgap for Fe₂O₃ reported in literature is wider than for Fe₃O₄.⁶² DRS analysis also showed that nanocomposite 2 presented a higher bandgap value than nanocomposite 3, corroborating with the observed by XRD analysis. On the contrary, nanocomposite 1 did not perform better than bulk Fe_3O_4 . This behavior can be explained by the combination of the results obtained in the characterization section. FESEM-EDX (Table 1) and EDX mapping (Figure S2) showed that nanocomposite 1 presented a high discrepancy in iron distribution through RGO sheets. This may lead to iron oxide agglomerates thus lowering its specific surface area, confirmed by textural analysis. Furthermore, the more pronounced formation of α -Fe₂O₃, and non-magnetic FeO_x, observed by XRD analysis and Mössbauer spectroscopy, may contribute to lower performance, due to its wider bandgap and higher electron-hole recombination rates.

The photo-Fenton heterogeneous IC discoloration with the Fe₃O₄/RGO nanocomposites can be summarized by equations 8-11. Firstly, when Fe₃O₄/RGO nanocomposite is irradiated by visible light, it absorbs a photon, photo exciting an electron from valence band to the conduction band. This phenomenon is responsible for creating an electron hole in the valence band (equation 8). The promoted electron (e^-) on RGO surface in contact with H₂O₂ and H⁺ generates the •OH radicals (equation 9), whereas the hole (h^+) in Fe₃O₄ combined with the water OH⁻, also results in •OH radicals. These structures attack the IC molecule, generating degradation products, leading to the discoloration of the solution.

$$\operatorname{Fe}_{3}O_{4}/\operatorname{RGO} + hv \to \operatorname{Fe}_{3}O_{4}(h^{+}) + \operatorname{RGO}(e^{-})$$
(8)

 $RGO (e^{-}) + H_2O_2 + H^+ \rightarrow \bullet OH + H_2O$ (9)

 $\operatorname{Fe}_{3}\operatorname{O}_{4}(h^{+}) + \operatorname{OH}^{-} \to \operatorname{Fe}_{3}\operatorname{O}_{4} + \bullet\operatorname{OH}$ (10)

Indigo carmine dye + •OH
$$\rightarrow$$
 degradation products (11)

Due to the best performance in IC discoloration, nanocomposite 3 was selected and a nanocomposite dosage variation study was conducted considering IC discoloration $(2.1 \times 10^{-5} \text{ mol } \text{L}^{-1})$ and H_2O_2 $(2.3 \times 10^{-1} \text{ mol } \text{L}^{-1})$ (Figures 10, S7 and Table S1, SI section). All IC discoloration curves for the three loads of nanocomposite 3 showed to be higher than the photolysis, with emphasis on 0.33 g L⁻¹ curve (IC discoloration of 99.7% at t = 30 min). Although nanocomposite 3 dosages of 0.17 and 0.07 g L⁻¹ resulted in discoloration curves higher than the photolysis test until t = 20 min, they became significantly close at the succeeding times. Therefore, these loads were not enough to observe the photocatalyst activity, and the dosage of 0.33 g $L^{\text{-}1}$ was fixed.



Figure 10. IC photo-Fenton discoloration with different dosages of nanocomposite 3.

Figures 11, S8 and Table S1 show the photocatalytic tests and results of nanocomposite 3 for different H_2O_2 inputs, performed with a photocatalyst dosage of 0.33 g L⁻¹ and 30 mL of IC solution (2.1 × 10⁻⁵ mol L⁻¹) nanocomposite. In this sense, two more tests varying the H_2O_2 concentration, and another without H_2O_2 were executed to observe if the H_2O_2 amount could be reduced in the heterogeneous photo-Fenton IC photocatalysis, without losing significant discoloration results.

