

## A RAPID ELECTROCHEMICAL PLATFORM FOR DETECTING THIAMETHOXAM USING A Ni-rGO CARBON PASTE COMPOSITE

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### **Abstract**

*Neonicotinoids, such as thiamethoxam (THMX), are widely used in agriculture, leading to water and environmental contamination. Hence, the main aim of this study is to develop an innovative and cost-effective sensing material for pesticide detection. To achieve this goal, an electrochemical sensor based on reduced graphene oxide functionalized with nickel was designed. The sensor was characterized via cyclic voltammetry (CV), differential pulse voltammetry (DPV), transmission electron microscopy (TEM), energy-dispersive X-ray spectroscopy (EDS) and Fourier-transform infrared spectroscopy (FT-IR). The differential pulse voltammetry results indicate that the incorporation of nickel into reduced graphene oxide structure enhances the sensor's performance compared to the unmodified carbon paste electrode. Under optimal conditions, the Ni-rGO/CPE sensor exhibited a sensitivity of 0.66  $\mu\text{A/ppm}$ , with a detection limit of 3.96 ppm. A high correlation coefficient ( $R^2 = 0.9993$ ) suggests a strong linear relationship between thiamethoxam concentration and the sensor's electrochemical response within a linear range of 6 -93 ppm, making the sensor suitable for rapid and portable detection applications. The sensor applied to river water samples in a recovery test showed a recovery of approximately 109.94%. These results highlight the potential of carbon-based nanomaterials for the efficient, cost-efficient and simple detection of neonicotinoids in complex water matrices.*

**Key words:** *Reduced graphene oxide, electrochemical, nickel, nanomaterials, thiamethoxam.*

**Përmbledhje:**

Neonikotinoidët, siç është thiamethoxami (THMX), përdoren gjerësisht në bujqësi, duke shkaktuar ndotje të ujit dhe mjedisit, prandaj janë një objektiv kryesor i kërkimit shkencor. Qëllimi kryesor i këtij studimi është zhvillimi i një materiali inovativ dhe me kosto të ulët për detektimin e pesticideve. Për këtë qëllim, është dizenuar një sensor elektrokimik bazuar në oksid grafeni të reduktuar, të funksionalizuar me nikel. Karakterizimi i sensorit është realizuar përmes teknikave të voltametrisë ciklike (CV), voltametrisë me puls diferencial (DPV), mikroskopisë TEM, spektroskopisë EDS dhe spektroskopisë FT-IR. Rezultatet e përftuara nga DPV tregojnë se inkorporimi i nikelit në rGO çon në përmirësimin e performancës analitike të sensorit krahasuar me elektrodën pastë karboni të pamodifikuar. Ky përmirësim lidhet me rritjen e sipërfaqes elektroaktive dhe përshpejtimin e transferimit të elektronit në sipërfaqen e elektrodës. Në kushte optimale, sensori Ni-rGO/CPE shfaq një ndjeshmëri prej  $0.66 \mu\text{A/ppm}$ , me kufi diktimi dhe  $3.96 \text{ ppm}$ . Një koeficient i lartë korelacioni ( $R^2 = 0.9993$ ) sugjeron një lidhje lineare të fortë midis përqendrimit të thiamethoxamit dhe përgjigjes elektrokimike të sensorit, me një zonë lineare prej  $6\text{-}93 \text{ ppm}$ , duke e bërë sensorin të përshtatshëm në zhvillimin e pajisjeve portative për detektimin e shpejtë të pesticideve në terren. Për më tepër, shkalla e rekuperimit e përfitar në mostra reale uje, konsiderohet e pranueshme. Këto rezultate theksojnë potencialin e nanomaterialeve me bazë karboni për detektimin efikas dhe të ndjeshëm të neonicotinoidëve në matrica komplekse uji.

**Fjalë kyçe:** Oksid grafeni i reduktuar, elektrokimi, nikel, nanomateriale, thiamethoxam.

**1. Introduction**

Pesticides have played a vital role in controlling pests and diseases in agriculture for thousands of years (Sharma et al., 2019). The advent of synthetic pesticides, (Abubakar et al., 2020) in the 20th century led to a significant rise in their usage, particularly neonicotinoids, which now account for more than a quarter of global insecticide consumption (Klingelhöfer et al., 2022). However, excessive pesticide use can pose risks to crops, the environment and human health, as residues accumulate in agricultural products. To address these concerns, the World Health Organization has established maximum residue limits of  $0.1 \mu\text{g/L}$  for individual pesticides and  $0.5 \mu\text{g/L}$  for total pesticide residues (World Health Organization, 2019).

Thiamethoxam (THMX), a second-generation neonicotinoid insecticide, is commonly used in agriculture for pest, weed and pathogen control through sprays or seed treatments (Obregon et al., 2022). However, with a half-life ranging from 16.2 to 35.1 days, THMX residues persist in the environment well after its application (Maienfisch, 2006). In the last 15 years, the concentration of THMX residues in water systems has risen, reflecting its increasing use worldwide (Sánchez-Bayo et al., 2016). As a result of its widespread application, water solubility and prolonged half-life THMX can accumulate in both agricultural areas and natural water bodies, potentially harming non-target organisms. This highlights the need for a simple, effective, real-time and cost-effective monitoring system to detect THMX in environmental samples, such as water samples.

Traditional analytical techniques, including liquid chromatography (HPLC), mass spectrometry (MS), thermal lens spectrometry (TLS), enzyme-linked immunosorbent assay (ELISA) etc., have been developed for pesticides detection (Samsidar et al., 2018). While these methods offer high reproducibility and low detection limits, they require specialized personnel, expensive equipment and are time-consuming with low throughput, making them less suitable for real-time detection (Narenderan et al., 2020). In contrast, electrochemical methods provide a rapid, simple, cost-effective, portable, stable and sensitive approach for pesticide detection in various environmental samples (Xu et al., 2022). As a result, there is an increasing demand for the development of portable and stable electrochemical devices that are sensitive to pesticide detection. Along with others, voltametric methods being frequently used for electrochemical detection of thiamethoxam (Zhai et al., 2017; Ajermoun et al., 2021; Kapoor & Rajput 2023).

