

Synthesis of GO/ γ -Fe₂O₃ for Application in Solid-Phase Dispersive Magnetic Microextraction for Determination of Pesticides at Ultra-Trace Levels in River Water Samples by HPLC-DAD

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Nanocomposites of GO/ γ -Fe₂O₃ were used for magnetic dispersive solid-phase microextraction (m-d- μ -SPE) of six pesticides from river water samples, followed by the determination using high-performance liquid chromatography-diode array detection. The synthesis of the nanocomposites is described and characterized using Fourier transform-infrared spectroscopy, X-ray diffraction, and scanning electron microscopy. A central composite design was used to optimize the extraction time, sample solution pH, and adsorbent amount. The solvent type and volume for desorption and the effect of the ionic strength for adsorption were also investigated. The optimum adsorption conditions were achieved at 84 min of extraction time, pH 5.4, 115 mg of adsorbent, and 1% (m/v) of NaCl, while the desorption solvent selected was 1.0 mL of methanol-acetic acid (9:1, v/v). The limits of detection ranged from 0.1 to 0.9 $\mu\text{g L}^{-1}$, and a good precision was achieved with relative standard deviation (RSD) lower than 7.6% (n = 10). The accuracy of the method was accessed by recovery tests ranging from 82 to 117% (n = 3, RSD < 8%).

Keywords: graphene oxide, pesticides, pre-concentration, high-performance liquid chromatography, experimental design

Introduction

Brazil is the one of the largest pesticide consumer in the world,¹ in 2022, 652 new products were authorized by the Brazilian government, totaling 2182 new products approved in the last four years. The Conselho Nacional do Meio Ambiente (CONAMA) is the government agency responsible for monitoring water quality by the resolution No. 357/2005;² however, there are still few actions to monitor and remediate residues of these contaminants in the aquatic environments.³ On the other hand, some studies³⁻⁹ have pointed to the occurrence of several pesticide residues in aqueous matrices throughout Brazil, including drinking water. As a result, the development of sensitive analytical methods that are also simple for monitoring pesticide residues in aqueous matrices is crucial, particularly in surface water.

Generally, pesticides in environmental samples are determined by chromatographic techniques such as gas chromatography (GC) and high-performance liquid chromatography (HPLC).¹⁰ Due to its low concentration ($\mu\text{g L}^{-1}$ and ng L^{-1}) and matrix coexisting interference in real samples, a sample pretreatment step prior to instrumental analysis may be necessary.¹¹ Sample preparation and pre-concentration methods could enrich the target analytes, significantly lowering the limit of detection (LOD) and separating the analyte for potentially interfering species from the matrix.¹² Solid phase extraction (SPE) is one of the most commonly used techniques for the pre-concentration of pesticides due to its desirable features, including higher enrichment factor and low consumption of organic solvents.^{13,14} However, SPE is time-consuming, and relatively expensive.¹⁵ One of the variations of SPE, dispersive solid phase extraction (d-SPE), reduces sample preparation time because the sorbent is placed directly in contact with the liquid sample containing the analytes.¹⁶ In recent years, magnetic nanoparticles (MNPs) have been used as sorbents for magnetic d-SPE (m-d-SPE).¹⁷⁻²⁰

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Compared with conventional d-SPE, m-d-SPE has advantages such as easier and faster separation, and the MNPs can be reused or recycled.^{17,21} Additionally, some applications of m-d-SPE use small amounts of sorbents (mg or μ g). The m-d-SPE in a miniaturized format is called magnetic dispersive solid-phase microextraction (m-d- μ -SPE).^{16,18}

Recently, graphene-based magnetic materials, especially graphene oxide (GO), have been reported^{19,20,22-24} as one of the most widely used sorbents in the m-d-SPE procedure for the extraction of pesticides from water. Graphene oxide consists of a carbon network based on hexagonal rings with an extensive delocalized π -electron system and many oxygen functional groups.¹⁴ This structure offers good adsorption capability due to strong π - π interactions between the aromatic ring of GO and the organic pollutants and the interactions involving the oxygen functional groups, electrostatic interaction, and hydrogen bonding.²⁵ Furthermore, the GO sheet protects the MNPs against oxidation and inhibits the leaching of nanoparticles into the aqueous solution.²⁶ Generally, iron oxides such as magnetite (Fe₃O₄) and maghemite (γ -Fe₂O₃) are the MNPs mainly used in m-d-SPE due to their low cost, low toxicity to human health, and environmental friendliness.^{16,27} Despite the many studies concerning using nanocomposite GO/iron oxide in the m-d-SPE to extract pesticides in water, most works focus on developing methods for pre-concentration of pesticides from a single class. The studies for determining mixtures of pesticides from different chemical classes in environmental samples are minimal, so we focused our work on that. Six pesticides from different chemical classes, i.e., acetamiprid, atrazine, diuron, imidacloprid, thiacloprid, and thiamethoxam (chemical structures displayed in Figure S1, presented in the Supplementary Information (SI) section), were selected for this work. Atrazine and diuron are herbicides of the triazine and phenyl urea classes used worldwide. Acetamiprid, imidacloprid, thiacloprid, and thiamethoxam are neonicotinoid insecticides and have been the fastest-growing class of insecticides on the global market.

Hence, this study aimed to develop a new method for pre-concentration and determination of pesticides at ultra-trace levels in river water samples using GO/ γ -Fe₂O₃ nanocomposite as solid phase extraction sorbent and analysis by high-performance liquid chromatography-diode array detector (HPLC-DAD). The GO/ γ -Fe₂O₃ sorbent is an environmentally friendly material with a relatively simple synthesis route and possible reuse. The proposed method presented a high sample throughput, high sensitivity, and is relatively simple.