As can be seen in Figure 11, S8, and Table S1 (SI section), reducing the H₂O₂ concentrations to 1.2×10^{-1} mol L⁻¹ and 0.6×10^{-1} mol L⁻¹, leads to a decrease in IC discoloration at t = 5 min, to 87.3% (k_{app} = 6.94×10^{-2} min⁻¹) and 70.1% (k_{app} = 5.02×10^{-2} min⁻¹), respectively for the nanocomposite 3. Furthermore, if H₂O₂ is completely removed from this system, a drastic activity drop is observed (IC discoloration at t = 5 min equal to 39.4% and k_{app} = 0.30×10^{-2} min⁻¹). The results found for the H₂O₂ concentration study with nanocomposite 3 (0.33 g L⁻¹), compared with the tests without a heterogeneous photocatalyst, clearly indicate that the presence of the Fe₃O₄/RGO nanocomposite is responsible for facilitating the •OH radical formation, thus improving the IC discoloration.

Fe₃O₄/RGO nanocomposite reuse tests

The reuse tests for nanocomposite 3 are shown in Figure 12. In Figure 12a, it is observed that nanocomposite 3 remained its outstanding activity (ca. 99%) after 30 min for, at least, three recycles or four runs, while Figure 12b reflects the UV-Vis spectra of the withdrawn aliquots.



Figure 11. IC photo-Fenton discoloration with different H_2O_2 concentrations and nanocomposite 3 (0.33 g L⁻¹) (a), UV-Vis absorption spectra obtained for each time interval for IC photo-Fenton discoloration with nanocomposite 3 (0.33 g L⁻¹) with the following concentrations: [IC] = 2.1×10^{-5} mol L⁻¹, and [H_2O_2] = 2.3×10^{-1} mol L⁻¹.



Figure 12. IC photo-Fenton discoloration curves for nanocomposite 3 recycling tests (a), UV-Vis absorption spectra obtained for each time interval for IC photo-Fenton discoloration with the third reuse of nanocomposite 3 (0.33 g L⁻¹) with the following concentrations: $[IC] = 2.1 \times 10^{-5} \text{ mol } L^{-1}$, and $[H_2O_2] = 2.3 \times 10^{-1} \text{ mol } L^{-1}$ (b).

Figures 13a-13b show the XPS analysis of fresh nanocomposite 3, and after its third recycle. The Fe2p spectra comparison (Figure 13a) indicates that $Fe2p_{3/2}$ and Fe2p_{1/2} photoelectron peaks did not have any significant displacements for both samples, as well as the spin-orbit splitting, which remained at 13.6 eV. After a thorough $Fe2p_{3/2}$ peak fitting with the parameters described by Biesinger et al.,63 it was observed that the Fe^{III}/Fe^{II} ratio persisted at 1.9. These results are strong evidence that RGO stabilizes the Fe^{III}/Fe^{II} pair, maintaining its activity, and by mitigating the electron (e^{-}) -hole (h^{+}) recombination, a critical phenomenon that is responsible for the deactivation of photocatalysts.^{55,56,58} However, higher RGO amounts, as observed by XRD for nanocomposites 2 and 1, lead to α-Fe₂O₃ formation, changing the nanocomposite physicalchemical properties, thus reducing its photocatalytic activity. Moreover, other works that synthesized different semiconductor oxides/RGO nanocomposites observed that adding low amounts of RGO is crucial for maintaining their photocatalytic activity,^{22,24,64} supporting that higher RGO contents above an optimal RGO load result in lower performances.

Critical assessment of IC discoloration with Fe $_{3}O_{4}/RGO$ nanocomposites

One concern about heterogeneous Fenton-like reactions with H_2O_2 is that the generated •OH radicals have very short half-life, meaning that these structures can be rapidly transformed before attacking the pollutant molecule in bulk solution, thus reducing the system efficiency.⁶⁵ In this sense, Xu *et al.*⁶⁶ designed a nanoreactor of halloysite



Figure 13. Fe2p XPS photoelectron spectra (a), and Fe2p_{3/2} peak fitting (b) of fresh and reused (3 recycles, or 4 runs) nanocomposite 3.