Recent studies have highlighted the potential of graphene-related materials, in the realm of nanotechnology portable devices (Nalepa et al., 2024; Wu et al., 2021; Peng et al., 2021). GO, a derivative of graphene featuring hydroxyl, carboxyl and epoxy groups is created through the oxidation of graphite and subsequent dispersion in solvents (Georgakilas et al., 2012). These oxygenated groups enable GO to generate stable solutions, rendering it advantageous for thin-film electrodes modification. Reduced graphene oxide (rGO) exhibits exceptional qualities for electrochemical sensing, including a large surface area, pronounced hydrophilic properties, and elevated surface-to-volume ratio (Chamoli et al., 2020; Su et al., 2019). Nevertheless, obstacles such as limited electrocatalytic activity and sluggish charge transfer may impact sensor performance (Zhou et al., 2022). The integration of metal nanoparticles and

nanomaterials enhances electrocatalytic efficacy, charge transfer rate, durability and sensor precision, addressing these issues (Saleh & Hassan 2023; Wang et al., 2020). Metal based nanoparticles have attracted significant scientific interest due to their ability to enhance sensor performance in thiamethoxam detection (Maheshwaran et al., 2024; Ajermoun et al., 2023). To our best knowledge, the incorporation of Ni to rGO for thiamethoxam determination has not been explored.

Within this context, the aim of this study is to develop a new material based on reduced graphene oxide (rGO) functionalized with nickel (Ni) for electrochemical thiamethoxam determination. Initial results showed a significant improvement in the electrochemical performance of rGO-modified carbon paste electrodes (rGO/CPE) when combined with nickel nanoparticles. This enhancement is attributed to both synergic effect of rGO and nickel incorporation. The proposed sensor demonstrated appreciable recovery in the direct analysis of water samples, showing its potential for practical applications.

## **2. Materials and methods**

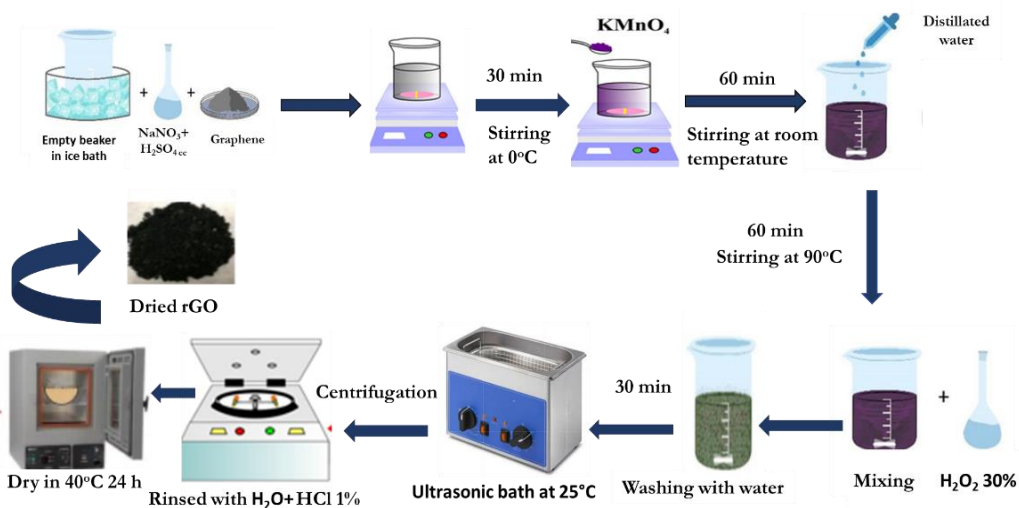
### **2.1 Chemicals and experimental set up**

Thiamethoxam and imidacloprid were procured from Sigma-Aldrich. Phosphate-buffered saline (PBS) pH=6.76 was used as the supporting electrolyte for electrochemical studies. All chemicals were of analytical grade and used without further purification. In this experiment, deionized water was used for solution preparation and washing purposes. Electrochemical experiments were performed in a classic three-electrode cell using a PalmSens4 device. A carbon paste electrode (CPE) modified with Ni-rGO was utilized as the working electrode, Ag/AgCl electrode as the reference electrode and a platinum wire as the counter electrode. All tests were carried out at room temperature.

### **2.2 Synthesis of partial reduced graphene oxide**

Reduced graphene oxide (rGO) was prepared using a modified Hummer method (Zaaba et al., 2017), (Fig.1), as detailed in our previous work (Kulla et al., 2024). Briefly: A mixture of graphene, sodium nitrate ( $\text{NaNO}_3$ ), and sulfuric acid ( $\text{H}_2\text{SO}_4$ ) was stirred in an ice-water bath, followed by the addition of potassium permanganate ( $\text{KMnO}_4$ ) and stirring for an hour. The mixture was then heated at  $90^\circ\text{C}$ , followed by the addition of  $\text{H}_2\text{O}_2$  and water. When heating graphene oxide and adding  $\text{H}_2\text{O}_2$ , a reduction process is facilitated and

the oxidation effect of  $\text{KMnO}_4$  is partially inhibited. The solution underwent ultrasonic treatment and centrifugation and the partial reduced graphene oxide (rGO) was dried for 24 hours.



