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NANOSTRUCTURED MODIFIED CARBON PASTE ELECTRODE AS VOLTAMMETRIC SENSOR FOR ISOPROTURON TRACE ANALYSIS IN WATER

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Abstract

A new electrochemical sensor based on nanostructured carbon paste electrodes (CPEs) is developed for the sensitive detection of Isoproturon in water. The CPEs were nanostructured by incorporation of carbon nanotubes (NTCs) and synthesized copper oxide nanoparticles (CuO). They were characterized using the X-ray diffraction spectroscopy (XRD), scanning electron microscopy (SEM) and voltammetric methods. Electrochemical experiments showed that the adsorption of Isoproturon on to (GC-NTC-CuO)-CPE, associated with nanomaterials (NTCs and CuO), provided remarkable analytical performances of the sensor such as a large quantification range from 1 to 200 $\mu\text{g}\cdot\text{L}^{-1}$ with a detection limit of 0.1 $\mu\text{g}\cdot\text{L}^{-1}$ of Isoproturon and no interferences of some another pesticides tested (specificity of ISO adsorption in acidified water). The tests carried out on real samples of water are conclusive. The analytical performances of the sensor showed that it is suitable for the specific determination of pesticide traces in water.

Keywords : Carbon Paste Electrode; nanostructured composite material; trace analysis; Isoproturon; cyclic voltammetry.

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1. INTRODUCTION

The use of pesticides, although necessary to protect crops and minimize losses, is detrimental to the ecosystem and human health by the pollution it generates. Because of their physicochemical properties, these compounds can migrate to groundwater and surface water and alter the quality of water and food. Among others, Isoproturon (ISO) is an herbicide of the substituted urea family, widely used in cereal agriculture to control weeds. It is a toxic product, likely to harm human health [1]. WHO recommends a threshold concentration of $9 \mu\text{gL}^{-1}$ of ISO for water quality [2]. In addition, the European Union has set its maximum allowable concentration at $0.1 \mu\text{gL}^{-1}$ in drinking water [3]. Many pesticide analysis techniques have been developed such as capillary electrophoresis [4, 5], chromatographic techniques [6, 7, 8-10] and chromatography coupled to mass spectroscopy. Although they are very sensitive and reliable but have strong drawbacks such as complex and long processing samples and can only be performed by highly qualified personnel.

In this context, electrochemical based sensing devices are a promising alternative, offering great potentials for a broad range of analytical applications. These tools are very sensitive and reliable, selective, fast, inexpensive and are suitable for on-site analysis.

Most of the research developed in pesticides analysis has focused on enzymatic quantification [11-13], while current works are moving towards direct detection [14, 15]. Moreover, the development of nanotechnology has paved the way for the manufacture of new, efficient and inexpensive electrode materials [16, 17]. Indeed, electrochemical sensors have increasingly used nanoparticles because of their special properties that increase the surface area of electrodes, accelerate mass transport, control the microenvironment of electrodes and allow efficient catalysis [16, 17]. The use of carbon, in its various forms (graphite, nanotubes, graphene, etc.), in the design of electrochemical sensors and biosensors is widespread [18-20]. In order to improve their properties, particularly the selectivity towards target analytes, nanostructured materials can be mixed with carbon-based materials. Furthermore, it is well documented that materials containing nanocomposites such as copper oxide (CuO), zinc oxide (ZnO), manganese oxide (MnO_2) and others [21-23] are exploited in the detection of pesticides in order to interact specifically with the analyte and to facilitate the charge transfer.

The aim of this work is to develop a new sensor based on carbon paste consisting of a GC powder nanostructured by NTC and CuO in order to enhance the sensitive and selective Isoproturon analysis in aqueous solution using the CV method.

2. Materials and methods

2.1 Reagents and Materials

All reagents used are of analytical grade. Nujol (mineral oil), graphite powder ($< 20 \mu\text{m}$), carbon nanotubes (DxL: 110-170 nm x 5-9 μm), sulfuric acid (for analysis EMSURE, 98%), ethanol(99%), acetone, Isoproturon (analytical standard 99.9%) were purchased from Sigma-Aldrich, and ammonium carbonate $(\text{NH}_4)_2\text{CO}_3$, copper sulphate pentahydrate $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, sodium hydroxide NaOH were provide by Prolabo. All aqueous solutions were prepared with deionized (DI) 18.2 M Ω .cm (25 °C) water from Millipore Direct-Q Water system. Stock solutions of Isoproturon (0.1M) were prepared with ethanol and subsequent dilutions were

prepared daily with ultrapure water and stored at 4°C in the dark. Standard solutions of pesticides used as potential interferences of Isoproturon detection were prepared with deionized water and employed during the interference study. All experiments were performed at room temperature ($20 \pm 1^\circ\text{C}$). All reagents were used as received.