Experimental

Chemicals and materials

Graphite powder (Grafin 996100) was provided by Nacional Grafite Company (São Paulo, Brazil). Sulfuric acid (H₂SO₄, 95 wt.%), acetic acid (C₂H₄O₂, 99.7 wt.%), ammonium hydroxide (NH₄OH, 28 wt.%), and ferric nitrate nonahydrate (Fe(NO₃)₃·9H₂O) were acquired from Vetec (Rio de Janeiro, Brazil). Sodium chloride (NaCl), sodium nitrate (NaNO₃), potassium permanganate (KMnO₄), phosphoric acid (H₃PO₄, 85 wt.%), and hydrogen peroxide (H₂O₂, 30 wt.%) were obtained from Isosfar (Duque de Caxias, Brazil). Ferrous sulfate heptahydrate (FeSO₄·7H₂O) was purchased from Sigma-Aldrich (São Paulo, Brazil). HPLC-grade acetone, acetonitrile, and methanol were obtained from Vetec (Rio de Janeiro, Brazil), Êxodo Científica (Sumaré, Brazil), and Dinâmica Química Contemporânea (Indaiatuba, Brazil), respectively.

Analytical standards acetamiprid, diuron, imidacloprid, thiacloprid, and thiamethoxam were purchased from Dr. Ehrenstorfer GmbH (Augsburg, Germany), and for atrazine, the analytical standard was purchased from Sigma-Aldrich (São Paulo, Brazil). To prepare stock solutions of the pesticides (1000 mg L⁻¹), a suitable mass of the analytes in acetonitrile was dissolved, and an appropriate dilution of these solutions was applied to obtain the work solution daily. Ultrapure water was collected from a Gehaka purification system (São Paulo, Brazil). All standard solutions were stored at 4 °C in light-protected flasks.

Instrumentations and chromatographic conditions

The sorbent was synthesized and characterized before being used for pre-concentration and analysis of pesticides. To confirm the phases formed in the composite, X-ray diffraction (XRD) was performed (Rigaku Miniflex II diffractometer; Rigaku, Japan), using Cu K α radiation ($\lambda = 1.5405 \text{ \AA}$), in the range of $5^\circ < 2\theta < 70^\circ$ and step size of 0.05° . The morphology of magnetic nanoparticles was observed using a JSM-7100F microscope (FE-SEM, JEOL, Japan) with an acceleration voltage of 15 kV and without a metallic covering. Fourier transform infrared (FTIR) spectroscopy (Spectrum One, PerkinElmer, USA) of the nanoparticles was recorded using KBr discs, 4000 to 400 cm⁻¹ range, 4 cm⁻¹ of resolution, and 20 scans.

Chromatographic analyses were carried out in a HPLC system (Agilent 1260 Infinity, Agilent Technologies, USA) equipped with a degasser, a high-pressure quaternary pump, an autosampler with 20.0 μ L sample loop, and a diode array detector. ChemStation software was utilized to control the

system and to acquire and analyze the data. The separation was conducted on a reversed-phase Pursuit 5 C18 column (250 mm \times 4.6 mm internal diameter (id), 5.0 μ m, Agilent Technologies, USA) at 25 °C. The mobile phase was (A) water containing 0.05% phosphoric acid and (B) acetonitrile at a flow rate of 1.0 mL min⁻¹. The gradient elution was performed as follows: from 0 to 3 min, 75% A; from 3 to 13 min, a linear gradient from 25 to 90% B; from 13 to 17 min, 90% B; from 17 to 24 min, 75% A. The DAD monitoring wavelengths were chosen at 220 nm for atrazine, 270 nm for imidacloprid, 244 nm for acetamiprid and thiacloprid, and 250 nm for diuron and thiamethoxam, respectively. The sample injection volume was 20.0 μ L. A pHmeter, model 350M (Analyser, Brazil), was used to regulate the pH of the sample solution. To carry out the adsorption experiments, an SK 180-PRO horizontal orbital shaking (Scilogex, USA) at 400 rpm was used, while for the desorption experiments, a vortex agitator, model AV (Sieger, Brazil), was used.

Synthesis of GO/ γ -Fe₂O₃

The Hummers method²⁸ synthesized the graphene oxide after some modifications, as reported by Soares *et al.*²⁹ Firstly, graphite was treated with HCl (1.37 mol L⁻¹) to remove impurities. Graphite (0.2 g) and NaNO₃ (0.25 g) were mixed in a 500 mL round bottom flask. Then, 11.5 mL of H₂SO₄ (95 wt.%) was added to the flask, which was immersed in an ice bath followed by magnetic stirring. An amount of 1.5 g KMnO₄ was added gradually under stirring, and the mixture temperature was kept below 10 °C. After that, the ice bath was removed, and the temperature was increased to 35 °C and stirred for 2 h. Then, 80 mL of distilled water was added and stirred at 90 °C for 30 min. So, 60 mL of H₂O₂ (2.94 mol L⁻¹) was added and stirred for 60 min. Finally, the GO was separated by centrifugation and washed with 20 mL of H₂O₂ (2.94 mol L⁻¹), 20 mL of H₂SO₄ (0.5 mol L⁻¹), and distilled water until pH 6. After washing, the solution was filtered in a 0.45 μ m nylon membrane and dried at 50 °C for 15 h to obtain GO powder.