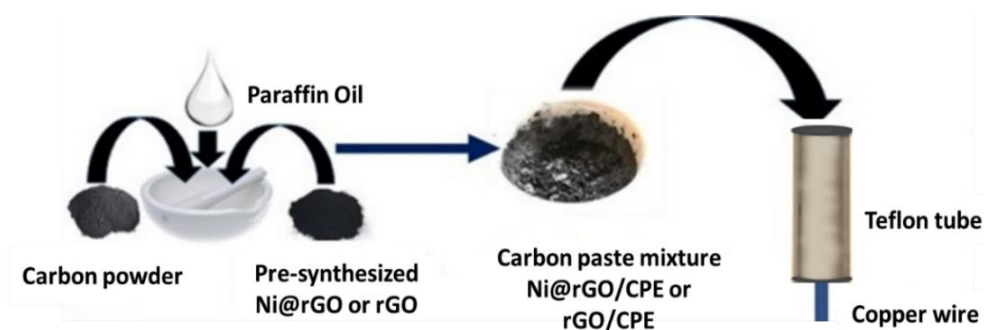
**Figure 1.** Schematics synthesis of rGO mostly based in Hummer's method.

### 2.3 Synthesis of reduced graphene oxide functionalized with Ni

To initiate the experimentation process, a solution was prepared by mixing 0.30  $\text{NiSO}_4$ , 0.102 g of previously synthesized rGO and 20 mL of distilled water in a 75 mL beaker. The mixture was then stirred using a magnetic stirrer set at level 4 for a duration of 2 hours, before being subjected to an ultrasonic bath for 4 hours. Subsequent to this step, the solution was centrifuged for 5 minutes at a speed of 5000 revolutions. The resulting precipitate was then subjected to drying in a thermostat at  $800^\circ\text{C}$  for a few minutes.

### 2.4 Sensor fabrication

The Ni-rGO composite was prepared by mixing 2 g of carbon powder, 200 mg of Ni@rGO, and 600  $\mu\text{l}$  of paraffin oil in a porcelain mortar for 1 hour. The paste was refrigerated for 24 hours and stored in a dry place. For electrochemical measurements, 1 g of the paste transferred into a Teflon tube, connected to a conductive wire (Fig.2). The same procedure was followed for rGO electrode fabrication.



**Figure 2.** Schematic preparation of Ni-rGO/CPE and rGO/CPE sensors.

## 2.5 Water sample preparation

Water samples from the Langarica River in Albania were collected and stored in dark glass bottles. The samples were then filtered through 1  $\mu\text{m}$  glass filters to remove any suspended particles and refrigerated at 4  $^{\circ}\text{C}$  to preserve their quality before analysis. Next, the samples were mixed with standard PBS buffer (pH 6.7) in a 50:50 ratio and 1.3 mL of the sample were added to a 15 mL electrochemical cell. The river samples were spiked with 1 mM thiamethoxam before performing DPV experiments utilizing a PalmSens4 device.

To calculate the recoveries was used the linear regression equation:

$$\text{Rate of Recovery}(RR, \%) = \frac{\text{Amount of TMX found}}{\text{Amount of TMX added}} \times 100$$

Equation 1.

## 2.6 Characterization methods

The sensor was characterized using cyclic voltammetry (CV), transmission electron microscopy (TEM), energy-dispersive X-ray spectroscopy (EDS), and Fourier-transform infrared spectroscopy (FT-IR). CV measurements were performed in 5 mM  $[\text{Fe}(\text{CN})_6]^{4-}/[\text{Fe}(\text{CN})_6]^{3-}$  with a potential range of -0.5 V to 0.5 V, scan rate of 100 mV/s, Estep of 0.01 V. FT-IR spectra were recorded using an ALPHA II spectrometer with OPUS software at room temperature. TEM images were captured with a JEOL JEM-2100 instrument, with samples prepared by placing a droplet of diluted solution onto copper grids coated with Formvar carbon film.

## 2.7 Electrochemical measurements

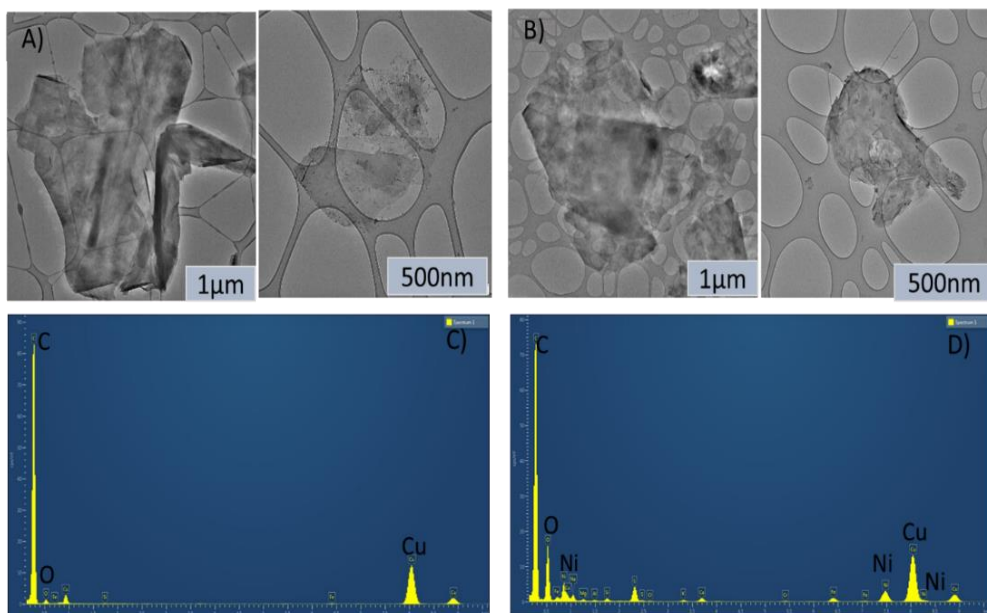
Cyclic voltammetry measurements of 100 ppm thiamethoxam was performed within a potential range of +1.5 V to -1.5 V,  $E_{\text{step}}$  0.01 V and scan rate 100 mV/s. For differential pulse voltammetry experiments, the parameters were as follows: scanning -0.8 V to -1.4 V,  $t_{\text{equilibration}}$  10 seconds,  $E_{\text{step}}$  0.01V,  $E_{\text{pulse}}$  0.05 V,  $t_{\text{pulse}}$  0.05 s and scan rate of 50 mV/s. Argon gas was bubbled through the solution throughout the electrochemical measurements to eliminate any interference from dissolved oxygen.