2.2 Instrumentation

X-ray powder pattern was collected with a Panalytical Empyrean powder diffractometer (θ – θ Bragg–Brentano geometry) working with the Cu $K\alpha$ radiation ($\lambda K\alpha_1 = 1.5406 \text{ \AA}$, $\lambda K\alpha_2 = 1.5444 \text{ \AA}$) selected with a flat multilayer X-ray mirror (Bragg-Brentano HD[®]). Data were collected with a Pixel 1D silicon-strip detector, in the angular range 10–80° (2 θ) (step size $\sim 0.013^\circ$ (2 θ)). The surface morphology of the prepared samples was characterized by scanning electron microscope (JEOL JSM-7100F, Detector EDS Oxford Instrument 50 mm²). All electrochemical experiments were performed with a PGSTAT20 Metrohm potentiostat/galvanostat in combination with the NOVA 2.1 software, at room temperature, using a traditional three-electrode electrochemical cell with a working electrode, Ag/AgCl (3 M KCl) as reference electrode, and a platinum wire counter electrode.

2.3 CuO nanoparticles synthesis

The CuO nanoparticles were synthesized by the hydrothermal method described by M. Ben Ali et al [23]. 10 mL of a freshly prepared solution of copper sulfate 1 mol L⁻¹ (CuSO₄·5H₂O) was added dropwise to a stirred solution of 5 mL of 1M ammonium carbonate solution in 35 mL of deionized water. Then, 1 mol L⁻¹ sodium hydroxide aqueous solution was added dropwise to the previous mixture to form a white precipitate at pH=11. After 30 minutes of magnetic stirring, the mixture was transferred to a teflon-coated stainless steel autoclave of 45 mL capacity for 16 hours at 160 ° C. The nanoparticles obtained were washed and then dried at 90 ° C. for 24 hours. The powder obtained was then calcined at 600 ° C for 4 hours.

2.4 Preparation of the CPEs

The carbon pastes (CPs) have been prepared by mixing the components in desired proportions with a binder (Nujol) for about thirty minutes to have a homogeneous mixture. The resulting paste was then packed into the cavity (2 mm deep) at the end of homemade Teflon cylindrical tube of 3 mm (internal diameter) surrounding hermetically a graphite bar acting as electrical contact. The surface was smoothed off by rubbing the electrode several times slowly across a paper. Four CPs of different compositions were prepared: and composed in mass % of (i) graphite powder (85%) and binder (15%) (GC-CP), (ii) graphite powder (60%), binder (15%) and carbon nanotubes (25%) (GC_NTC)-CP), (iii) graphite powder (60%), binder (15%) and nanoparticles of copper oxide (25%) ((GC-CuO)-CP) and (iv) graphite powder (60%), binder (15%), carbon nanotubes (10%) and copper oxide nanoparticles (15%) ((GC-NTC-CuO)-CP). The percentage of added binder was previously optimized and the value of 15% allowed maintaining the compacted pastes in the electrode cavity while retaining its electrical properties. In order to compare the different nanostructured pastes the proportion of graphite powder was kept at 60%.

3. Results and discussion

3.1 Characterization of CuO nanoparticles and (GC-NTC-CuO)-CP

Figure 1 shows the collected X-ray powder diffraction pattern of the synthesized CuO. Dirac peaks below the pattern indicate the positions of the reflexions of CuO tenorite from the ICDD PDF-2 database. No additional diffraction line neither angular shift are observed, which clearly indicates the purity of the crystallized compound.

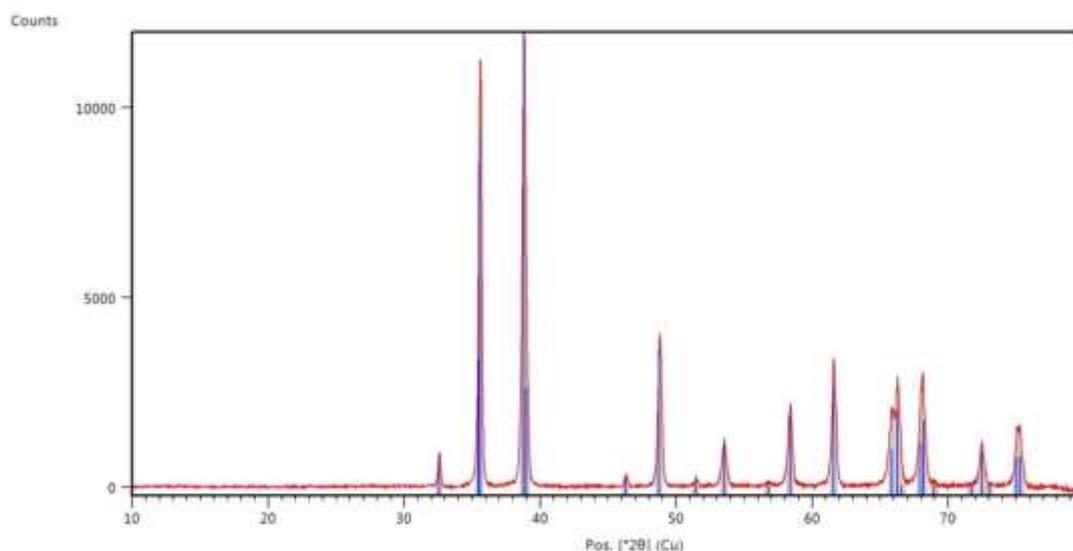


Figure 1: XRD pattern of the synthesized CuO powder (red) compared to the theoretical pattern of CuO tenorite (blue)

The morphology of the components of the CPs was studied by scanning electron microscopy and in the mixture for (GC-NTC-CuO)-CP (see Figure 2). The synthesized CuO material (SEM image (C)) shows as clusters of roughly spherical particles at sub-micrometric sizes. In the SEM image (A) graphite carbon appears as particles of graphite sheets with dispersed sizes lower than 20 μm . In the SEM image (B) the carbon nanotubes are looking tangled. For (GC-NTC-CuO)_CP, SEM image (D) clearly shows that the paste is composed of a mixture of GC, CNTs and CuO nanoparticles closely linked insuring electrical contact between all the components in (GC-NTC-CuO)-CP. It can also be seen that this mixture gives a very rough and spongy surface of the CP which could provide a large contact area for subsequent interaction with the analyzed pesticides.

