Electrochemical determination of fenuron herbicide in water environmental samples by electro-reduced graphene oxide sensor

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Research Article

Keywords: fenuron, herbicide, sensor, graphene

Posted Date: October 13th, 2023

DOI: https://doi.org/10.21203/rs.3.rs-3428577/v1

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Additional Declarations: No competing interests reported.

Version of Record: A version of this preprint was published at Journal of Applied Electrochemistry on February 16th, 2024. See the published version at https://doi.org/10.1007/s10800-024-02073-4.
Abstract

Fenuron (FEN) is a herbicide that acts as a weed growing inhibitor in crops. Due to its persistence and good solubility in water, its presence in water bodies is emerging as a concern for aquatic species. Herein, we propose a simple development of an electrochemically reduced graphene oxide (rGO) sensor for the monitoring of FEN in water samples. The electrochemical determination of FEN showed the best performance in a 0.1 mol L$^{-1}$ NaCl solution (pH = 2.5). Differential pulse voltammetry (DPV) was performed using optimal parameters and resulted in two linear ranges (0.4–12 µmol L$^{-1}$ and 20 to 50 µmol L$^{-1}$) with high sensitivities of 6.83 and 1.9 µA µmol$^{-1}$ L, respectively, and a low LD of 0.34 µmol L$^{-1}$. Stability, reproducibility, and interference tests showed that rGO is sufficiently reliable to be used as a sensor of FEN in real samples. Spiked tap and canal water samples returned recoveries close to 100%, exhibiting no statistically significant difference when compared to a UV-Vis method by an average paired t-test, attesting the viability of the rGO modified electrode as a promising sensor of FEN in environmental water samples.

1 Introduction

Fenuron (1,1-dimethyl-3-phenylurea) is a herbicide of the phenylurea class that acts by eliminating undesirable weeds by inhibition of their photosynthetic process. It is relatively persistent in the environment due to its difficult degradation by microbial activity or through poor natural photolysis promoted by the sunlight. Moreover, the polar characteristic of fenuron (FEN) promotes its easy solubilization in water, which facilitates its presence in surface and groundwater. FEN is considered highly toxic and, along with its good solubility and chemical stability properties, it becomes an alarming issue for water bodies.$^1$–$^3$ Therefore, it is of significant importance to sensitively monitor the presence and concentration of FEN in environmental samples.

Different methods are available for the determination of FEN in water samples such as electrochemistry,$^2$ liquid chromatography,$^4$ mass spectrometry,$^5$ photo-induced fluorescence,$^6$ and electrophoresis.$^7$ Among these, the electrochemical method exhibits lower cost, simpler handling and faster analysis, besides the exclusion of organic reagents usage, and returning notable analytical parameters such as a wide concentration range and high sensitivity.$^2,^8$ Furthermore, the electrochemical response can be improved through the use of modifying agents at the surface of the electrode that is used as a detector. The increase of the signal relative to the target molecule is associated with the electron transfer kinetics of the modifier species, and its structure can be related to the selectivity of the method.$^9$

Graphene (and its derivatives) is one of the most widely used materials as electrode surface modifiers because of its capability to mediate the electron transfer at a fast rate. The pristine graphene is constituted by a bidimensional network of sp$^2$-hibrizided carbon atoms, while its derivatives possess different structural characteristics, such as defects and functional groups, which play an important role in electrocatalytic applications.$^{10}$ Graphene oxide (GO) is the best known derivative of graphene due to its tuneability, applicability, and higher yield of production. The abundant presence of functional groups all
over its structure avoids the free conductivity of electrical current, which is an issue for electrochemical applications. The removal of these functional groups in an interesting route to recover the electrical conductivity once it is able to restore the sp²-carbon atoms network.[11]

The elimination of the functional groups from the GO carbon structure can be done by thermal,[12] chemical,[13] photocatalytic,[14] and electrochemical[15] reduction methods. Although this procedure promotes the increase of electrical conductivity compared to GO, some functional groups are too stable to be removed from the structure. However, for electroanalytical purposes, the presence of some of these are essential, once they work as catalyst sites for electrochemical reactions to occur.[10] The electrochemical reduction of GO presents itself as a fast, simple, and environmentally friendly method to produce large amounts of good quality reduced graphene oxide (rGO). Moreover, by controlling the electrochemical parameters and composition of the colloidal suspension of the GO precursor, it is possible to tune the properties of the final material for specific applications.[16]