The GO/ γ -Fe₂O₃ nanocomposite was synthesized by chemical coprecipitation *in situ* of Fe²⁺ and Fe³⁺ ions using NH₄OH (28 wt.%) in the presence of GO.³⁰ The magnetic nanocomposite was prepared by suspending 0.6 g GO in 300 mL of a solution containing 6.3 g FeSO₄·7H₂O and 18.3 g Fe(NO₃)₃·9H₂O at room temperature under an N₂ atmosphere. After stirring the solution for 5 min, 25 mL of NH₄OH (28 wt.%) was added dropwise, followed by additional stirring for 30 min. Then, the composite was separated by centrifugation and washed with distilled water until pH 6. Subsequently, the nanocomposite was dried by vacuum, and finally, 5.9 g of GO/ γ -Fe₂O₃ was obtained.

Sample collection

Surface water samples were collected from rivers near agricultural areas located in Minas Gerais and Rio de Janeiro states, Brazil, and named as P1, P2, P3, P4, and P5 (sampling sites are presented in Table S1 and Figure S2, SI section). The water samples were collected in pre-cleaned glass bottles, filtered through a 0.45 μ m membrane filter, and stored no more than a week in dark containers at 4 °C until analysis.

Extraction procedures for selected pesticides

Optimization of the m-d- μ -SPE conditions

The optimum conditions for the extraction method were determined in two steps. The domain of the factors time of extraction, pH of sample solution, and amount of adsorbent was optimized using a central composite design consisting of eight points in the kernel part (2³), six points in the star part, and six replicates of the central point. The experimental parameters were optimized as follows: the different amounts of adsorbent (20 to 120 mg) were dispersed in 50 mL of water and spiked with 1.0 mg L⁻¹ of each pesticide. Then, the pH of the sample solutions was adjusted in the range of 3.0-8.0. The extraction of analytes was achieved by shaking the sample for times ranging from 20 to 120 min. Then, HPLC-DAD was used to determine the concentration of pesticides in the supernatant. All data treatment was carried out using RStudio software version 3.5.3.³¹

Afterward, the effect of desorption solvent type, volume, and ionic strength were investigated one at a time to obtain the highest extraction efficiency for the m-d- μ -SPE approach. All experiments were performed in triplicate. Briefly, 20 mg of adsorbent was dispersed into 10 mL of sample aqueous solutions containing pesticides at 50 μ g L⁻¹. After stirring for 84 min, the adsorbent was collected, and the eluent was added to desorb the analytes. Several solvents, including acetone, acetonitrile, a mixture of acetonitrile-water/phosphoric acid (2.5:7.5, v/v), methanol, and methanol-acetic acid (9:1, v/v), were evaluated for desorption of pesticides. The influence of the solvent volume on the desorption efficiency of the analyte was investigated. To evaluate the effect of this parameter, 0.5, 1.0, and 1.5 mL of solvent were utilized. Finally, the effect of salt concentration (NaCl, m/v%) was investigated from 0 to 10% m/v.

Magnetic dispersive solid-phase microextraction procedure

The optimized procedure was, firstly, adjusting the pH (5.4) and ionic strength (NaCl, 1% m/v) of the water sample.

For the m-d- μ -SPE procedure, 115 mg of GO/ γ -Fe₂O₃ was dispersed in a centrifuge tube with 50 mL of the water sample, and then the extraction was performed under constant shaking on a slow-moving platform shaker at 400 rpm for 84 min. A neodymium magnet was placed on the outside bottom of the tube to collect the adsorbent, and then the supernatant was discarded. After that, the desorption procedure encompasses the use of 0.5 mL of methanol and acetic acid mixture (9:1, v/v) for 1 min to desorb the analytes for two times. The two desorption solutions were combined, transferred to a 2 mL microcentrifuge tube, and then dried under a mild stream of nitrogen. Finally, the residue was reconstituted in 100.0 μ L of acetonitrile and water/phosphoric acid (2.5:7.5, v/v) mixture, and 20.0 μ L was injected into the HPLC for analysis.

Adsorption study

After optimizing conditions, the adsorption capacity for GO/ γ -Fe₂O₃ was determined by measuring the residual pesticide concentration in water. The studies were carried out by preparing standards at concentrations ranging from 0.5–12.0 mg L⁻¹ by diluting the stock solution (100 mg L⁻¹) with ultrapure water. The GO/ γ -Fe₂O₃ nanocomposite (115 mg) was dispersed in 50 mL of aqueous pesticide solutions (pH 5.4, NaCl 1% m/v). After shaking at room temperature for 84 min, the solid phase was separated by an external magnetic field. The supernatant was filtered and then analyzed by HPLC-DAD to determine the concentration of pesticides. Subsequently, the adsorption was calculated using equation 1:

$$q_e = \frac{V}{m}(C_0 - C_e) \quad (1)$$

where q_e is the adsorption capacity (mg g⁻¹), V is the volume of the sample (L), m is the mass of adsorbent (g), C_0 is the initial concentration (mg L⁻¹), and C_e is the residual concentration (mg L⁻¹) of analytes in the solution produced after adsorption.

The experimental data investigated were fitted to the two most common isotherm models of Langmuir and Freundlich (equations 2 and 3).³² OriginPro 2016³³ software was used to obtain the adjusted non-linear adsorption isotherms.

$$q_e = \frac{q_m K_L C_e}{(1 + K_L C_e)} \quad (2)$$

$$q_e = K_F C_e^{1/n} \quad (3)$$

where C_e is the residual concentration of analytes (mg L⁻¹), q_e is the experimental adsorption capacity (mg g⁻¹), q_m is the maximum adsorption capacity (mg g⁻¹), K_L is the Langmuir constant (L mg⁻¹), K_F (L g⁻¹) and n are the Freundlich constants that represent the adsorption capacity and intensity, respectively.