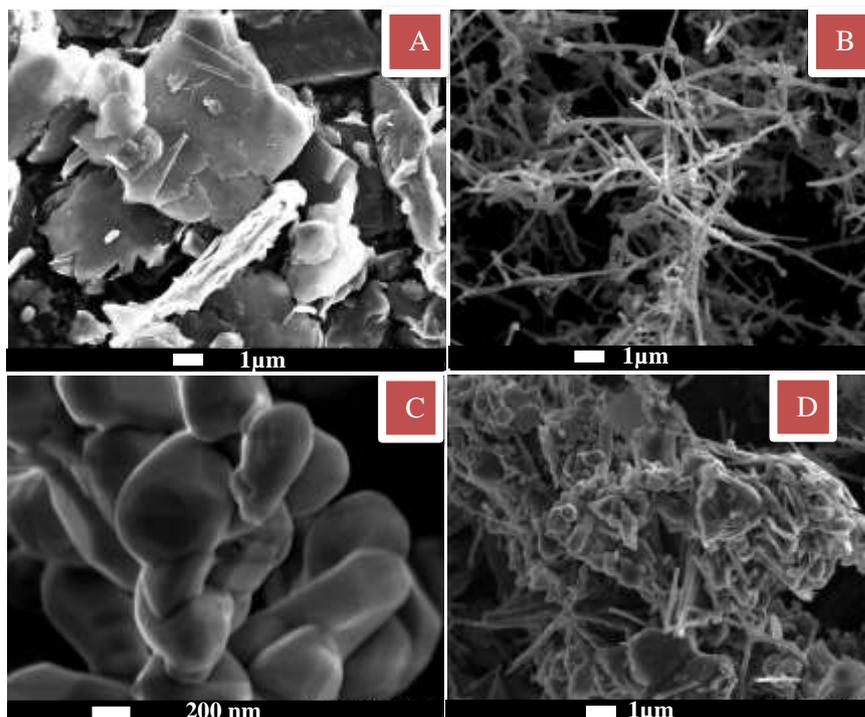


Figure 2: SEM images of the various compounds used for the CPEs preparation, CG (A), NTC (B), CuO (C) and constituent mixtures (CG-NTC-CuO)–CP (D)

3.2 Cyclic voltammetric studies at CPEs

3.2.1 Effect of the paste composition on CPE response of Isoproturon

The electrochemical behavior of Isoproturon (ISO) on different CPEs was investigated by CV. Figure 3 presented the CVs of the GC-CPE (curve 1), (GC-NTC)-CPE (curve 2), (GC-CuO)-CPE (curve 3) and (GC-NTC-CuO)-CPE (curve 4) in $0.5 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$ electrolyte solution in the presence of $10^{-4} \text{ mol L}^{-1}$ of Isoproturon. This electrolyte with a pH about 1, was the optimized composition given a quasi-rapid electron transfer (well defined peak) with an optimum current intensity.

As can be seen, all the recorded voltammograms show an oxidation peak around 1.0 V of variable intensity without reduction peak at the reverse scan (non-reversible electrochemical system). The current response depends on the composition of the paste. Indeed, the most intense current intensities were recorded when CuO nanoparticles were incorporated in the CPE, indicating that adsorption of ISO is favored by CuO. In addition, by comparison of curve 1 and 2, we can observe a significant increase in the oxidation current due to the presence of NTC in the paste. This enhancement of sensitivity is probably brought out by the increase of the specific active surface of the electrode and by the paste nanostructuration, which improves the electrical contact of the powder material and facilitates the charge transfer. This effect of the NTCs was also observed for CPEs integrating CuO nanoparticles (curve 3 and 4). The best response is thereby obtained by (CG-NTC-CuO)-CPE with a gain of about 30 in sensitivity in comparison with classical CP-CPE.