There are many publications in the literature employing different carbon materials as an electrode for the determination of several phenylurea herbicides.[17–22] However, only the publication of Mani and collaborators[17] uses a carbonaceous material to detect and quantify FEN. Their work is based on the drop casting of a GO-multiwalled carbon nanotube (MWCNT) dispersion on a glassy carbon electrode (GCE) surface to evaluate its performance to determine FEN and diuron in environmental water samples. The number of publications involving the electrochemical detection of FEN in the literature is scarce, providing only a few papers using varied materials for this purpose.[17, 23, 24]

Apart from the usage of GO-MWCNT-modified electrode as FEN electrochemical sensor, there are no other publications in the literature regarding this application using carbonaceous materials as detectors. Moreover, there is only two more published works that focus on electrochemical sensing of FEN. Abraham and Vasantha prepared a hollow polypyrrole composite as catalyst for FEN voltammetric determination in agriculture water samples.[23] In another work, Bhalla et al. detected FEN along with several other phenylurea-based herbicides through impedimetric technique using a biosensor composed of screen-printed electrodes decorated with gold nanoparticles and functionalized with anti-diuron antibodies, although this one is not a analytical study.[24]

The necessity to monitor this toxic herbicide in environmental waters along with the lack of studies developing electrochemical sensors for FEN are, fundamentally, the motivational point for the development of the present work. Therefore, we propose a simple route to produce a rGO electrode material that is able to produce notable electroanalytical parameters for FEN determination. Also, this publication presents the capability of the developed material to be employed in environmental samples, detecting the herbicide in tap water and water collected from a canal.

2 Experimental

2.1 Reagents
All the reagents employed were of analytical grade and used without any purification procedures. Graphite (≥ 99%), FEN (≥ 98%), hydrochloric acid (37%), potassium ferricyanide (≥ 99%), potassium chloride (≥ 99%), sodium chloride (≥ 99%), sodium phosphate monohydrate monobasic (≥ 98%), sodium sulphate (≥ 99%), sodium acetate (≥ 99%), sodium hydroxide (≥ 97%), sodium fluoride (≥ 99%), magnesium chloride (≥ 99%), and barium chloride (≥ 99%) were acquired by Sigma-Aldrich. Cobalt chloride hexahydrate (≥ 99.9%), copper chloride dihydrate (≥ 99%), and nickel chloride hexahydrate (≥ 98%) were purchased from Fisher Scientific. Sulphuric acid (≥ 95%), potassium permanganate (≥ 99.7%), and ethanol (≥ 99.5%) were obtained by Hexis Científica (Brazil), Quimis (Brazil), and Êxodo Científica (Brazil), respectively. Sodium iodide (≥ 99.5%) was acquired by Alfa Aesar (USA), while sodium carbonate (≥ 99.5%) was by Honeywell (USA), as well as aluminium chloride hexahydrate (≥ 99%). Sodium nitrate (≥ 99.5%), hydrogen peroxide (29%), and calcium chloride (≥ 94%) were purchased from Merck (Germany), Synth (Brazil), and VWR International (USA).

2.2 Instrumental

Electrochemical synthesis of rGO and cyclic voltammetry (CV) measurements were conducted with a Solartron 1285 potentiostat (USA) using a three-electrode system. Glassy carbon (geometric area = 0.071 cm²), lab-made Ag(s)/AgCl(s)/Cl⁻(aq) [25] and platinum wire were used as working, reference, and auxiliary electrodes, respectively. For microscopic and spectroscopic characterizations, the carbon material was deposited over a fluoride-doped tin oxide (FTO) glass electrode. Electrochemical impedance spectroscopy (EIS) and differential pulse voltammetry (DPV) measurements were performed with a CH1660E potentiostat from CH Instruments (USA).

Scanning electron microscopy (SEM) images were acquired by a Vega3 microscope from Tescan (Czech Republic) applying 20 kV of voltage and using a secondary electrons detector. Fourier-transform infrared (FTIR) spectroscopy was performed in a Frontier MIR/FIR equipment by PerkinElmer (USA) in a range between 500 and 4000 cm⁻¹ equipped with an attenuated total reflectance (ATR) accessory by Pike Technologies (USA). Raman spectroscopy was executed in a LabRAM HR Evolution by Horiba (Japan) under incidence of a 514 nm Ar laser operated at 5% of potency.