## 3. Results and discussion

### 3.1 Morphological and Structural characterization of rGO and Ni-rGO Composites

The synthesized rGO and Ni-rGO was characterized using: TEM, EDS and FT-IR. TEM was employed to investigate the overall morphology of the material. In the TEM images, fig.3A and fig.3B, the dark areas were identified as graphene oxide sheets, which is typical due to their structure and density while the "light" spots in fig.3B, were attributed to the presence of metallic nickel.

To further confirm the elemental composition, EDS analysis was performed. The EDS data verified the presence of nickel, indicating that Ni was effectively incorporated into the rGO structure. In addition to nickel, the EDS spectra revealed the presence of that (C) and (O), which are characteristic components of GO (Liaros et al., 2013). The spectra of fig.3C and fig.3D also showed the presence of other elements (K, Na, Cl, etc.) suggesting impurities from the material synthesis and copper (Cu) from supporting tape.

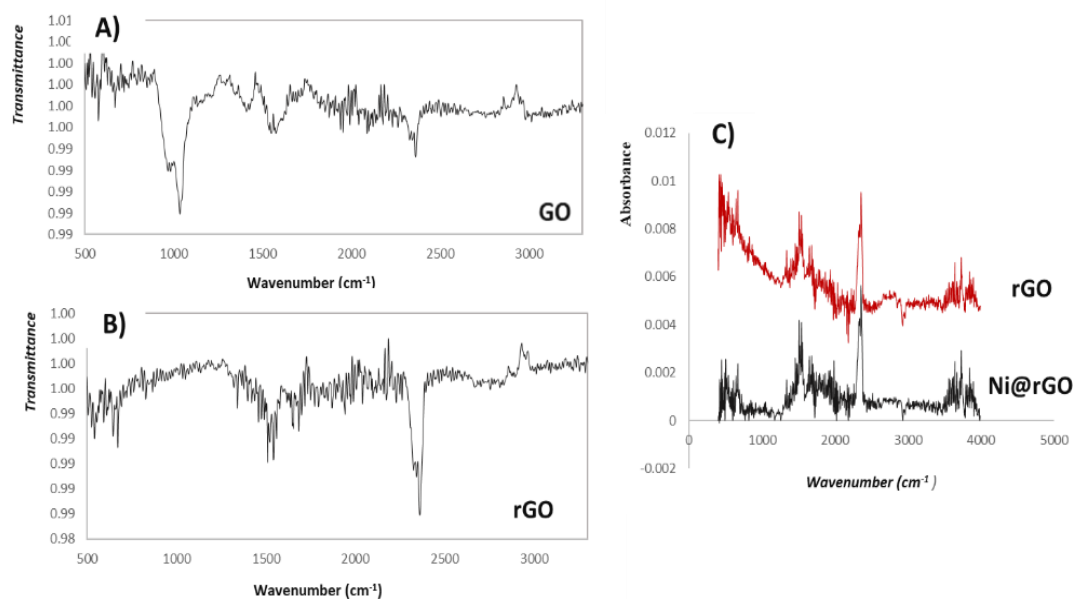


**Figure 3.** TEM images of: A) reduced graphene oxide (rGO) and B) reduced graphene oxide functionalized with Ni (Ni-rGO). EDS analysis of: C) reduced graphene oxide and D) reduced graphene oxide functionalized with Ni.

FT-IR analysis was conducted to study the structural properties of reduced graphene oxide and nickel-functionalized rGO, as illustrated in Fig.4. In Fig.4A, the FT-IR spectrum of rGO depicted the presence of characteristic peaks for C-H bending ( $600-700\text{ cm}^{-1}$ ), C-C bending ( $2400-2200\text{ cm}^{-1}$ ), C=O stretching ( $1750\text{ cm}^{-1}$ ), C-OH bending ( $1408-1574\text{ cm}^{-1}$ ) and C-O stretching ( $1000-1290\text{ cm}^{-1}$ ), indicating the presence of oxygenated functional groups typical of GO.

After reduction (Fig.4B), these peaks showed decreased intensity or were absent, suggesting a successful partial removal or reduction of oxygenated groups (Ickecan et al., 2017; Zaaba et al., 2017). In Fig. 4C, the spectrum of Ni@rGO revealed that the incorporation of Ni affected the vibrational energies, leading to a decrease in peak intensities compared to pure rGO, such findings align with previous studies that observed similar changes (Sahu et al., 2015).