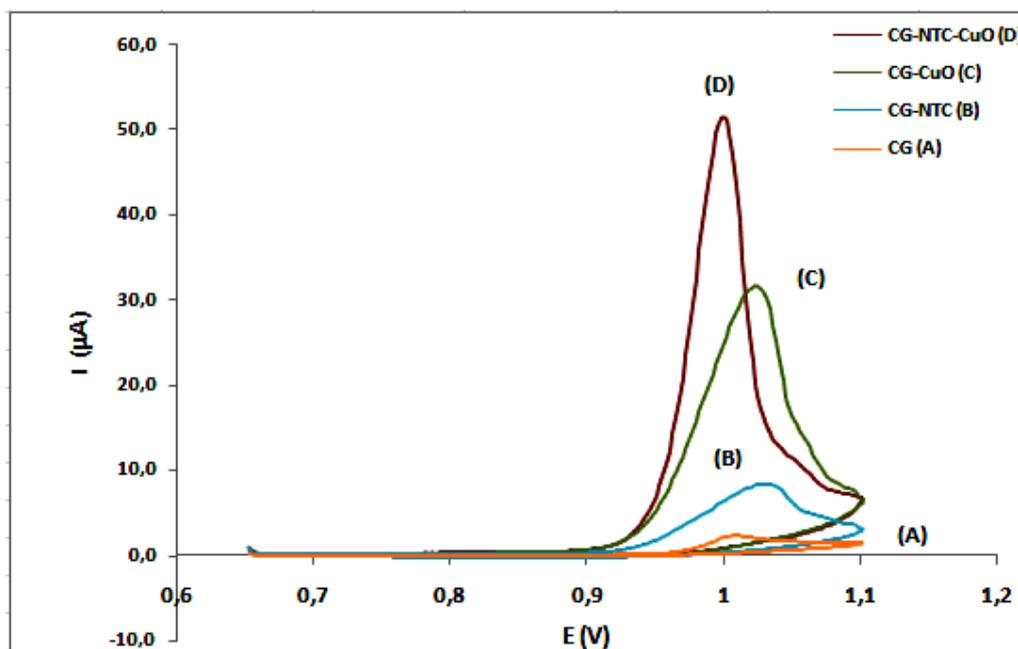


Figure 3: Cyclic voltammetry obtained with the (GC)-CPE (A), (CG-CNT)-CPE (B), (CG-CuO)-CPE (C) and (CG-NTC-CuO)-CPE (D) for 10^{-4} mol L $^{-1}$ ISO in H $_2$ SO $_4$ solution (0.5 mol L $^{-1}$) with scan rate of 10 mV s $^{-1}$

The peak shape in CV (in particularly with the presence of CuO nanoparticles in the paste) is characteristic of the oxidation of adsorbed Isoproturon on electrode material (see figure 3). A first study for a large range of 3 Isoproturon concentrations (10^{-6} , 10^{-5} and 10^{-4} mol L $^{-1}$) indicates a good linearity of the peak current versus concentration in this 3 decades range (insert on figure 4). The best sensitivity is recorded for the (CG-NTC-CuO)-CPE indicating the promising use of nanostructured materials for the sensitive voltammetric detection of Isoproturon.

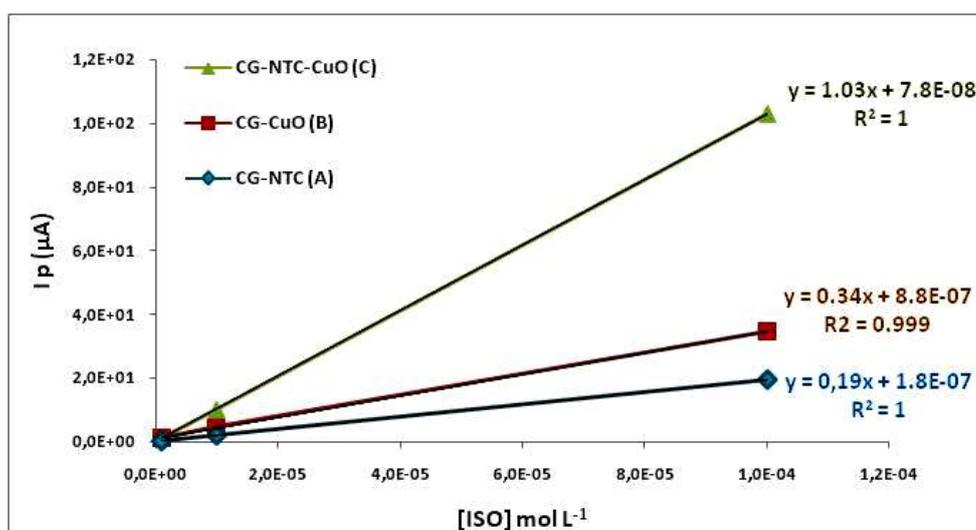


Figure 4: variation of current intensity as a function of the ISO concentration (10^{-6} , 10^{-5} and 10^{-4} mol L $^{-1}$), for the different paste electrodes (CG-NTC)-CPE (A), (CG-CuO)-CPE (B) and (CG-NTC-CuO)-CPE (C) in H $_2$ SO $_4$ solution (0.5 mol L $^{-1}$) with scan rate of 10 mV s $^{-1}$

3.2.1 Influence of the scan rate in CV

The effect of the potential scan rate on the CV peak currents for a solution of Isoproturon $5.10^{-7} \text{ mol L}^{-1}$ in H_2SO_4 (0.5 mol L^{-1}) was examined over the range of $5\text{--}40 \text{ mVs}^{-1}$, upper scan rates implicates CV distortion due to the ohmic drop and greater capacitive currents. As displayed by the figure 5, the voltammograms (only the forward scan presented) present the same shape for the oxidation of the Isoproturon with an increasing of the capacitive current. The variation of the anodic peak currents (I_p) as a function of the scan rates (v) (figure 5) shows linear relation ($r^2=0.999$) in this scan rate range indicating that the process at the electrode is not controlled by the diffusion of Isoproturon but by the oxidation of a quantity of Isoproturon on the electrode surface. This suggests an adsorption step of Isoproturon before its oxidation on the electrode (typical electrochemical behavior of thin layer adsorbed compounds [25]).