Recovery and reuse of the adsorbent

The reusability of the GO/ γ -Fe₂O₃ adsorbent was carried out by performing adsorption-desorption experiments. After each extraction process, the used adsorbent (115 mg) was washed with 30 mL of deionized water, followed by 40 mL of methanol (10 mL \times 4). The adsorbent was magnetically collected and dried at 50 °C for 2 h. The retrieved GO/ γ -Fe₂O₃ was applied for the extraction experiment under the optimized conditions. Each extraction experiment used 50.0 μ g L⁻¹ of pesticide sample solution. The retrieved GO/ γ -Fe₂O₃ were analyzed using FTIR.

Results and Discussion

Characterization of GO/ γ -Fe₂O₃

The X-ray diffraction measurements for GO (Figure 1a) show a characteristic profile with a strong diffraction peak at 2θ around 10.9°, corresponding to the interlayer distance (d) of 0.814 nm. The typical diffraction peak for graphite at $2\theta = 26^\circ$ was not found, showing that the prepared GO was completely oxidized.³⁴ As shown in Figure 1b, the characteristic diffraction peak of the graphene oxide was not observed in the XRD pattern of GO/ γ -Fe₂O₃, which may be due to the low content of graphene oxide in the nanocomposite.^{30,35} Meanwhile, several peaks at 2θ of 30.5° (220), 35.8° (311), 43.9° (400), 54.2° (422), 57.5° (511), and 62.9° (440) are related to the γ -Fe₂O₃ nanoparticles, which agreed with the standard XRD data cards of maghemite (JCPDS 39-1346). The diffraction peak at $2\theta = 35.8^\circ$ (311) with a d -spacing of 0.252 nm was used to calculate the crystallite size of the γ -Fe₂O₃ nanoparticle using the Debye-Scherrer equation.³⁶ The calculated value was 9.7 nm, confirming the formation of nanoparticles.

The FTIR spectra (KBr) of GO, γ -Fe₂O₃, and GO/ γ -Fe₂O₃ samples are shown in Figure 2. In the spectrum of graphene oxide, the characteristic vibrational modes at around 1719 cm⁻¹ (C=O stretching) and 1055 cm⁻¹ for C–O confirms the GO formation.^{37,38} The bands at 628, 441, and 560 cm⁻¹ attributed to the Fe–O bond of maghemite are observed in the spectrum of γ -Fe₂O₃ nanoparticles, corroborating with the XRD data.^{30,39} In the spectrum of GO/ γ -Fe₂O₃,

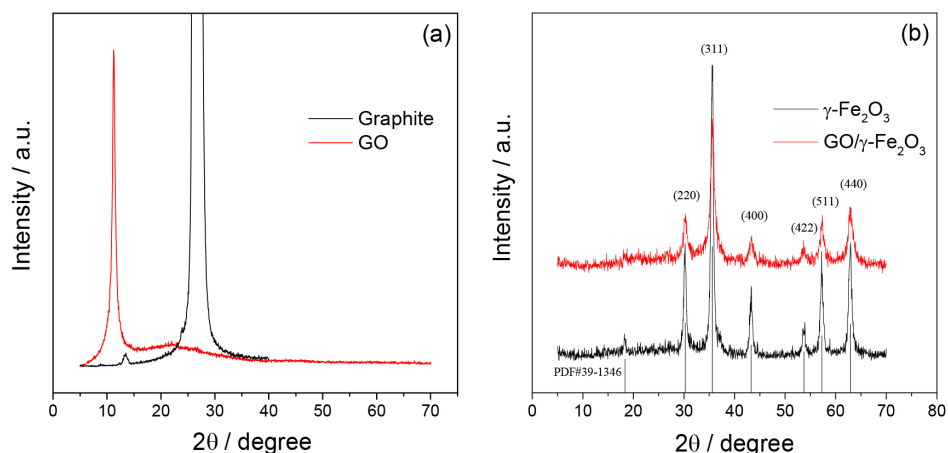


Figure 1. X-ray diffraction pattern of GO (a), γ -Fe₂O₃ and GO/ γ -Fe₂O₃ (b).

the characteristic absorption bands γ -Fe₂O₃ are observed. However, the band disappeared at 1719 cm⁻¹. It suggests that the addition of the MNPs on the graphene oxide involved chemical interactions between γ -Fe₂O₃ and GO through the carbonyl groups on the GO surface. All three materials exhibit a broad peak at 3400 cm⁻¹, attributed to the stretching vibration mode of the O–H bond from adsorbed water molecules.^{37,40}

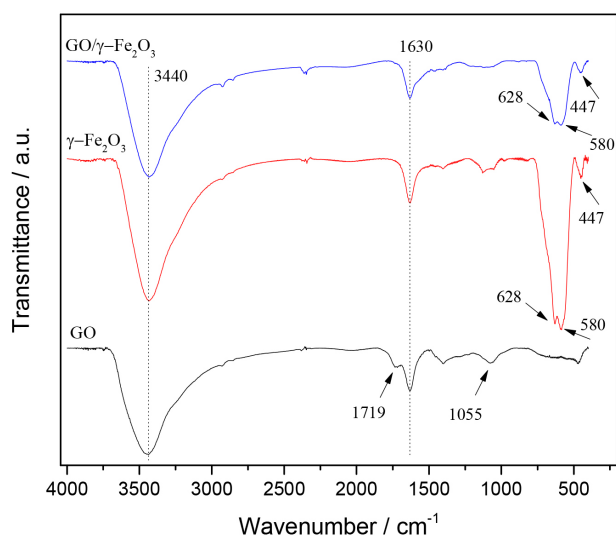


Figure 2. FTIR spectra (KBr) of GO, γ -Fe₂O₃, and GO/ γ -Fe₂O₃.