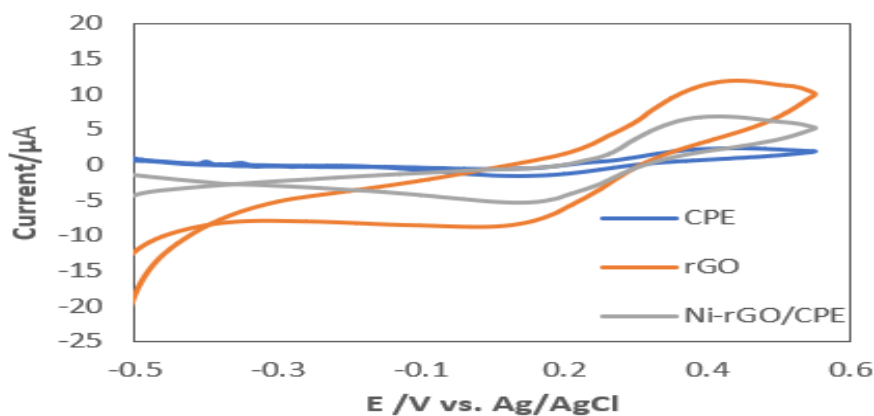




**Figure 4.** FT-IR spectrum of: A) graphene oxide, B) reduced graphene oxide and C) Ni@rGO and rGO.

### 3.2 Electrochemical properties of rGO/CPE and Ni-rGO/CPE

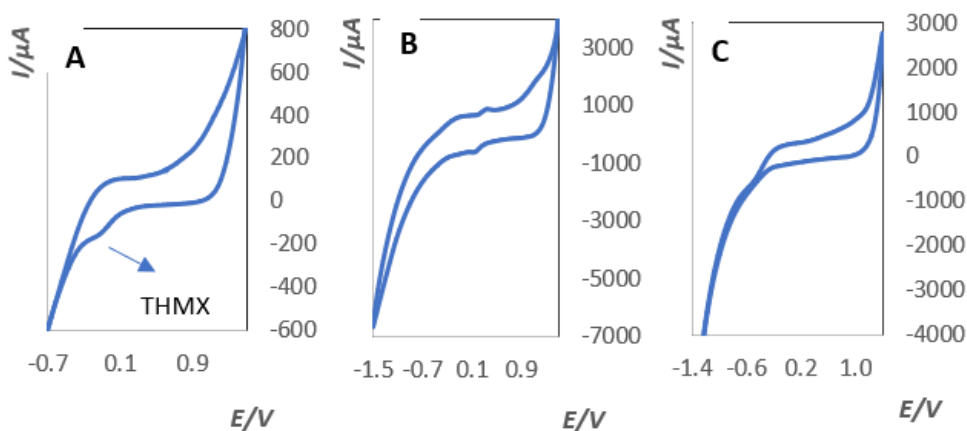
Cyclic voltammetry was used to evaluate the electrode with optimal electron transfer kinetics. All electrodes exhibited both cathodic and anodic peaks, confirming the redox activity of the system, as illustrated in Fig.5. The peak-to-peak separation ( $\Delta E_p$ ) for the Ni-rGO/CPE electrode was 180mV, while for the rGO/CPE and CPE electrodes, were 190 mV and 210mV, respectively. Furthermore, the ratio of anodic to cathodic peak currents ( $I_a/I_c$ ) was 1.17 for the Ni-rGO/CPE, whereas it was 1.12 and 1.9 for the rGO and CPE electrodes. This observation of an  $I_a/I_c$  ratio approaching 1 for Ni-rGO/CPE and rGO/CPE indicates a more quasi-reversible redox process, which is a characteristic of improved electron transfer kinetics. The observed improvement is attributed to the synergistic effects of Ni and rGO, which effectively increase the electrode surface area and promote more efficient electron transfer.



**Figure 5.** Cyclic voltammetry responds to 5mM  $[\text{Fe}(\text{CN})_6]^{4-}/[\text{Fe}(\text{CN})_6]^{3-}$ , obtained with: CPE (blue curve), rGO/CPE (orange curve) and Ni@rGO/CPE (grey curve).

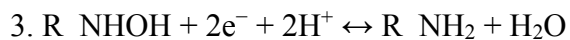
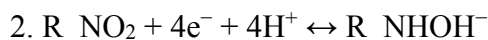
### 3.3 Electrochemical behaviour of thiamethoxam: CV and DPV

The study, via CV, aimed to assess the electrode's effectiveness in detecting THMX and its associated electrochemical properties. The CV curves in fig.6A revealed that the Ni-rGO/CPE electrode exhibited a distinct reduction peak specific to THMX, which was not observed in the unmodified CPE or rGO/CPE electrodes (Fig. 6B,6C). It is noted that the CV curves revealed no reversible peak, assuming that the electro-reduction of THMX is irreversible (Zhai et al., 2017).



**Figure 6.** CV voltammograms of 100 ppm THMX in PBS pH=6.7 at: A) Ni-rGO/CPE, B) rGO/CPE and C) CPE.

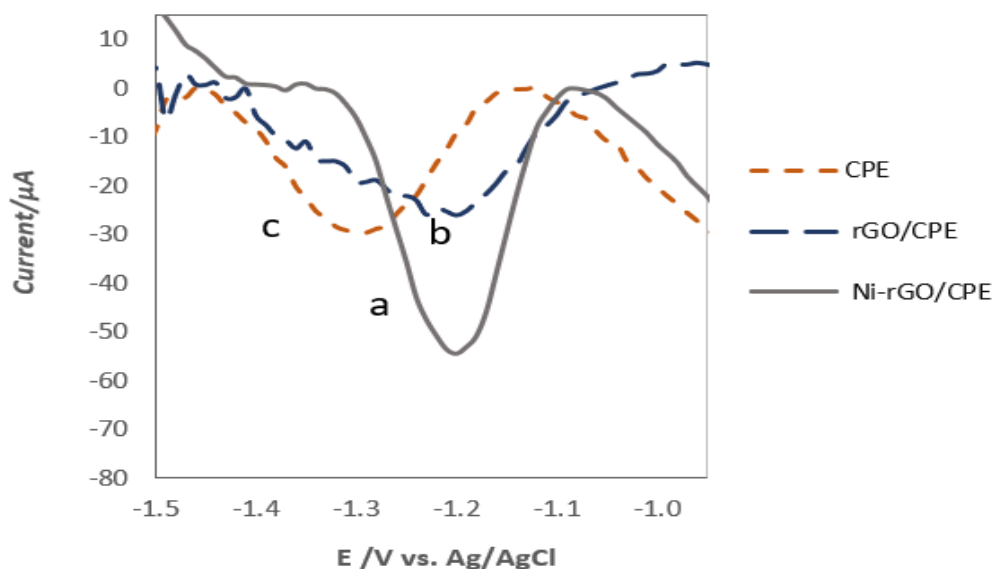
Based on current knowledge, the nitro-group is usually reduced in a two-step process: first to hydroxylamine (Eq. (2)) and then to amine (Eq. (3)). (Junqueira et al., 2013 ).