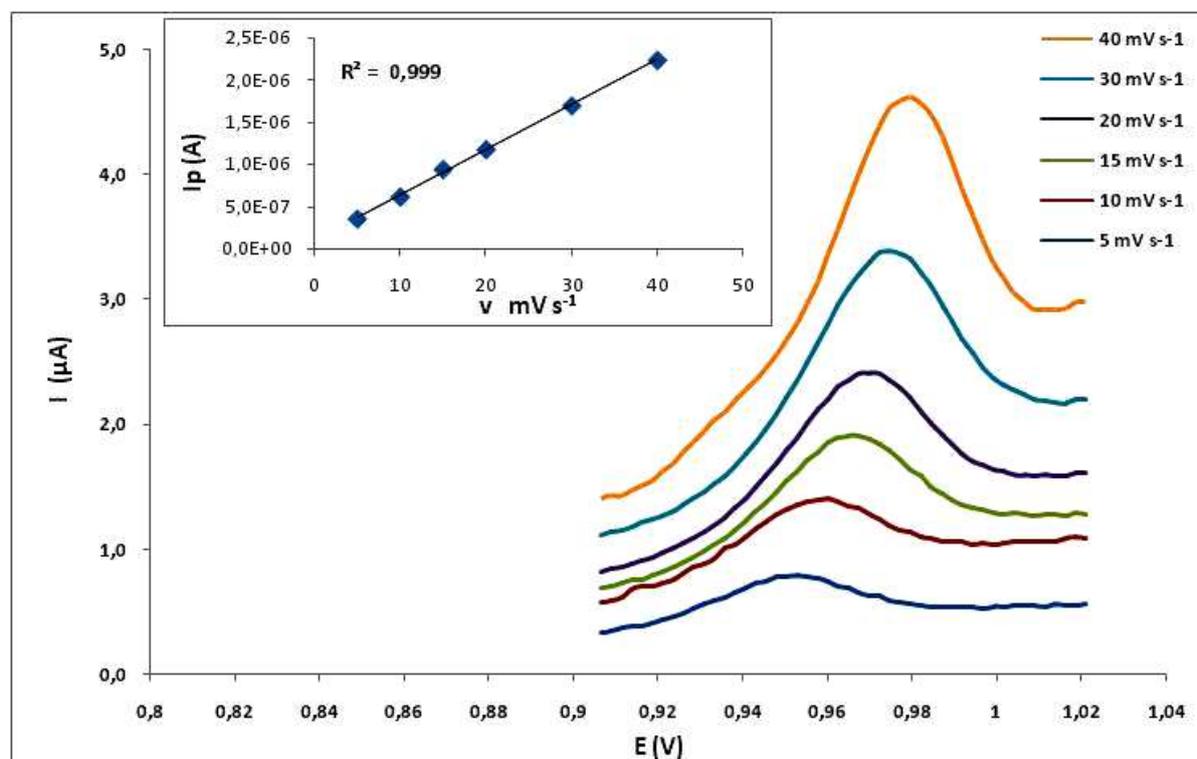


Figure 5: Cyclic voltammetry for different potential scan rates at the (CG-NTC-CuO)-CPE electrode in $0.5 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$ for $[\text{iso}] = 5.10^{-7} \text{ mol L}^{-1}$. Insert: oxidation peak current in function of scan rate

3.2.2 Effect of pre-concentration time

Since the detection of Isoproturon trace levels depends on its adsorption on CPE, the waiting time before the analysis in CV can significantly affect the current intensity of ISO oxidation. Figure 6 exhibits the effect of the adsorption time under magnetic stirring (300 rpm) before the CV analysis on the sensor response for an Isoproturon concentration of $10^{-6} \text{ mol L}^{-1}$ in solution. The current intensity of the oxidation peak increases in function of the adsorption time, and reaches a maximum after 12 minutes (no change for the current intensity at 12 and 17 minutes) indicating the obtain of adsorption equilibria of Isoproturon at (CG-NTC-CuO)-CPE. It is near the same for lower concentrations than $10^{-6} \text{ mol L}^{-1}$.