2.3 Graphene oxide preparation and its electrochemical reduction

GO was prepared using a modified Hummers method proposed by Chen et al.[26] Firstly, a mixture containing 1.0 g of graphite, 1.0 g of sodium nitrate, and 46.0 mL of sulphuric acid was stirred in an ice bath for 4 h. Then, 6.0 g of potassium permanganate was carefully added to the mixture, which was continuously stirred for an additional 2 h at room temperature. After that, 92.0 mL of deionized water was added dropwise and then the reaction flask was submitted to a hot water bath (95°C) for 15 min. Then, 200 mL of deionized water (40°C) and next 20.0 mL of hydrogen peroxide were added. The generated sludge-like suspension was centrifuged and washed several times with hydrochloric acid (10%) and deionized water. The precipitate was dried for 36 h at 50°C, then crushed to a fine powder with a pestle and mortar.
The rGO material was deposited electrochemically by CV using a single procedure. As precursor, a 10 mL aqueous dispersion containing 1.0 mg mL\(^{-1}\) GO was prepared using 0.1 mol L\(^{-1}\) of sodium sulphate as supporting electrolyte. The dispersion was submitted to ultrasonic agitation for 10 min before every deposition. The three-electrode system was immersed in the GO dispersion and the electrodeposition was carried out over a glassy carbon electrode (GCE) surface applying 10 cycles, in a potential range from −0.5 to -1.5 V, at 10 mV s\(^{-1}\). The electrochemical deposition was performed under magnetic stirring. After that, the rGO modified electrode was carefully washed with deionized water twice to remove the excess of the supporting electrolyte salt. Then, the electrode was dried at room temperature and before every measurement, it was submitted to 20 voltammetry cycles, at 50 mV s\(^{-1}\), in a 0 to +1.2 V potential window in a 0.1 mol L\(^{-1}\) NaCl solution (pH = 2.5).

### 2.4 Water samples preparation

Two different water samples were used to evaluate the presence of FEN. Tap water was directly collected from the lab, while the canal water was collected straight from the Royal Canal in Maynooth (Ireland) by using falcon tubes. The samples were centrifuged and filtered to remove insoluble and heavy particles. A stock solution of FEN of well-defined concentration was previously prepared and added to the water samples. Finally, aliquots of the samples were diluted with the supporting electrolyte so their concentrations fell within the linear range of the proposed analytical method.

### 3 Results and discussion

#### 3.1 rGO preparation and characterization

The deposition of GO was performed by CV at 10 mV s\(^{-1}\) for 10 cycles between −0.5 and −1.5 V, and the electrochemical profile is presented in Fig. 1a. Firstly, two cathodic peaks around −0.97 and −1.34 V, which are related to the reduction of functional groups, are marked by the grey dashed lines. However, there are some functional groups that are too stable to be reduced by the conditions used in this electrochemical method. The consecutive enhancement of current at each cycle indicates the increasing amount of electro-conducting material over the working electrode surface, attesting the formation of rGO. [27, 28] Furthermore, the successful deposition is clearly observed as a black film on the surface of the electrode, with the color differing from the brownish dispersion of the higher oxidation degree precursor – the GO (not shown).[29]

The electrodeposited rGO was characterized by FTIR and Raman spectroscopies, as well as its GO precursor, and the spectra are shown in Fig. 1b. The infrared spectrum of the GO (black) shows several peaks related to the presence of oxygen functional groups generated by the process of oxidation of graphite promoted by the modified Hummers method. The peaks at 1040 and 1164 cm\(^{-1}\) are related to stretching vibrations of edge and basal-localized epoxy groups. The peaks shown at 1217 and 1363 cm\(^{-1}\) are usually assigned to the presence of epoxy, hydroxyl, and phenolic groups.
Amid 1600 and 1800 cm$^{-1}$ two clear intense peaks are observed. The one at 1617 cm$^{-1}$ can be related to vibrations of ketone groups and of the bonds in water molecules, while above 1700 cm$^{-1}$ the peak can be assigned to the stretching of carbonyl bonds from different functional groups, such as ketones and carboxylic acids. At wavenumbers higher than 2900 cm$^{-1}$ the broad peak is assigned to vibrations of structurally bound hydroxyl groups or even from adsorbed water molecules, as the oxygen functional groups in GO permit good interaction of the material with polar solvents.[30, 31]

The FTIR spectrum of rGO (orange) shows a lack of peaks related to functional groups, indicating that the electrochemical process is efficient at removing most of them, although there are some weak residual peaks that are still observable. Moreover, a weak peak at 1549 cm$^{-1}$ is evident and this is assigned to the vibration of double bonds between sp$^2$ carbon atoms that constitute the graphitic structure that is only noticeable due to defects in their vicinities, inducing a difference in the dipole moment between the atoms.[32]