In this case, the analysing peak corresponds to the second step of nitro group TMX electro-reduction at Ni-rGO / CPE.

The electrochemical behaviour of 100 ppm thiamethoxam was studied using DPV with CPE, rGO/CPE and Ni-rGO/CPE electrodes in 0.1 mM PBS (pH=6.7). As shown in Fig.7, a distinct reduction peak at -1.15 V was observed for Ni-rGO/CPE electrode while for rGO/CPE and CPE electrodes, similar peaks appeared at -1.18V and -1.25 V, respectively, suggesting that Ni-rGO play a key role in enhancing the electrode's response, as evidenced by the shift of the peak to a more positive potential.

Additionally, the Ni-rGO/CPE exhibited a significant increase in peak current 89 $\mu$ A compared to the rGO 11 $\mu$ A and CPE 28  $\mu$ A, indicating that the incorporation of Ni into rGO structure significantly enhances the sensor sensitivity. This may be attributed to the incorporation of Ni into the rGO structure which can improve the electrochemically active surface area offering improved conductivity and charge transfer across the electrode-electrolyte interface (Wang et al., 2023).

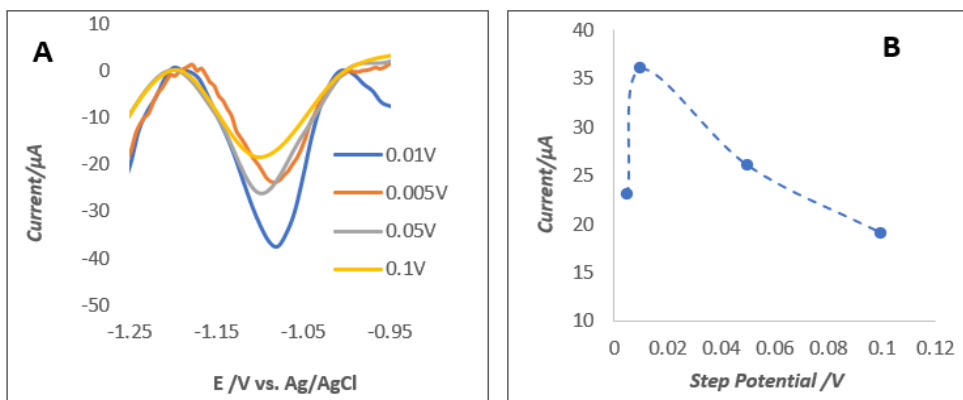


**Figura 7.** DPV voltammograms of 100 ppm THMX in PBS buffer solution pH=6.7 at: a) Ni-rGO/CPE, b) rGO/CPE and c) CPE.

### 3.4 Optimization of working conditions

#### 3.4.1 The effect of step potential

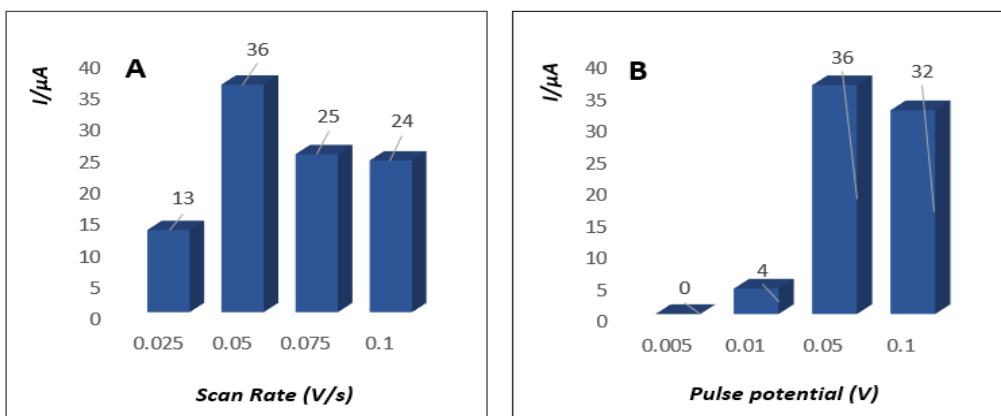
The electrochemical reduction of THMX at the surface of Ni-rGO/CPE was directly influenced by the potential step. DPVs voltammograms were obtained at step potentials of 0.005V, 0.01V, 0.05V, and 0.1V. Fig.8A, shows the voltammograms of peak current and respective potentials. Based on the results shown in Fig.8B, a step potential of 50mV, which exhibited the maximum current in, was identified as the optimal step potential.



**Figure 8.** (A) DPV voltammograms of of Ni-rGO/CPE in 50 ppm at step potential of 0.005V, 0.01V, 0.05V and 0.1V and (B) Relationship between reduction peak current versus step potentials.

### 3.4.2 Optimization of Scan rate and $E_{\text{pulse}}$ ( $t_{\text{pulse}}$ ) of DPV

The optimization of scan rate and pulse potential (the same value for  $t_{\text{pulse}}$ ) in DPV for thiamethoxam detection was performed to achieve the best sensitivity and peak resolution. Fig.9A illustrates the correlation between scan rate and peak current, leading to the determination of the optimal scan rate as 50mV. Adjusting the  $E_{\text{pulse}}$  ( $t_{\text{pulse}}$ ) ensured optimal peak sharpness and minimal noise, improving the overall detection accuracy of THMX. The best value for  $E_{\text{puls}}$  is 0.05 V and  $t_{\text{pulse}}$  0.05s, which can be found in fig.9B.