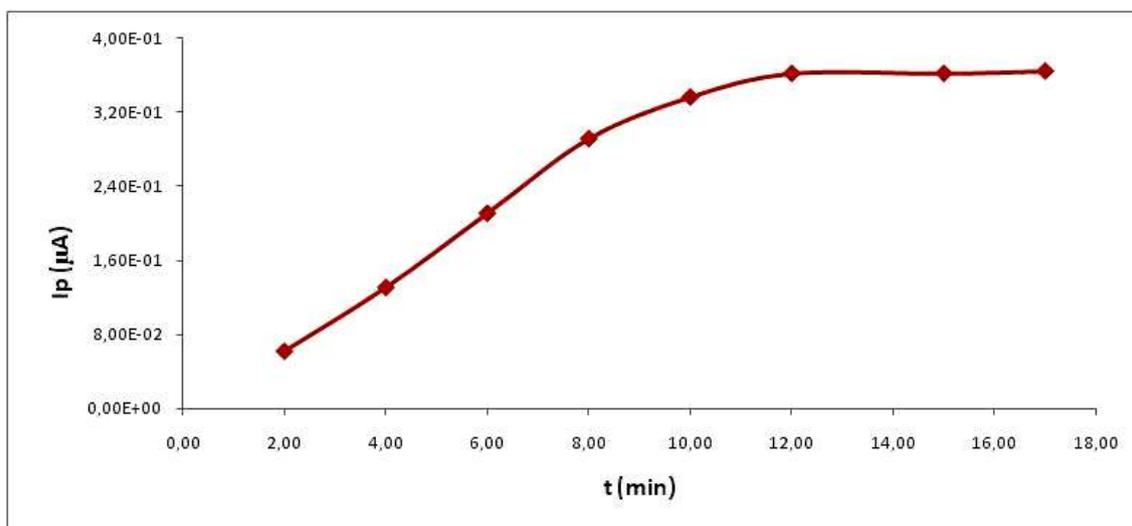


Figure 6: Influence of the adsorption time under stirring on the peak current intensity obtained in CV for Isoproturon oxidation at (CG-NTC-CuO)-CPE in H_2SO_4 (0.5 mol L^{-1}), $[\text{ISO}] = 10^{-6} \text{ mol L}^{-1}$, $v = 10 \text{ mV s}^{-1}$

3.3 Sensor application to Isoproturon analysis

3.3.1 Performances of the (CG-NTC-CuO)-CPE sensor

The calibration of the CG-NTC-CuO sensor was investigated using cyclic voltammetry, under optimized conditions (potential range: 0.65-1.1 V; sweep rate 10 mV.s^{-1} ; waiting time 12 min under stirring H_2SO_4 (0.5 mol L^{-1}) as the supporting electrolyte). Figure 7 shows a well-defined peak with an oxidation current linearly proportional to the concentration of Isoproturon, in the concentration range of 10^{-8} - $10^{-6} \text{ mol L}^{-1}$ ($r^2=0.998$). The detection and quantification limits, calculated as the concentration of ISO that gave a signal equal to respectively three and ten times the standard deviation of the background current, were found to be in the nano-molar level respectively $5 \cdot 10^{-10} \text{ mol L}^{-1}$ and $1.5 \cdot 10^{-9} \text{ mol L}^{-1}$.

The interference study of the Isoproturon CG-NTC-CuO sensor was carried out by comparing the current response for $5 \cdot 10^{-5} \text{ mol L}^{-1}$ of Isoproturon in 0.5 mol L^{-1} sulfuric acid solution before and after adding some potential interfering pesticide such some class of phenyl urea herbicides (linuron), other herbicides (propazine, tetrazine and metazachlore) and chlordecone at $5 \cdot 10^{-5} \text{ mol L}^{-1}$ concentrations. The results showed negligible interferences of these substances (lower than 2% on the value of oxidation peak current) and indicated that this sensor is specific to the detection of Isoproturon.

Table 1 shows the comparison of the analytical performance of GC-NTC-CuO carbon paste sensor with other reported sensors or analytical methods in the literature. The voltammetric results from this work present a good linearity range and low detection limit for ISO. These observed analytical results indicate that the proposed electrochemical sensor seems to be attractive and suitable for trace analysis of ISO.

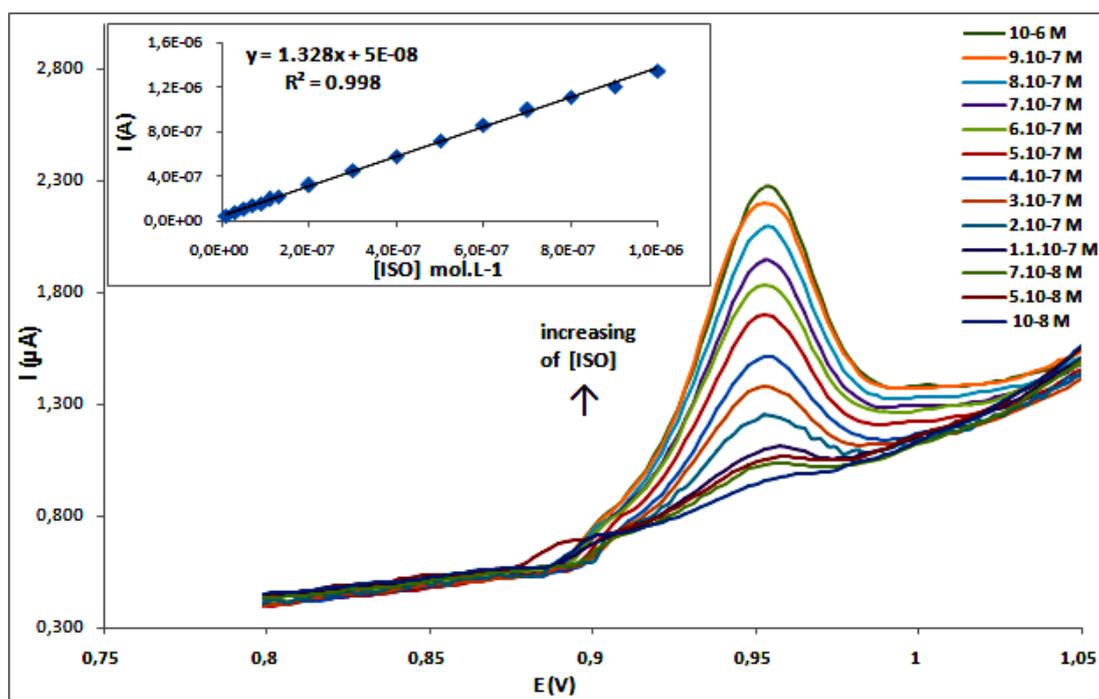


Figure 7: Cyclic voltammograms at (CG-NTC-CuO)-CPE in 0.5 mol L⁻¹ H₂SO₄ ($v=0.01$ V s⁻¹) and Calibration curves for different Isoproturon concentrations from 10⁻⁸ to 10⁻⁶ mol L⁻¹