The SEM image of GO (Figure 3a) displayed a wrinkled sheet-like morphology, characteristic of graphene-based materials,²⁷ while maghemite (Figure 3b) exhibits aggregated particles with an irregular morphology. As shown in Figure 3c, graphene oxide sheets were not observed in the nanocomposite, suggesting growth of the γ -Fe₂O₃ nanoparticles over the GO surface. It confirms the FTIR results, which indicate that the γ -Fe₂O₃ was deposited on the GO surface, forming the nanocomposite successfully.

Optimization of the m-d- μ -SPE conditions

Optimization of extraction factors

The successful application of m-d- μ -SPE as a microextraction method depends on the proper optimization of the factor that can play an important role in the extraction, encompassing the time of extraction, pH of sample solution, and amount of adsorbent.^{5,41} Optimization of these parameters using a multivariate approach is recommended because it enables the simultaneous study of several variables at different levels with few experiments.⁴² This study employed a 2³ central composite design consisting of 20 experiments. The design matrix and the response (% adsorption) obtained in each experiment are shown in Table S2 (SI section).

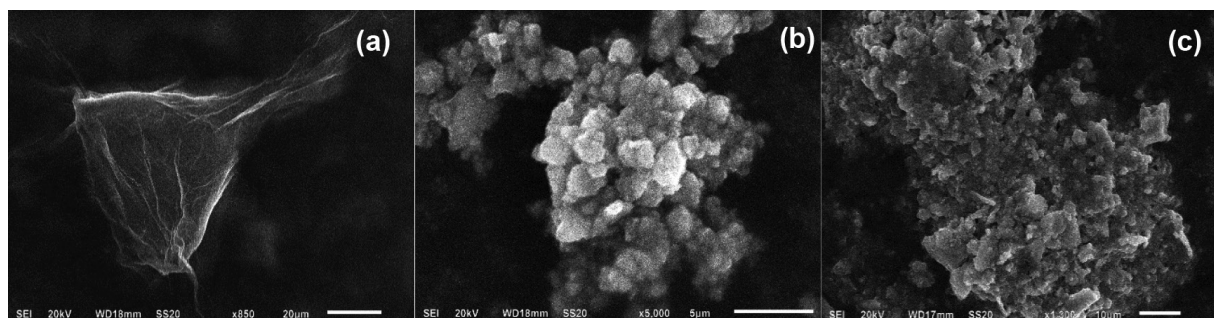


Figure 3. Scanning electron microscopy images of GO (a), γ -Fe₂O₃ (b), and GO/ γ -Fe₂O₃ (c).

The mathematical models were generated according to the experimental data, whose statistical significance of each factor and their interactions on analytical response was evaluated by the analysis of variance (ANOVA). The *p*-value was employed to estimate the statistical significance, and when the *p*-value was less than 0.05, the parameter was regarded as significant. The refined models are presented in Table S3 (SI section). According to ANOVA, the *F*-test and the *p*-values confirmed the statistical significance of the regression terms for the model and the absence of lack of fit at a 95% confidence level. The adjustment of the model was also checked through the coefficient of determination (R^2) and the residues of the models. This study of the adjusted R^2 value ranged from 0.9601-0.9933, demonstrating that the model did not explain only 1 to 4% of the total variations. The residues of the models were proven to follow a normal distribution according to a Shapiro-Wilk test (*p*-value = 0.05). The contour plot for the refined models are illustrated in Figure S3 (SI section).

The desirability function was used to obtain the optimum values for the extraction and pre-concentration methods. The desirability profile considers values between 0 and 1, where 0 indicates an undesirable response and 1 represents a completely desirable value.⁴² The optimum conditions were the extraction time of 84 min, pH of 5.4, and amount of adsorbent of 115 mg with an overall desirability of 0.991. The maximum percentage of adsorption values ranged from 46.5 to 92.0%. Figure 4 exhibits the response surface of the overall desirability function *versus* the affecting factors.

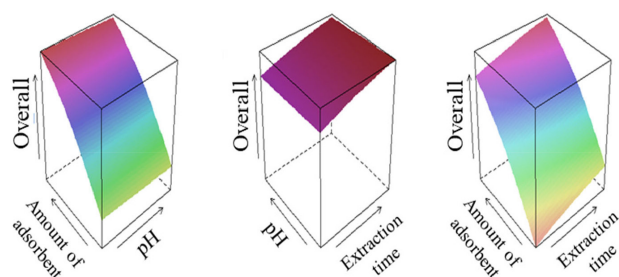


Figure 4. Response surfaces for the overall desirability obtained from the 2³ central composite designs for optimization adsorption procedure and determination of pesticides in supernatant by HPLC-DAD. Conditions: sample volume, 50 mL; concentration of the analytes, 1.0 mg L⁻¹.

Desorption conditions

Effective elution of the analytes depends significantly on the solvent, mainly for extraction of analytes with different polarities. Initially, four organic solvents, namely, acetone, acetonitrile, methanol, and a mixture of acetonitrile-water/phosphoric acid (2.5:7.5, v/v) were used for desorption of the analytes from the GO/ γ -Fe₂O₃. The results (Figure 5a) showed that methanol had better

elution ability for most pesticides, which is similar to some studies^{11,43,44} that applied graphene-based materials as adsorbents for pesticides. The elution with methanol-added acetic acid was tested to increase the efficiency of pesticide desorption. As shown in Figure 5b, methanol-acetic acid (9:1, v/v) was the best eluting solvent compared to other solvents studied. Therefore, methanol-acetic acid (9:1, v/v) was chosen for further experiments.