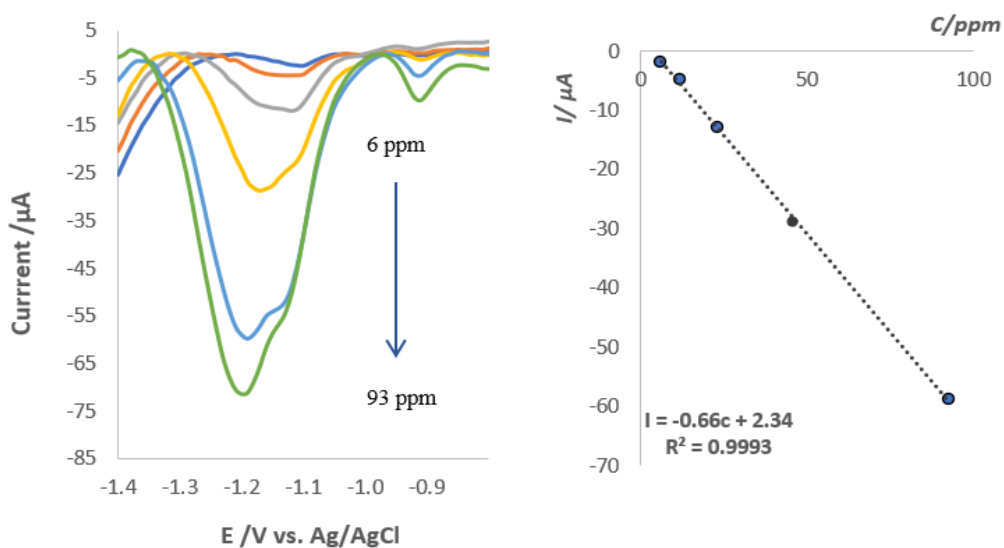


**Figure 9.** Correlation between: A) scan rate and peak current and B) pulse potential and peak current.

### 3.5 Calibration plots and interference study

#### 3.5.1 Electrochemical detection of thiamethoxam

The THMX determination was conducted at modified electrode Ni-rGO/CPE under the optimal conditions. Fig.10 shows the DPVs responses of THMX with the series of different concentrations, illustrating an increase in the current response of thiamethoxam reduction with increasing concentrations.



**Figure 10.** DPV responses to increasing concentration of thiamethoxam (left) and corresponding linear regression (right). All measurements were performed in PBS, pH=6.76 with Ni-rGO/CPE.

Fig.10 demonstrate a strong linear correlation between peak currents and pesticide concentration within the range of 6 -93 ppm. The relationship is represented by the equation  $I = -0.66c + 2.34$ , with a correlation coefficient of 0.9993. Also, from the voltammograms is shown that an unamplified peak is appeared at almost -0.95V, this may come as a results of pesticide polymerization. The limit of detection (LoD) for THMX was calculated using the equation:  $LoD = 3 \times (s/S)$ , where (s) is the standard deviation of the response

and (S) the slope. Consequently, the LoD value was determined to be 3.96 ppm.

The reproducibility of thiamethoxam detection at 93 ppm using the Ni-rGO/CPE electrode was evaluated, yielding a relative standard deviation (RSD) of 7.5%. The 7.5% RSD suggests a reliable and stable electrochemical response, making the Ni-rGO/CPE electrode suitable for practical analytical applications in THMX detection. A summary of these parameters is provided in Table 1.

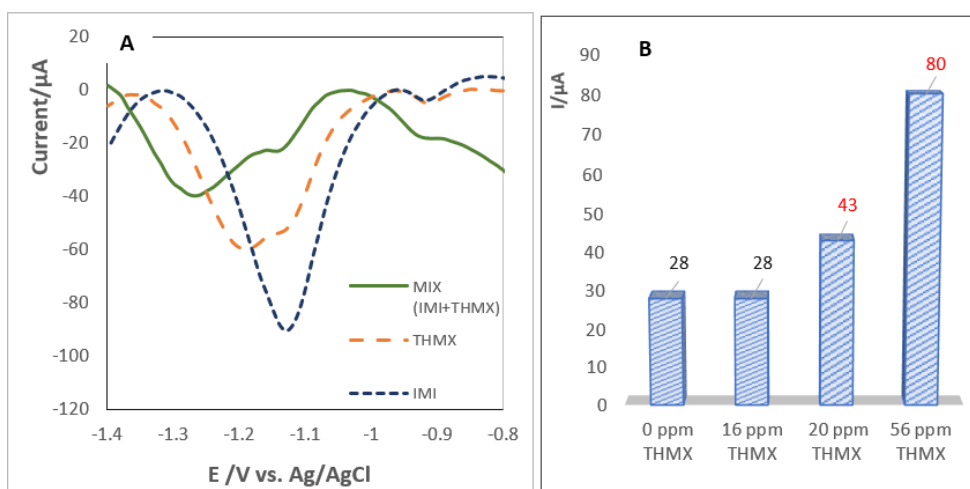
**Table 1.** Summary of analytical performance parameters.

Sensor	CPE/ Ni-rGO
Pesticide	Thiamethoxam - THMX
Voltammetry technique	DPV
Sensitivity	0.66 ( $\mu\text{A/ppm}$ )
Linear range	6-93 (ppm)
LoD	3.96 (ppm)
%RSD	7.5%
$R^2$	0.9993

### 3.5.2 Interference study

The selectivity of the Ni-rGO/CPE electrode was evaluated by analysing thiamethoxam in the presence of other nitro-aromatic pesticide compounds, such as imidacloprid (IMI), to see study the selectivity of the sensor in similar structure pesticide. As shown in Fig.11A, the reduction peaks for IMI and THMX were found to overlap and the reduction potential shifted negatively compared to the individual peaks of them.