The Raman spectra of GO (black) and rGO (orange) exhibit the typical D, G, and 2D bands for graphitic-structured materials. The G band ($\approx$ 1580 cm$^{-1}$) is assigned to the first order scattering of the skeletal carbonaceous sp$^2$ hybridized structure and it is commonly referred as the graphitic band. On the other hand, the D band ($\approx$ 1350 cm$^{-1}$) requires structural defects for its activation. It consists of a second order scattering generated by the breathing mode of the 6-atom carbon rings, and it indicates the presence of heteroatoms, cleaved bonds, sp$^3$-hybridized carbon atoms, and other types of defect sources. Another essential Raman signal for graphitic materials is the 2D band ($\approx$ 2700 cm$^{-1}$), also known as G’. This band provides important information about the number of layers, their stacking, and the structural quality of the carbon rings.[33–35] The intensity ratio between the D and G bands is strictly associated to the degree of disorder of the graphitic species. For the studied materials, the rGO material showed a higher $I_D/I_G$ ratio of 1.68 in comparison to its GO precursor (1.59), indicating an enhancement in the degree of defects. Moreover, it is clear that this effect can be related to the formation of a higher number of smaller sized sp$^2$ carbon atom domains promoted by the electrochemical reduction process.[36, 37] The $I_{2D}/I_G$ ratio also informs the number of layers that are present, where $I_{2D}/I_G \approx 2$ is the parameter value for monolayer graphene. A ratio between 1 and 2 suggests the existence of bilayer graphene, while values lower than 1 indicate multilayer graphene. The presented materials both consist of multilayer graphene, although the higher $I_{2D}/I_G$ of 0.35 for rGO demonstrates a fewer number of graphene layers compared with GO (0.13), which is a consequence of the exfoliation and reduction processes.[38, 39]

Morphological studies of GO and rGO surfaces were performed by using SEM images and they can be visualized in Fig. 1c and d. The GO micrograph (Fig. 1c) exhibits wrinkled sheet-like morphology that is directly related to the high amount of oxygen functional groups generated by the chemical oxidation of the graphite precursor. After the electrochemical reduction process, the rGO morphology (Fig. 1d) is slightly altered. The extent of wrinkling is clearly higher, indicating the formation of a larger number of defects, such as smaller sizes of sp$^2$ carbon domains, and residual functional groups.[40] Furthermore, it is possible to observe its higher degree of transparency due to the observation of FTO particles above the
carbonaceous sheets. Lastly, it can be concluded that the electrochemical reduction produces a material with a higher degree of defects and a lower number of graphene sheets.

The electrochemistry of the unmodified GCE, GO, and rGO were studied using $K_3Fe(CN)_6$ as the electrochemical probe. The CV and EIS data were recorded in a 0.1 mol L$^{-1}$ NaCl solution using 5.0 mmol L$^{-1}K_3Fe(CN)_6$, and these data are illustrated in Fig. 2a and 2b, respectively. Regarding the CV test, it is clear that the rGO modified electrode shows higher anodic and cathodic currents as a result of its higher electroconductivity due to its larger electroactive surface area. The GO modified electrode exhibited the lowest current due to its larger number of functional groups that creates resistivity for electron flow. At 50 mV s$^{-1}$, the three materials provided satisfactory reversibility criteria, with $I_{pa}/I_{pc} = 0.99, 1.05,$ and 0.95, and $\Delta E_p (E_{pa} - E_{po}) = 130, 77,$ and 89 mV for GCE, GO, and rGO electrodes, respectively, demonstrating good electron transfer capability for all electrodes, but with lower peak-to-peak separations for the rGO. [41, 42] The electroactive surface areas of the electrodes were estimated by fitting the scan rate data to the Randles-Sevcik equation (Eq. S1). The current intensities of the redox pairs were analyzed at 10, 25, 50, 75, 100, 150, 200, and 300 mV s$^{-1}$ and the $I_{pa}$ and $I_{pc}$ vs square root of the scan rate ($v^{1/2}$) plots for GCE, GO, and rGO materials can be visualized in Fig. S1a, b, and c, respectively. Considering the electroactive species concentration ($c$) of $5.0 \times 10^{-6}$ mol cm$^{-3}$, its diffusion coefficient ($D$) of $7.3 \times 10^{-6}$ cm$^2$ s$^{-1}$, the number of transferred electrons ($n$) of 1, and the average of the $I_p/v^{1/2}$ slopes, it was possible to calculate the electroactive surface areas of the materials as 0.044 cm$^2$ for GCE, 0.008 cm$^2$ for GO, and 0.063 cm$^2$ for rGO, indicating a much higher electroactive surface area for the rGO modified GCE.