Analytical methods	Linear range	Detection limit	Ref
Fluoro-immunosensor with enrichment in a sol-gel immunosorbent	0.05-0.5 μg L ⁻¹	9.7 ng L ⁻¹	[26]
SWSV (graphene-based sensor)	0.02-10.0 mg L ⁻¹	0.02 mg L ⁻¹	[27]
SG-IS combined with HPLC/ MS	5-2.2 μg L ⁻¹	5 ng L ⁻¹	[28]
Flow Injection Analysis with Amperometric immunosensor	1-3000 μg L ⁻¹	0.84 μg L ⁻¹	[29]
SWSV with montmorillonite clay-modified electrode	1-300 μg L ⁻¹	1 μg L ⁻¹	[30]
DPSV (PANI/MWCNT/GCE)	0.01-100 mg L ⁻¹	0.1 μg L ⁻¹	[31]
CV ((CG-NTC-CuO)-CPE)	0.3 - 200 μg L ⁻¹	0.1 ug L ⁻¹	This work

SWSV: square wave stripping voltammetric; SG-IS: sol-gel immunosorbent ;DPSV: Differential pulse stripping voltammetry; PANI/MWCNT: Polyaniline/multi-walled carbon nanotubes

Table 1: Comparison with subsequent works

3.3.2 Repeatability and reproducibility study

Repeatability and reproducibility are important criteria for any developed sensor. Therefore, the repeatability and reproducibility of the designed sensor for determination of Isoproturon were studied using four concentrations (1, 3, 7, and $9 \cdot 10^{-8}$ mol L⁻¹). This was evaluated by CV by performing three determinations of peak current intensity with the same standard solutions of Isoproturon. The results are summarized in Table 2.

The repeatability of the (CG-CuO-NTC)-CPE was evaluated by using the same electrode in the optimal conditions for CV experiments. It appears that the relative standard deviations (RSD) did not exceed 3.6%. The reproducibility was estimated by using three modified electrodes independently prepared by the same procedure. In this case, the RSD of peak current intensities for ISO oxidation did not exceed 6.3%. These results indicate that the proposed sensor has good repeatability and reproducibility.

Concentration of Isoproturon ($\times 10^{-8}$ mol L ⁻¹)	Repeatability of Ip values	Reproducibility of Ip values
	RSD* (%)	RSD* (%)
1	2.1	3.4
3	3.6	5.1
7	3.6	5.7
9	2.0	6.3

* ($n = 3$)

Table 2: Study of repeatability and reproducibility for the proposed CV method with (CG-NTC-CuO)-CPE in the Isoproturon concentration range of 10^{-8} – 10^{-7} mol L⁻¹

3.3.3 Application to real samples

To illustrate the practical application of (CG-CuO-NTC)-CPE, the electrode was applied to Isoproturon detection in local tap water. As the voltammograms in CV of acidified tap water (0.1 mol L⁻¹ H₂SO₄) did not give an observable peak in the potential window corresponding to ISO oxidation ($< 0.1 \mu\text{g L}^{-1}$), two tap water samples were spiked at 0.2 and $0.6 \mu\text{mol L}^{-1}$. Voltammetric studies under the optimum experimental conditions were carried out to determine ISO in these water samples. The standard addition method was used for the quantification of ISO in these spiked samples and three replicates were done. The presented data in Table 3 show excellent recovery rates that are in the 96.4 – 101.7 range with $\text{RSD} < 4\%$. This indicates that the proposed method with (CG-CuO-NTC)-CPE was successfully applied for determination of Isoproturon in tap water samples as indicated.

Samples (spiked Tap water)	Spiked concentration of ISO ($\mu\text{mol L}^{-1}$)	Mean founded concentration of ISO ($\mu\text{mol L}^{-1}$)	RSD* (%)	Recovery from spiked water sample (%)
A	0.2	$0.18 \pm 0.01^{**}$	3.1	96.7
B	0.6	$0.61 \pm 0.03^{**}$	3.7	101.4

* ($n=3$); ** Confidence interval for $\alpha=0.05$.

Table 3: Analysis of two tap water samples spiked with Isoproturon by applying CV method with (CG-NTC-CuO)-CPE. Standard addition determination for 3 replicates

4. Conclusion

In this present work, an electrochemical sensor was developed for ISO detection in water. It consists of a carbon paste mixed with nano-materials (NTCs and CuO) in order to produce a nanostructured sensitive surface of the CPE. The CV method was used to detect ISO following the measurement of the oxidation peak current at $E_p = 0.89 \text{ V/Ag/AgCl}$. This sensor is characterized by a wide concentration range, a good sensitivity and a low detection limit due to the adsorption of ISO onto this nanostructured carbon paste. The tests carried out on contaminated real samples of water are conclusive, thus the developed sensor could be used for the trace detection of ISO in water as a sensitive, selective and inexpensive device.