It was observed that when the concentration of THMX was equal to or greater than that of IMI, the intensity of the overlapping reduction peak increased and the peak broadened (Fig. 11B). The overlapping of peaks for THMX and IMI can occur due to similar redox potentials or similar electrochemical properties. This suggests that while the Ni-rGO/CPE electrode can detect THMX in the presence of IMI, the overlapping peaks present a challenge for accurate quantification in complex mixtures.



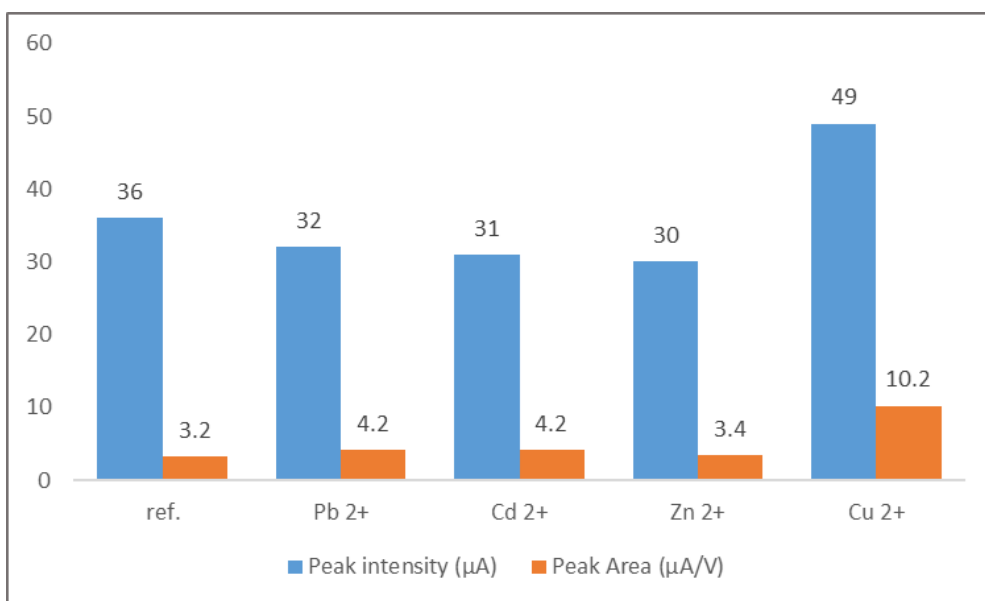
**Figure 11.** DPV voltammograms in 0.1M PBS pH=6.7 and: A) Mix solution of THMX and IMI (blue curve), THMX (orange curve) and IMI (grey curve) and B) the relationship between the current peak and a concentration of 20ppm IMI along with various concentrations of THMX.

The selectivity of the electrochemical detection was further evaluated by introducing various toxic metals, such as  $\text{Pb}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Cd}^{2+}$ , and  $\text{Cu}^{2+}$ , into the electrolyte. The results (Fig.12) indicated that the current intensity for thiamethoxam remained relatively stable, although a slight shift in the peak was observed in all cases. So, the electrode exhibited good selectivity for detecting thiamethoxam, except in the presence of copper ions.

Copper ions can interact with thiamethoxam molecules altering the electrochemical behaviour of thiamethoxam and affecting its reduction process. As is indicated form Fig.12, the electrochemical peak for



thiamethoxam becomes broader (as the surface area is increased) or shifts, with an increase in current, likely due to the formation of a complex with  $\text{Cu}^{2+}$  ions, (Da Silva Santos et al., 2020) or the generation of pesticide isomers (Liu et al., 2007). If  $\text{Cu}^{2+}$  ions form stable complexes with thiamethoxam, it may slow down electrochemical reactions due to additional molecular interactions or intermediate states. Copper ions can also facilitate multi-step reactions or introduce intermediate states of THMX reduction.



**Figure 12.** Interferences study of toxic metals on the reduction signal of 50 ppm thiamethoxam.

### 3.6 Spiked recovery study

The proposed method's applicability was assessed by using it to detect thiamethoxam insecticide in water samples. The samples underwent analysis using DPV. A calibration curve was constructed by adding specified quantities of thiamethoxam insecticide (sample preparation details are provided in the experimental section). The recovery rate was determined to be 109.94 %, indicating the effectiveness of our sensors in detecting THMX insecticide in water samples matrix. The obtained results are summarized in Table 2.

**Table 2.** The recovery of spiked THMX with Langarica River matrix.

Pesticides	Spiked Concentration	Founded Concentration	Recovery	%RSD ( $n=3$ )
THMX	1mM	1.0994 mM	109.94 %	3.35 %

## Conclusions

In our research, we introduced a novel approach utilizing reduced graphene oxide functionalization with nickel nanoparticles for electrochemical sensing. This approach highlights the potential of Ni-rGO/CPE electrodes for selective and sensitive electrochemical detection of nitroaromatic compounds like THMX. The incorporation of nickel nanoparticles into the rGO structure enhances electron transfer and the increased electroactive surface area from rGO modification, improve the overall electrochemical response.

The method has several advantages, such as simplicity, low cost and the rapid production of the Ni-rGO composite material. Our differential pulse voltammetry results, based on the irreversible electrochemical reduction of THMX, demonstrated good reproducibility (7.5%) and high linearity ( $R^2=0.9993$ ). The sensor beside the benefits mention above offers a broad linear range of 6 to 93 ppm, making it a suitable option for future portable devices. Moreover, it effectively detects THMX in complex water matrix with good accuracy and minimal interference from common contaminants, aside from complex forming metals such as copper. In conclusion, the Ni-rGO composite material provides a promising, cost-effective, fast, simple-to-prepare and environmentally sustainable solution for electrochemical THMX detection in polluted environments.

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