The materials were further analyzed using EIS. The spectra were acquired using 10 mV of amplitude in a range of frequencies from 10 mHz to 30 kHz under open-circuit conditions (Fig. 2b). The three spectra, represented by the Nyquist plots, exhibit a semi-circle at the higher frequencies followed by a Warburg element at the lower frequencies. These two elements are connected to the interfacial electron transfer and ionic semi-infinite diffusion, respectively. On fitting the experimental data to equivalent circuits, the solution resistances ($R_s$) were computed as 109.6, 106.1, and 108.0 $\Omega$ for GCE, GO, and rGO electrodes, respectively. Likewise, the charge transfer resistance values ($R_{ct}$), in the presence of the electroactive species, were estimated as 2846, 27836, and 352 $\Omega$ for GCE, GO, and rGO, respectively, clearly showing a more facilitated electron transfer for the rGO. The standard rate constant ($k_0$), calculated by Eq. S2, also corroborates with that conclusion. The equation involves the molar gas constant ($R = 8.3145$ J K$^{-1}$ mol$^{-1}$), thermodynamic temperature ($T = 298$ K), Faraday constant ($F = 96485$ C mol$^{-1}$), concentration of electroactive species ($c = 5.0 \times 10^{-6}$ mol cm$^{-3}$), number of transferred electrons ($n = 1$), electroactive surface area ($A = $ previously calculated). Using this relationship, the charge transfer resistance ($R_{ct}$) was used to calculate the $k_0$ values. The GCE, GO, and rGO materials showed $k_0$ values of $4.25 \times 10^{-4}$, $2.39 \times 10^{-4}$, and $2.4 \times 10^{-3}$ s$^{-1}$, respectively, resulting in a near 10-fold improvement when the GO precursor is reduced by the electrochemical method.[43]
3.2 Electrochemical oxidation of FEN by rGO modified electrode

3.2.1 Media optimization

The electrochemical oxidation of FEN by rGO was initially studied regarding the composition of the supporting electrolyte, as shown in Fig. 3a. The process was tested in five different sodium salts: NaCl, NaNO₃, NaAc, Na₂SO₄, and Na₂HPO₄ keeping the concentration of Na⁺ constant (0.1 mol L⁻¹) without changing the pH value. The anodic current peak associated with the oxidation of 100 µmol L⁻¹ FEN oxidation in the NaCl electrolyte showed the highest current intensity, providing more sensitive electrocatalytic behavior. Therefore, this electrolyte was used in all subsequent measurements.

The effect of pH over the peak potential and current of 100 µmol L⁻¹ FEN electrooxidation was also studied by CV in a 0.1 mol L⁻¹ NaCl solution that was adjusted using HCl and NaOH with assistance of a pH-meter. In Fig. 3b, it is possible to observe the peak current intensity (left y-axis; black line plots) and peak potential (right y-axis; grey line plots) of FEN electrochemical oxidation in several pH values. The most acidic pH value (2.5) exhibited the highest peak current intensity, so it was chosen to carry out the next tests due to being the better media for analytical purposes. It can be observed that the peak potential does not considerably shift from pH = 2.5 to pH = 10.0 (Eₚ/pH unit ≈ 0), which is very different to that observed by Abraham and Vasantha. The electrooxidation of FEN on the rGO modified electrode surface does not show the usual influence of the number of protons in the solution media in the mentioned pH range.

The GCE, GO, and rGO electrode materials were tested in the optimum media (0.1 mol L⁻¹ NaCl, pH = 2.5) towards electrooxidation of FEN at a concentration of 100 µmol L⁻¹ to compare their electrocatalytic activities. The results observed in Fig. 3c show that the peak potential for the oxidation of FEN shifts from 1.11 to 1.09 V when GCE was modified with GO precursor. Similarly, the current intensity increases by a factor of 1.58, proving that not only the electroconductivity of the materials are important, but their composition as well. The GO is composed of functional groups that act as catalytic sites for electrochemical reactions. The presence of reactive sites with improved electrical conductivity provides even greater results, as shown by the anodic peak of FEN detected by the rGO modified material. In this case, the peak potential is observed at 1.04 V, while the current intensity is 3.58 times higher compared to GO. This can be related to the high electrical conductivity of the rGO combined with a larger electroactive surface area, corroborating to the better performance of rGO as an electrochemical sensor.