In addition, the influence of methanol-acetic acid (9:1, v/v) volume on the desorption efficiency of the analytes was also investigated. Figure 5b results reveal that the peak area increased with the increase of eluent from 0.5 to 1.0 mL (0.5 mL \times 2), and no noticeable difference was observed with increasing the volume of eluent from 1.0 to 1.5 mL. Therefore, 1.0 mL was selected as the optimum volume of desorption solvent.

Influence of ionic strength

Generally, adding salt can increase extraction recovery once it decreases the solubility of the analytes in the aqueous phase due to the salting-out effect. On the other hand, it can also increase the viscosity of the solution, which causes a decrease in the adsorption that may induce a decrease in extraction recoveries at higher salt concentrations.^{14,45} Different concentrations of NaCl (0, 1, 2.5, 5, and 10% m/v) were added to the sample solution to examine the influence of ionic strength on the extraction efficiency. As shown in Figure 5c, when salt content increased from 0 to 1%, the peak area of all pesticides increased. However, when salt concentration increased (i.e., 10%), the peak areas of the investigated pesticides decreased. Similar results have been reported in pesticide extraction studies^{14,17,45} by magnetic graphene-based materials. Therefore, the optimum NaCl concentration in the sample solution was fixed at 1% (m/v).

Adsorption isotherms

Adsorption isotherms allow a correlation between the amounts of solute adsorbed *per* unit amount of the adsorbent (q_e) and the residual concentration of adsorbate in solution (C_e). The adsorption isotherms of the pesticides on the GO/ γ -Fe₂O₃ nanocomposite and the isotherms fitting curves are shown in Figure 6. Table S4 (SI section) presents the key values extracted from the non-linear fitting of the data to the equations of the Langmuir and Freundlich models.

The determination coefficient obtained by the Langmuir equation ($0.9725 \leq R^2 \leq 0.9921$) is higher than that obtained by the Freundlich equation ($0.7151 \leq R^2 \leq 0.9657$),

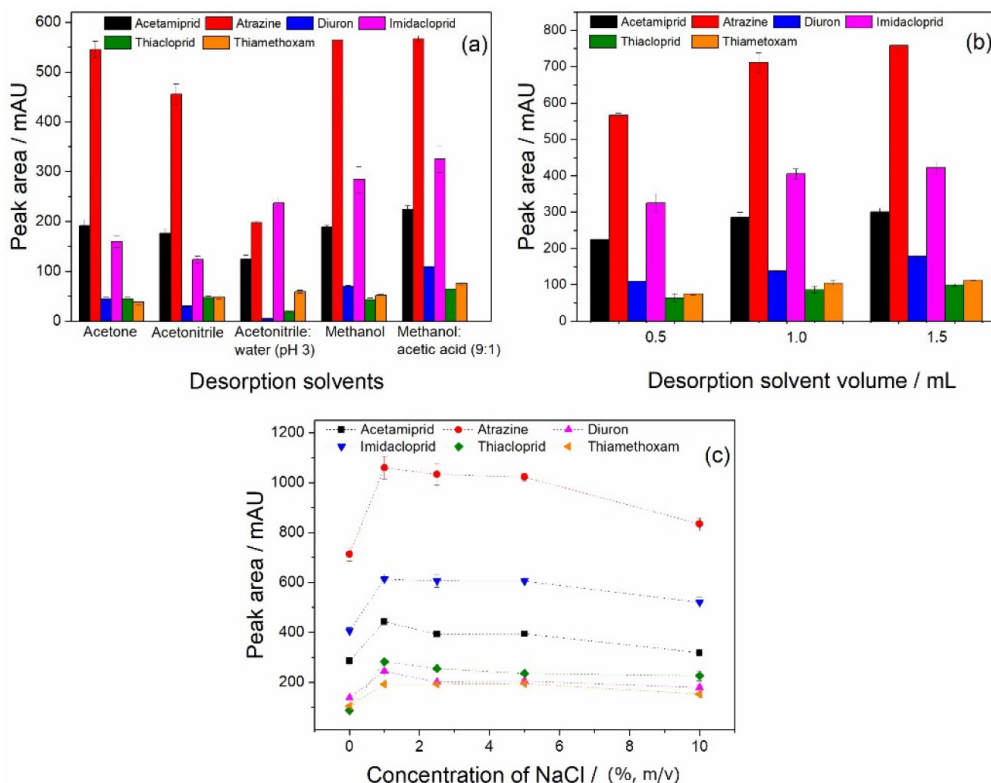


Figure 5. Effect of different parameters on the extraction efficiency of pesticides: (a) types of desorption solvent, (b) volume of desorption solvent, and (c) concentration of salt. Conditions: sample volume, 10 mL; concentration of the analytes, 50.0 $\mu\text{g L}^{-1}$; extraction time, 84 min; pH of the sample, 5.4; adsorbent amount, 20 mg; vortex time for desorption, 1 min.