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References

1. P.J. John, A. Prakash, *Environ. Contam. Toxicol.*, **2003**, 70, 1013–1016.
2. Guidelines for Drinking-water Quality, 4th ed., World Health Organization press, **2011**, pp183.
3. A.C. Johnson, T.J. Besien, C. Lal Bhardwaj, A. Dixon, D.C. Goody, A.H. Haria, C. White, *J. of Contaminant Hydrology*, **2001**, 53, 101–117.
4. Y. Wang, L. Xiao, M. Cheng, *J. Chromatog. A* **2011**, 1218, 9115–9119.
5. J. Dominguez-Alvarez, M. Mateos-Vivas, D. Garcia-Gomez, E. Rodriguez-Gonzalo, R. Carabias-Martinez, *J. Chromatog. A*, **2013**, 1278, 166–174.
6. X.-M. Xu, S. Yu, R. Li, J. Fan, S.H. Chen, H.-T. Shen, J.-L. Han, B.-F. Huang, Y.-P. Ren, *Food Chem.*, **2012**, 135, 161–169.
7. C. Anagnostopoulos, G.E. Miliadis, *Talanta*, **2013**, 112, 1–10.

8. M. Godejohann, J.-D. Berset, D. Muff, *J. Chromatog. A* **2011**, 1218, 9202–9209.
9. J. Vichapong, R. Burakham, S. Srijaranai, K. Grudpan, *J. Sep. Sci.*, **2011**, 34, 1574–1581.
10. Y. Wen, J. Li, F. Yang, W. Zhang, W. Li, C. Liao, L. Chen, *Talanta* **2013**, 106, 119–126.
11. M. Shi, J. Xu, S. Zhang, B. Liu, J. Kong, *Talanta*, **2006**, 68, 1089–1095.
12. A. Attar, A. Amine, F. Achi, S. Bourouina-Bacha, M. Bourouina, L. Cubillana-Aguilerac, J. M. Palacios-Santander, A. Baraket, A. Errachid, *Int. J. Environ. Anal. Chem.* **2016**, 96, 515–529.
13. A. Amine, H. Mohammadi, I. Bourais, G. Palleschi, *Biosens. Bioelectron.*, **2006**, 21, 1405–23.
14. S.J. Shahtaheri, F. Faridbod, M. Khadem, *Procedia Technology*, **2017**, 27, 96–97.
15. D.J.E. Costa, J. C.S. Santos, F. A.C.S. Brandão, W.F. Ribeiro, G.R. Salazar-Banda, M. C.U. Araujo, *J. Electroanal. Chem.*, **2017**, 789, 100–107.
16. J. Gong, L. Wang, X. Miao, L. Zhang, *Electrochem. Commun.*, **2010**, 12, 1658.
17. H. Li, C. Xie, S. Li, K. Xu, *Colloids Surf. B/ Biointerfaces*, **2012**, 89, 175–181.
18. Z.J. Papp, V.J. Guzsvany, S. Kubiak, A. Borowski, L.J. Bjelica, *J. Serbian Chem. Soc.*, **2010**, 75, 681–687.
19. M. Sbaï, H. Essis-Tome, U. Gombert, T. Breton, M. Pontié, *Sens. Actuat. B-chem.*, **2007**, 124, 368–375.
20. K.P. Prathish, M.M. Barsan, D. Geng, X. Sun, C.M.A. Brett, *Electrochim. Acta.*, **2013**, 114, 533–542.
21. M. Wang, Z. Li, *Sens. Actuat. B-chem.*, **2008**, 133, 607–612.
22. D. Huo, Q. Li, Y. Zhanga, C. Houa, Y. Leib, *Sens. Actuat. B chem.*, **2014**, 199, 410–417.
23. M. Nithya, *J. Biosens. Bioelectron.*, **2015**, 6, 1–9.
24. M. Ben Ali, F. Barka-Bouaifel, B. Sieber, H. Elhouichet, A. Addad, L. Boussekey, M. Ferid, R. Boukherroub, *Superlattices and Microstructures.*, **2016**, 91, 225–237.
25. P. Manisankar, G. Selvanathan, C. Vedhi, *Intern. J. Environ. Anal. Chem.*, **2005**, 85, 409–422.
26. P. Pulido-Tofino, J.M. Barrero-Moreno, M.C. Perez-Conde, *Anal. Chim. Acta.*, **2006**, 562, 122–127.
27. P. Noyrod, O. Chailapakul, W. Wonsawat, S. Chuanuwatanakul, *J. Electroanal. Chem.*, **2014**, 719, 54–59.
28. X. Zhang, D. Martens, M. Petra. K. Amer, A. Kettrup, X. Liang, *J. Chromatog. A.*, **2006**, 1102, 84–90.
29. E.H. Damian, F. Baskeyfield, N. Magan Davis, E.I. Tohill, *Anal. Chim. Acta.*, 2011, 699, 223–231.
30. P. Manisankar, G. Selvanathan, C. Vendhi, *Talanta*, **2006**, 68, 686–692.
31. P. Manisankar, P.L. AbiramaSundari, R. Sasikumar, S.P. Palaniappan, *Talanta*, **2008**, 76, 1022–1028.