3.2.2 Scan rate diagnostics

The electrochemical behavior of 100 µmol L⁻¹ FEN was studied by CV in a 0.1 mol L⁻¹ NaCl solution (pH = 2.5) using the rGO modified electrode at several scan rates (5, 10, 15, 25, 35, 50, 65, 80, and 100 mV s⁻¹) and the results can be visualized in Fig. 4. The CV of the process (Fig. 4a) suggests that FEN
electrochemically oxidizes in an irreversible path due to the presence of an anodic peak around 1.0 V that shifts towards higher potentials as the scan rate increases. It is possible to observe a redox pair forming at approximately 0.47 V that appears to be related to the adsorption of electroactive dimers produced by the electrochemical oxidation of phenylurea-type herbicide molecules.[46, 47]

The intensity of the anodic peak current of FEN ($I_p$) was analyzed against the scan rate ($v$) and the square root of the scan rate ($v^{1/2}$) and compared to understand the kinetic process that drives the electrochemical reaction. It was found that both curves present good linear relationship between the variables, as shown by the $R^2$ of the fitting curves of Fig. 4b, suggesting that the process can be controlled by both semi-infinite and surface diffusion paths. To confirm which process is predominant, the logarithm of $I_p$ was plotted versus the logarithm of $v$, where a slope close to 0.5 indicates a semi-infinite diffusion-controlled process, while a slope close to 1.0 means an adsorptive-controlled process. On fitting the curve using linear regression, as shown in Fig. 4c, a slope value of 0.66 was obtained, which proves the occurrence of a mixed-controlled diffusion process, although with predominance of the semi-infinite diffusion pathway.[48]

The plot of the anodic peak potential ($E_p$) against the logarithm of the scan rate (log $v$), shown in Fig. 4d, provides the estimation of the number of electrons involved in the rate-determining step of the reaction through the Tafel slope analysis (Eq. S2). The slope of the curve fitting applied to Eq. S3 results in a Tafel slope (b) of 86 mV, which is related to the transference of one electron in the rate-determining step of the reaction.[49] To corroborate this result, the Tafel slope was also extracted from the rising part of the electrooxidation of FEN at 10 mV s$^{-1}$, resulting in a Tafel slope of 88 mV, as can be observed in Fig. S2.

More details on the mechanism of the oxidation of FEN were obtained using the Equation S3.[49] Using the Tafel slope extracted from Eq. S3 and the $E_p$ vs log $v$ plot depicted in Fig. 4d, and assuming a transfer of one electron ($n = 1$) in the rate-determining step of the reaction, the electron transfer coefficient ($\alpha$) could be computed from the Eq. S4, returning in a result of $\alpha = 0.69$. Figure 5 illustrates the mechanism of the electrochemical oxidation of FEN by rGO modified electrode involving one electron and with no participation of protons, as previously verified in the pH studies.[50, 51] Additional scan rate studies were performed for the redox pair around + 0.47 V, which slopes of log $v$ vs log $I_p$ close to 1.0 (Fig. S3) confirmed a process related to the surface-confined dimer formed after successive oxidation of FEN.[46, 47]

### 3.2.3 Electroanalytical performance of rGO modified electrode for FEN determination

Electroanalytical studies for the determination of FEN by the rGO modified electrode were performed by CV at 25 mV s$^{-1}$ in a 0.1 mol L$^{-1}$ NaCl solution (pH = 2.5). The corresponding data are shown in Fig. 6a. The increase of anodic peak current around 1.05 V showed good response towards the injection of increasing concentrations of FEN producing two linear ranges: from 2.0 to 50.0 µmol L$^{-1}$ ($R^2 = 0.992$) and from 65 to 160 µmol L$^{-1}$ ($R^2 = 0.9831$). Moreover, the curve fitting (Fig. 6a, inset) provided sensitivities of
0.2 and 0.06 µA µmol\(^{-1}\) L for the former linear range and the latter, respectively. The limit of detection was estimated using Eq. S5, where \(S\) is the sensitivity and \(s_b\) is the standard deviation of 10 measurements of the blank. By applying these parameters, a LOD of 0.6 µmol L\(^{-1}\) could be found for the method.\[52\]

The electrochemical determination of FEN was also performed by the DPV technique in order to develop a more sensitive and selective method to evaluate the detection of the herbicide in water samples. Initially, the main parameters regarding the DPV technique were optimized, such as the amplitude potential (AmpE), the increment potential (IncE), and the pulse width (PW), varying one factor while keeping both others constant. The AmpE was studied from 60 to 160 mV (IncE = 8 mV; PW = 7 ms); the IncE was analyzed from 5 to 10 mV (AmpE = 120 mV; PW = 7 ms); and the PW was carried out from 4 to 9 ms (AmpE = 120 mV; IncE = 8 mV). The DPV profiles and the current intensity extracted from the data can be verified in Fig. S4, that leads to the optimum results of AmpE = 120 mV, IncE = 10 mV, and PW = 7 ms, parameters which was used for all further measurements.