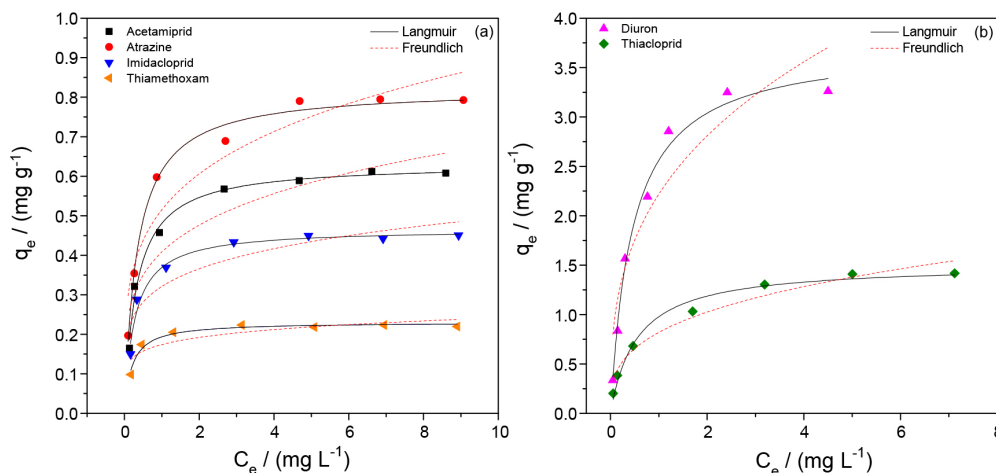


Figure 6. Experimental adsorption capacity of GO/ γ -Fe₂O₃ and Langmuir and Freundlich isotherms fitting curves for acetamiprid, atrazine, imidacloprid, and thiamethoxam (0.5–10.0 mg L^{-1}) (a); diuron (1.0–12.0 mg L^{-1}) and thiacloprid (0.5–10.0 mg L^{-1}) (b). Conditions: sample volume, 50 mL; extraction time, 84 min; pH of the sample, 5.4; adsorbent amount, 115 mg; salt concentration, 1% (m/v) NaCl.

indicating that the Langmuir model was more suitable than Freundlich for the adsorption process of selected pesticides onto the GO/ γ -Fe₂O₃. Thus, the maximum adsorption capacity (q_m) measured from the Langmuir equation for acetamiprid, atrazine, diuron, imidacloprid, thiacloprid, and thiamethoxam was calculated to be 0.63, 0.82, 3.73, 0.47, 1.51, and 0.23 mg g^{-1} , respectively. The capacities calculated by the Langmuir equation were nearly similar to

the experimental results, which suggests that it is suitable to describe the adsorption process.

Adsorption mechanism

The mechanisms involved in the adsorption of pesticides are complex and associated with different interactions. In the case of pesticide adsorption on graphene oxide-based

magnetic adsorbents, the main mechanisms reported in the literature^{19,43,45-48} are π - π interaction, electrostatic interaction, and hydrogen bonding. According to the structure of the analytes (Figure S1, SI section), one of the possible adsorption mechanisms suggested is the π - π interactions between the aromatic rings in GO/ γ -Fe₂O₃ and the delocalized π -system of pesticides. Another probable mechanism is hydrogen bonding through N-containing functional groups of pesticides and the oxygenated function groups of the adsorbent. Also, at pH 5.4, the analytes, i.e., acetamiprid ($pK_a = 0.7$) and atrazine ($pK_a = 1.7$), are in a molecular form, and the adsorption appears to be unaffected by charges on the surface of the adsorbent, even for the case of this material, that presents the point of zero charge ranging from 4-6.²⁷ In addition, the electronegative atoms (such as Cl, O, and N) belonging to the pesticide molecules act as a Lewis base. They can promote the formation of covalent bonds with iron.⁴⁹ Therefore, the possible adsorption mechanism of GO/ γ -Fe₂O₃ toward pesticides can be mainly ascribed to π - π interactions, hydrogen bonds, and covalent bonds.

Reusability of adsorbent

The reusability of the adsorbent is essential for m-d- μ -SPE applications as it can reduce the total cost and increase the sustainability of the process. Therefore, repetitive adsorption/desorption cycles were performed. After the last cycle, no carryover was observed when the adsorbent was washed with deionized water (30 mL) and methanol (10 mL \times 4). The data showed that the adsorbent could be used 6 times, at least without a significant loss in the extraction recoveries (Figure S4a, SI section). The mean extraction recoveries of adsorbent towards the six pesticides were above 80%. As shown in the FTIR spectra in Figure S4b (SI section), the characteristic bands of γ -Fe₂O₃ remain in the retrieved adsorbent after the sixth cycle. These results indicated that GO/ γ -Fe₂O₃ is satisfactorily reusable and exhibit good stability.

Analytical performance

The proposed method was validated by figures of merit under optimum conditions (84 min of extraction time, pH 5.4, 115 mg of adsorbent, 1% (m/v) of NaCl, and 1.0 mL of methanol-acetic acid (9:1, v/v) as desorption solvent). The analytical parameters of the method such as the enrichment factor (EF), limit of quantification (LOD), limit of quantification (LOQ), and precision, are summarized in Table 1. Eight spiked levels (0.5, 1.0, 2.0, 5.0, 20.0, 30.0, 50.0, and 100.0 μ g L⁻¹) in ultrapure water were prepared

and analyzed by m-d- μ -SPE followed by HPLC coupled with DAD detection to obtain the working range of the method. Acetamiprid, atrazine, imidacloprid, thiacloprid, and thiamethoxam presented a good linearity over the concentration range of 0.5-100.0 μ g L⁻¹ and 1.0-100.0 μ g L⁻¹ for diuron with a coefficient of determination ranging from 0.9961-0.9995. The results of the ANOVA (*F*-test and *p*-values) confirmed the statistical significance of the regression terms for the model and the absence of lack of fit at a 95%, moreover, the residues of the models were proven to follow a normal distribution according to a Shapiro-Wilk test (*p*-value = 0.05).

Table 1. Analytical figures of merit for determination of pesticides in water samples after the magnetic dispersive solid-phase microextraction and analysis by HPLC-DAD

Analyte	LOD / (μ g L ⁻¹)	LOQ / (μ g L ⁻¹)	EF	RSD / % (n = 10)
Acetamiprid	0.1	0.3	112	6.2
Atrazine	0.2	0.4	125	7.0
Diuron	0.9	1.6	20	7.6
Imidacloprid	0.2	0.4	156	5.7
Thiacloprid	0.3	0.6	49	3.7
Thiamethoxam	0.3	0.7	107	5.0

LOD: limit of detection; LOQ: limit of quantification; EF: enrichment factor; RSD: relative standard deviation of intraday measurements (n = 10) at the concentration level of 20.0 μ g L⁻¹.