nanotubes internally loaded with Fe₃O₄ nanoparticles (Fe₃O₄@HNTs), aiming to increase the reaction medium confinement, thus improving radicals utilization in methyl orange (MO) dye discoloration. This author indeed observed that in the condition with nanoconfinement, MO discoloration was significantly improved. Furthermore, by using radical scavenging experiments, this author also observed that besides •OH radical, the formation of ¹O₂ also has crucial role in MO discoloration. Therefore, the presence of other reactive oxygen species cannot be discarded. Thus, quenching experiments are suggested to improve understanding of the IC degradation mechanism for further works.⁶⁷ Nevertheless, in our work, RGO was used to anchor and stabilize Fe₃O₄ nanoparticles, and especially for nanocomposite 3. Besides its high Fe₃O₄ load we can observe that it presented low nanoparticle mean size (Figure 1c and Table 1), improved textural properties such as high surface area (Table 1), and mesoporous structure (Figure S3, SI section). Thus, these properties may provide favorable conditions to the continuous reactive oxygen species generation and its further utilization, as well as the IC dye adsorption onto Fe_3O_4/RGO active sites, once these reactions are known to occur mostly on the heterogeneous catalyst surface.⁶⁸ This hypothesis can be endorsed by Figure 11a, which shows that the increase in $[H_2O_2]$ for nanocomposite 3 reflects in a higher and faster IC discoloration.

Table 5 brings information about IC discoloration in the presence of distinct photocatalysts from other works. References,⁶⁹⁻⁷² not discussed in the text, are displayed only in Table 5 for comparison purposes. Considering the maximum discoloration, the time to reach it, and

Table 5. Indigo carmine (IC) heterogeneous catalysis discoloration results of different works found in literature

Catalyst	IC/catalyst mass ratio	Maximum IC discoloration / %	$k_{app}^{a} / (10^{-2} \text{ min}^{-1})$	Recycles (discoloration) / %	Reference
Fe ₃ O ₄ /RGO	0.02	99.9 (5 min)	_	1 (ca.100)	30
Fe ₃ O ₄	0.03	97.8 (60 min)	6.13	-	present work
Fe ₃ O ₄ /RGO (nanocomposite 1)	0.03	96.3 (60 min)	3.69	-	present work
Fe ₃ O ₄ /RGO (nanocomposite 2)	0.03	99.2 (30 min)	8.51	-	present work
Fe ₃ O ₄ /RGO (nanocomposite 3)	0.03	99.7 (30 min)	8.99	3 (99.0)	present work
Pd-ZnS/RGO	0.02	100 (210 min)	2.19	-	55
Co-ZnS/RGO	0.02	100 (180 min)	3.10	-	56
WO ₃	0.5	90 (120 min)	1.83	3 (70.0)	57
ZnBi ₂ O ₄ /RGO	0.05	91 (75 min)	3.20	3 (84.6)	58
Sn/Al ₂ O ₃	0.05	100 (40 min)	-	-	69
g-C ₃ N ₄	0.04	ca. 100 (50 min)	3.74	-	70
ZnO-Fe ₃ O ₄ /Kaolonite clay	0.006	100 (70 min)	5.20	4 (98.0)	70
Ni-BaMo ₃ O ₁₀	0.01	98.0 (180)	4.29	4 (98.0)	72

^aPseudo-first order fitting. RGO: reduced graphene oxide.

the k_{app} values, the present work shows quick IC photo-Fenton discoloration, and very active Fe₃O₄/RGO nanocomposites, with emphasis on nanocomposite 3. Furthermore, some works listed in Table 5 also performed photocatalyst recovery and new IC discoloration cycles. As aforementioned, our Fe₃O₄/RGO nanocomposites possess a strong magnetic character, providing an easy recovery method for succeeding IC discoloration cycles. Comparing it with the literature on the recycling capability of nanocomposite 3, one can infer that this is promising. In addition, this work did not use any initial pH correction or sonification and was carried out at room temperature, leading to a simpler IC discoloration system.