The analytical curve for the DPV technique applying the optimized parameters was constructed with increasing volume injections of a FEN stock solution and the results can be observed in Fig. 6b. The baseline corrected DPV showed an increasing peak current with the increasing concentration of FEN with two identified linear ranges: from 0.40 to 12.0 µmol L\(^{-1}\) (\(R^2 = 0.9968\)) and from 20.0 to 50.0 µmol L\(^{-1}\) (\(R^2 = 0.9991\)). The most diluted linear range provided a remarkable sensitivity of 6.83 µA µmol\(^{-1}\) L while the higher concentration linear range showed a sensitivity of 1.9 µA µmol\(^{-1}\) L. Furthermore, the LOD was estimated through Eq. S5, and the value found was as 0.34 µmol L\(^{-1}\). The extracted parameters from the DPV and CV methods proposed in this work are compared with previous studies and this comparison is summarized in Table 1.

### Table 1
Analytical parameters determined by different methods in the literature for FEN electrochemical determination.

<table>
<thead>
<tr>
<th>Material</th>
<th>Technique</th>
<th>Linear range / µmol L(^{-1})</th>
<th>LOD / µmol L(^{-1})</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>GO-MWCNT</td>
<td>Amp</td>
<td>0.9–47.0</td>
<td>0.35</td>
<td>[17]</td>
</tr>
<tr>
<td>Hollow PPy/AAS</td>
<td>DPV</td>
<td>0.01–110.0</td>
<td>0.005</td>
<td>[23]</td>
</tr>
<tr>
<td>rGO</td>
<td>CV</td>
<td>2.0–50.0</td>
<td>0.6</td>
<td>This work</td>
</tr>
<tr>
<td></td>
<td></td>
<td>65–160.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>DPV</td>
<td>0.4–12.0</td>
<td>0.34</td>
<td>This work</td>
</tr>
<tr>
<td></td>
<td></td>
<td>20.0–50.0</td>
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GO-MWCNT: graphene oxide-multiwalled carbon nanotubes; PPy/AAS: Polypyrrole/alkyl aryl sulphonate; rGO: reduced graphene oxide; Amp: amperometry.
The rGO modified electrode exhibited good stability for FEN determination using the DPV technique for ten measurements in the lower concentration range and ten in the higher range. The relative standard deviation (RSD) for measurements with 4.0 µmol L\(^{-1}\) (n = 10) was 2.7%, while for measurements of 30.0 µmol L\(^{-1}\) (n = 10) it was 2.0% (Fig. 7a). The RSD was also evaluated between four different rGO modified electrodes (n = 4) returning a result of 5.1% (Fig. 7b). These results indicate good repeatability and reproducibility suggesting that the rGO is a reliable candidate for the monitoring of the FEN herbicide.

The interference test was performed using a 10-fold concentration of several ions that can be found in environmental water samples (Fig. 7c). The species studied were Ac\(^-\), Al\(^{3+}\), Ba\(^{2+}\), Ca\(^{2+}\), Co\(^{2+}\), CO\(_3^{2-}\), Cu\(^{2+}\), F\(^-\), I\(^-\), K\(^+\), Mg\(^{2+}\), Ni\(^{2+}\), NO\(_3^-\), PO\(_4^{3-}\), and SO\(_4^{2-}\). All species showed low interference (< 8%) in the anodic peak current for the oxidation of 8.0 µmol L\(^{-1}\) FEN except the I\(^-\) and SO\(_4^{2-}\) anions, that resulted in a change of the peak current intensity by 88.8% and 82.7%, respectively (Fig. 7d). Even though, it is possible to affirm that the rGO material could satisfactorily detect the FEN herbicide without great influence from the various ions that are relatively common in water samples.

Water samples from two different sources were collected, centrifuged, filtered, and spiked with a FEN stock solution to give a real sample solution of well-known concentration. Small aliquots of the samples were diluted in the 0.1 mol L\(^{-1}\) NaCl (pH = 2.5) supporting electrolyte to provide concentrations inside the linear range of the method. Two concentrations (4.0 and 8.0 µmol L\(^{-1}\)) were tested in tap and canal water samples and the results for the proposed method are presented in Table 2 and Fig. 8.