Table 1 presents the EF calculated considering the ratio between the analyte concentration in the reconstituted solution (100.0 μ L mixture acetonitrile-water/phosphoric acid (2.5:7.5, v/v)) and the initial analyte concentration in the aqueous sample. The values obtained for acetamiprid, atrazine, diuron, imidacloprid, thiacloprid, and thiamethoxam were 112, 125, 20, 156, 49, and 107, respectively. The LOD and LOQ were calculated according to the parameters of the analytical curve and the standard errors estimated for the measurements using the chemCal package of RStudio software version 3.5.3.^{31,50,51} The LODs and LOQs of the six pesticides were in the range of 0.1-0.9 and 0.3-1.6 μ g L⁻¹, respectively (Table 1). The LOD obtained for atrazine was below the maximum residue limit (MRL) set by CONAMA Resolution No. 357/2005 for river water (2 μ g L⁻¹).² For the other selected pesticides, such as acetamiprid, diuron, imidacloprid, thiacloprid, and thiamethoxam, there is no value of MRL in the Brazilian legislation for superficial water. The short-term precision of the proposed method was investigated using intraday measurements (n = 10). Relative standard deviation was assessed for pesticide extraction and pre-concentration from spiked river water samples

(20.0 $\mu\text{g L}^{-1}$). The relative standard deviation (RSDs) varied from 3.7 to 7.6%, indicating good repeatability.

The accuracy of the method was accessed through recovery tests. Spiking standards of the pesticides carried out recovery tests into the river water samples at three concentration levels (2.0, 20.0, and 50.0 $\mu\text{g L}^{-1}$). The obtained data are shown in Table S5 (SI section). The spiked recoveries were between 82 and 117% ($n = 3$, RSDs < 8%), which indicates that the developed method is accurate and reliable. Figure 7 shows the typical chromatogram of no-spiked and spiked river water samples with six pesticides after performing the m-d- μ -SPE/HPLC-DAD analysis, where it is also possible to observe no interferences in the chromatogram.

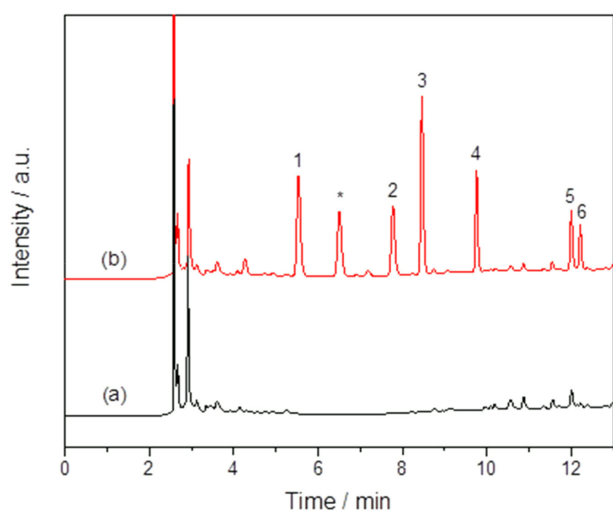


Figure 7. HPLC-DAD chromatograms (250 nm) of the river water sample extracted by GO/ γ -Fe₂O₃ based m-d- μ -SPE method for non-spiked (a) and spiked with each pesticide at the concentration of 20.0 $\mu\text{g L}^{-1}$ (b). Peak identification: (1) thiamethoxam, (2) imidacloprid, (3) acetamiprid, (4) thiacloprid, (5) atrazine, (6) diuron, (*) impurity.

Analysis of environmental water sample

The developed method was applied to analyze five surface water samples collected from rivers in the Rio de Janeiro and Minas Gerais states, Brazil. The results (Table S6, SI section) show that the neonicotinoids were undetected in river water samples (chromatograms presented in Figure S5, SI section). On the other hand, diuron was detected in one sampling point (P2), but the concentration was < LOQ. As for atrazine, it was detected in three sampling points (P3, P4, and P5 at 0.7, 1.9, and 4.4 $\mu\text{g L}^{-1}$, respectively), including the concentration in the P5 sample point that was about twice the maximum residue limit allowed by the Brazilian legislation. Therefore, the developed m-d- μ -SPE pretreatment step combined with HPLC-DAD showed satisfactory performance for analyzing pesticide residues in river water samples.

Conclusions

The use of GO/ γ -Fe₂O₃ demonstrated to be a straightforward approach for m-d- μ -SPE and determination of six pesticides in superficial water samples using HPLC-DAD analysis. The central composite design was a valuable tool for establishing the optimal extraction conditions of pesticides in the nanocomposite, also reducing interferences. The Langmuir model showed the best fit for the isotherms, and π - π interactions, hydrogen bonds, and covalent bonds were the possible adsorption mechanisms between GO/ γ -Fe₂O₃ and pesticides. The proposed method exhibited adequate LODs and acceptable accuracy and precision. The results for real samples confirmed the capacity of the method for pesticide determination in environmental conditions. In addition, the adsorbent could be recycled at least six times without significant changes in extraction recoveries. Therefore, this work demonstrated that the GO/ γ -Fe₂O₃ could be considered a promising adsorbent for the m-d- μ -SPE technique, which can potentially determine other classes of pesticides.

Supplementary Information

Supplementary data are available free of charge at <http://jbcbs.sbj.org.br> as PDF file.

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