A facile two-step method to anchor and disperse high loads of Fe₃O₄ over RGO sheets was successfully adapted from the Stöber-like³¹ method, resulting in very active nanocomposites for IC discoloration. With this approach, we were able to employ cost-effective reagents and mild temperature (60 °C) during iron particles nucleation, which are important aspects that could result in scalable processes for environmentally friendly nanocomposites production, as discussed elsewhere.⁷³⁻⁷⁶

In this sense, the facile synthesis, physical-chemical properties, reusability, and simplicity of the photo-Fenton system described, is a set of features that can be considered, aiming to contribute to the remediation of dye-containing wastewater. Furthermore, adding low amounts of RGO to iron oxide/RGO nanocomposites might be attractive once iron oxides are abundant, thus cost-effective.

Conclusions

 Fe_3O_4/RGO nanocomposites were synthesized with different precursor ratios (Fe(NO₃)₃.9H₂O:GO) and evaluated in the photo-Fenton discoloration of indigo carmine. The materials were characterized, and their physical-chemical properties were associated with their performances in the indigo carmine photo-Fenton discoloration.

Microscopic analysis showed that the nanocomposites with higher iron precursor loads resulted in well-distributed iron oxide nanoparticles on RGO sheets. In parallel, XRD patterns and Mössbauer spectra showed that lowering the Fe(NO₃)₃.9H₂O:GO ratio leads to the formation of a crystalline α -Fe₂O₃ phase, and formation of a non-magnetic FeO₃.

The photocatalyst with the best performance in indigo carmine $(2.1 \times 10^{-5} \text{ mol L}^{-1})$ photo-Fenton discoloration was the nanocomposite 3 ((Fe(NO₃)₃.9H₂O:GO) mass ratio of 17:1). With a photocatalyst dosage and H₂O₂ concentration of 0.33 g L⁻¹ and 2.3 × 10⁻¹ mol L⁻¹, respectively, IC discoloration reached 99.7% (k_{app} = 8.99 × 10⁻² min⁻¹), at

30 min of reaction. The well-dispersed Fe_3O_4 nanoparticles can explain this outstanding activity on RGO sheets, BET surface area (74 m² g⁻¹), and narrower bandgap.

The magnetic properties of the nanocomposites, proven by the VSM analysis, contributed to facilitate their removal from the system in the reuse tests. Nanocomposite 3 could be reused at least three times without significant activity loss. XPS analysis showed that the Fe^{III}/Fe^{II} surface ratio did not change after the third recycle, meaning that RGO sheets are responsible for stabilizing the Fe₃O₄ nanoparticles by hindering electron-hole recombination.

In conclusion, Fe_3O_4/RGO nanocomposites are proving to be promising photocatalysts. Their physical-chemical properties lead to remarkable dye discoloration results, and their reusability is important in reducing operational costs. Furthermore, their facile synthesis could motivate new studies such as scalability and other applications.

Supplementary Information

Supplementary information (EDX mapping, BET surface area and pore size distribution, IC discoloration curves and data) is available free of charge at http://jbcs. sbq.org.br as PDF file.

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Author Contributions

Arthur Gonçalves was responsible for conceptualization, methodology, investigation, formal analysis, writing-original draft, review and editing; Pedro Siciliano for methodology, investigation, writing original draft, review and editing; Carla Moreira for methodology, investigation, formal analysis, writing original draft; Odivaldo Alves for conceptualization, formal analysis, writing original draft; Alexander Caytuero for methodology, formal analysis, investigation; Elisa Saitovitch for conceptualization, methodology, formal analysis, writing-review and editing; Jochen Litterst for conceptualization, methodology, formal analysis, writing-review and editing; Deborah Cesar for conceptualization, methodology, investigation, formal analysis, supervision, writing-review and editing; Cristiane Henriques for conceptualization, methodology, funding acquisition, investigation, formal analysis, supervision, writing-review and editing; Alexandre Gaspar for conceptualization, methodology, funding acquisition, investigation, formal analysis, supervision, writing-review and editing.

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