For comparison, the proposed method was compared with the determination of FEN by UV-Vis technique. A paired t-test resulted in no statistically significant difference under 95% of level of confidence due to the lower calculated t-value (0.045) compared with the t-critical value (2.201) in a two-tailed test comparison. Thereby, the proposed method to determine FEN by the rGO modified electrode through the DPV technique proved remarkably reliability in environmental water samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Spiked / µmol L(^{-1})</th>
<th>Detected / µmol L(^{-1})</th>
<th>% of recovery</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tap water</td>
<td>4.0 µmol L(^{-1})</td>
<td>4.28 ± 0.08</td>
<td>107.01 ± 2.11</td>
</tr>
<tr>
<td></td>
<td>8.0 µmol L(^{-1})</td>
<td>8.07 ± 0.1</td>
<td>100.85 ± 1.28</td>
</tr>
<tr>
<td>Canal water</td>
<td>4.0 µmol L(^{-1})</td>
<td>4.48 ± 0.01</td>
<td>112.08 ± 0.3</td>
</tr>
<tr>
<td></td>
<td>8.0 µmol L(^{-1})</td>
<td>7.76 ± 0.12</td>
<td>97.04 ± 1.47</td>
</tr>
</tbody>
</table>

### 4 Conclusion

...
The present work showed a simple method of electrode modification aiming at the determination of FEN in water samples. Morphological and spectroscopic techniques showed that the rGO modified electrodes possess better characteristics including higher electrical conductivity and electron transfer rates when compared to GCE and GO as control materials. Using DPV, the rGO electrode showed satisfactory sensitivity and selectivity for the determination of FEN, with reliable applications in the monitoring of the herbicide in environmental water samples. The lack of publications for FEN electrochemical determination shows the necessity to develop sensors for that purpose, especially with simple materials such as rGO, that shows remarkable efficiency in the electrochemical detection of FEN.

### Declarations

### Acknowledgments

The authors are grateful to CAPES (financial code 001), FAPEMIG (APQ-01207-17), FINEP, and CNPq for financial support. We also thank RELAM multiuser laboratory from the Institute of Chemistry at the Federal University of Uberlândia for providing the equipment and technical support for experiments involving scanning electron microscopy and EDS. This work was partially supported by the Brazilian Institute of Science and Technology (INCT) in Carbon Nanomaterials.

### References


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Figures
Figure 1

(a) CV deposition of GO over GCE under magnetic stirring. Supporting electrolyte: 0.1 mol L\(^{-1}\) Na\(_2\)SO\(_4\);
Parameters: 10 mV s\(^{-1}\), -0.5 to -1.5 V, 10 cycles. (b) FTIR (top) and Raman (bottom) spectra of rGO and GO. SEM images of (c) GO and (d) rGO materials.
Figure 2

(a) CV and (b) EIS profiles of the materials in a 0.1 mol L\(^{-1}\) NaCl + 5.0 mmol L\(^{-1}\) K\(_3\)Fe(CN)\(_6\) solution.
Figure 3

(a) CV study of rGO modified electrode for the optimum supporting electrolyte composition ([Na⁺] = 0.1 mol L⁻¹) of FEN electrochemical oxidation and (b) pH effect on FEN electrochemical oxidation over its peak potential (right y-axis; grey line plot) and peak current intensity (left y-axis; black line plot). (c) Electrooxidation of 100 μmol L⁻¹ FEN in 0.1 mol L⁻¹ NaCl (pH = 2.5) by GCE, GO, and rGO electrodes.
Figure 4

(a) CV of electrochemical oxidation of 100 μmol L⁻¹ FEN by rGO modified electrode at 5, 10, 15, 25, 35, 50, 65, 80, and 100 mV s⁻¹ of scan rate. (b) Plot of the anodic peak current (I_p) versus scan rate (v – bottom x-axis; black line plot) and square root of scan rate (v^{1/2} – top x-axis; grey line plot). (c) Plot of log I_p vs log v. (d) Plot of the anodic peak potential (E_p) vs log v.
Figure 5

Proposed mechanism of FEN electrochemical oxidation.

Figure 6

(a) CV determination of FEN by rGO modified electrode at 25 mV s\(^{-1}\) in a 0.1 mol L\(^{-1}\) NaCl solution (pH = 2.5). (b) Baseline corrected determination of FEN by rGO electrode material through DPV technique. Parameters: Amplitude potential = 120 mV, Increment potential = 10 mV, and Pulse width = 7 ms. Inset: analytical curves and their respective equations.
Figure 7

(a) Repeatability and (b) reproducibility tests for DPV detection of FEN by rGO modified electrode. (c) DPV response of 10-fold concentration interferents study. (d) Relative peak currents of the interferents + FEN (I) against FEN (I₀).
Figure 8

(a) DPV of the environmental water samples spiked with FEN. (b) Peak current responses of the samples.

Supplementary Files

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- rGOforFENdeterminationSupportinginformationv4.docx